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Review Article

Applications and Preparation Methods of Copper Chromite Catalysts: A Review

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Abstract

In this review article various applications and preparation methods of copper chromite catalysts have been discussed. While discussing it is concluded that copper chromite is a versatile catalyst which not only catalyses numerous processes of commercial importance and national program related to defence and space research but also finds applications in the most concerned problem worldwide i.e. environmental pollution control. Several other very useful applications of copper chromite catalysts are in production of clean energy, drugs and agro chemicals, etc. Various preparation methods about 15 have been discussed which depicts clear idea about the dependence of catalytic activity and selectivity on way of preparation of catalyst. In view of the globally increasing interest towards copper chromite catalysis, reexamination on the important applications of such catalysts and their useful preparation methods is thus the need of the time. This review paper encloses 369 references including a well-conceivable tabulation of the newer state of the art.

Keywords: Copper chromite, Applications, Preparation methods, Review

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1. Introduction

The copper chromite ($CuCr_2O_4$) is one of the most efficient materials, has wide commercial application as catalysts being used in the unit processes of organic synthesis such as hydrogenation [1], dehydrogenation [2], hydrogenolysis [3], oxidation [4], alkylation [5], cyclization [6], etc. It can be used in the pollution abatement as the catalyst to remove aqueous organic wastes [7], volatile organic compound (VOC) [8] and vehicular primary emissions [9] such as CO, unburned hydrocarbon, NO_x and soot. In addition it has been used in various composite solid propellants as one of the efficient combustion supporting catalysts [10] in the domain of space vehicles (rockets) and weapon industries (high explosives, ballistic missiles). Furthermore, copper chromite has been proved as promising catalyst for the production of H_2 a clean energy carrier, by photo-catalytic phenomena [11-13], conversion of alcohols [14], water gas shift reaction [15], through sulphur based thermo-chemical water splitting cycles [16], etc. The next application of $CuCr_2O_4$ is catalyst for alternative fuels preparations, synthesizing methanol [17], an important hydrogen carrier; high alcohol synthesis (HAS) by hydrogenation of CO or CO_2, and fast pyrolysis of biomass [18] to bio-oil products. The catalyst is also helpful in the production of drugs and agro chemicals [19]. In fine chemicals industry for perfumery and synthesis of fragrances [20] $CuCr_2O_4$ is used as catalysts. The $CuCr_2O_4$ catalyst is useful in desulphurization sorbents for hot coal gas in integrated gasification combined cycle (IGCC) power plants [21,22]. Several other uses of $CuCr_2O_4$ are electrodes and sensors [23], semiconductors [24], heat-resistant pigment [25], etc.

Many research projects sanctioned [12, 26-29], several Ph.D. theses approved [30-34], a number of patents granted [35-39] and numerous studies [14,15,17,19,40-42] have been conducted on innovative preparation methods and utilizations of the copper chromite catalysts. However, preparation methods and utilizations of such catalysts have hardly been reviewed so far. Owing to the recurrently expanding interest the world over on the application of copper-chromite catalysts, this brief article is an attempt to summarise the applications of the copper chromite catalytic systems and to review their various useful preparation methods. This review paper will be beneficial to the research community as well as industries and national programs related to defence and space research in understanding the progress of preparation methods and applications of copper chromite catalysts.

2. Application of copper chromite catalysts

2.1 Commercial application

2.1.1 Hydrogenation

Catalytic hydrogenation is undoubtedly the most useful and widely applicable method for the reduction of chemical substances, and has found numerous applications in organic synthesis in research laboratories and industrial processes [42]. Copper chromite is an industrially important catalyst because of its ability to hydrogenate functional groups in aliphatic and aromatic compounds selectively. It is employed in both vapour-phase (e.g. hydrogenation of nitrobenzene and nitrotoluenes to their corresponding amines) and liquid phase (e.g. hydrogenation of carbonyl group in aldehydes, ketones and esters to the corresponding alcohol) commercial processes [43]. Copper chromite catalyst was first reported by Adkins et al. [44] to be active for the hydrogenation of a wide range of organic compounds. They tested the catalyst in the hydrogenation of a group of twenty-one organic compounds in the liquid state at temperature varying between 150-220 ^{0}C and pressure 100-150 atm, out of twenty-one compounds sixteen have been successfully hydrogenated in a batch reactor with 100% yield and 100% selectivity.

The catalysts of copper chromites (chromium wt.% > 25) have found extensive use in industrial processes for reducing furfural (C_4H_3O-CHO) to furfuryl alcohol (C_4H_3O-CH_2OH), butyraldehyde or crotonaldehyde to 1-butanol, partially reducing conjugated dienes to monoenes, and selectively reducing carbonyl group in vegetable oils and fatty acid with non-conjugated carbonyl and ethylenic bonds [45].

The selective hydrogenation of polyunsaturated organic compounds [46] attracts great interest from both industrial and academic point of view. In fine chemicals industry, we often need a semi-hydrogenation, for example with industrial foodstuffs and partial hydrogenation of edible oils and fatty acids [47] for perfumery and synthesis of fragrances which require the selective formation of allylic alcohols [48].

2.1.1.1 Hydrogenation of edible oils

Hydrogenation of edible oils is an important process because of its wide applications to produce margarine, frying oils, etc. Vegetable oils contain a mixture of saturated, monounsaturated, and polyunsaturated fatty acids. The mono- and polyunsaturated fatty acids have double bonds, all in the normal "cis" formation. These bonds can easily be broken down by oxygen. This produces compounds that make the oil rancid. Rancidity produces off-flavours in foods. To control this edible oil is hydrogenated in the food industry to produce fats and oils with desirable melting properties and an improved shelf life.

$$\text{Edible oil} + H_2 \rightarrow \text{Margarine} \quad (1)$$

Beside the desired hydrogenation reaction (eqn.1), trans-isomers of fatty acids are formed as well [49]. The trans-isomer has been reported to be undesirable for human diet due to adverse health effects [50]. It has similar effects as saturated fats increasing serum cholesterol levels in the blood, believed to be a major cause of heart disease [51]. The reduction and/or elimination and content of trans fatty acids in the food supply has attracted worldwide interest [52-56]. The options to reduce the trans levels in the hydrogenation of an edible oil are changing process conditions and applying selective low trans heterogeneous catalysts [57].

The copper chromite [44] has been extensively studied due to the high selectivity shown by this catalyst in the partial hydrogenation of vegetable oils [58,59]. In particular, many experiments have been done to correlate catalytic properties with operational parameters such as temperature [60], hydrogen pressure [60,61-63], hydrogen flow [64], catalyst concentration [61,63], substrate composition [62] and activation procedures [65].

Copper chromite catalysts have long been known in edible oils hydrogenation as the most selective for the reduction of linolenate $C_{18:3}$ to oleate $C_{18:1}$ leaving unaffected linoleate $C_{18:2}$, valuable component from the nutritional point of view [59]. The major factor responsible for the relative instability of soybean oil and other vegetable oils for food uses is widely recognized as the linolenate present in the oil [66]. A particular feature of the copper chromites is their high selectivity which has been used to advantage in the hydrogenation of edible oils and fats, where stronger hydrogenation catalyst, such as nickel can lead to excessive saturation and inferior nutritional quality of the final product [67]. Commercially employed Ni catalysts have limited linolenate selectivity in comparision to copper-chromite catalyst. Consequently, soybean oil hydrogenated over Ni catalyst to an iodine value (IV) of 110 contains 3% linolenate, while copper-chromite catalyst reducing it to 0.1% [66]. In room odour evaluations, copper chromite hydrogenated soybean oil gave higher scores and lower fishy responses than nickel-hydrogenated soybean oil after both had been exposed to fluorescent light [68].

The catalysts are usually charged into the oil in the oxidized form and are partly reduced to Cu(I) and/or Cu(0) during use. Pre-reduced copper chromites have found to be strongly deactivated in soybean oil hydrogenation due to disappearance of Cu(II) and Cu(I) species and to the decrement of Cu/Cr ratio on the catalyst surface [69]. Capece and co-workers [70] determined the oxidation states and surface composition of copper chromite at various stages of catalytic use and after reductive pre-treatments, and they concluded that Cu^1 is the active species for double-bond isomerization while Cu^0 is required for hydrogenation of conjugated dienes. According to Rieke et al. [71], activity and selectivity correlate well with the crystallinity of the copper chromite surface; they increase with decreasing crystallinity.

Szukalska and Drozdowski [72] hydrogenated rapeseed oils with different erucic acid contents with Adkins type copper-chromite catalyst. The tested rapeseed oils, after the elimination of linolenic acid by selective hydrogenation showed several times higher oxidative stability than the initial raw material and retained the liquid state at ambient temperatures.

2.1.1.2 Hydrogenation of aromatic compounds

Adkins copper chromite $CuO.CuCr_2O_4$ catalyst [73] is a rugged one commonly used in hydrogenations of ethylenic bonds, esters amides under high pressures and temperatures, but rarely employed to reduce aromatic compounds. It is less susceptible to poisons. With this catalyst phenanthrene [74] and anthracene [75] are converted to their dihydroderivatives, whereas naphthalene [76] was converted to tetralin. In general, copper chromite catalyst is employed in hydrogenations of compounds where reducible groups other than aromatic nucleus are to be hydrogenated in preference, e.g. hydrogenation of nitrobenzene to aniline [75].

Selective hydrogenation of aromatic nitrogroups to the corresponding aromatic amines is one of the most important reactions. There are three main categories of aromatic nitrogroup hydrogenations depending on the presence of other functional groups at the aromatic ring [77]:

a) The first category includes high volume products, such as aniline and toluene-diamines.

The largest end user of these products is the polyurethane industry;

b) Category two includes the hydrogenation of halonitroaromatic compounds. The corresponding haloanilines are used in the life science and specialty chemicals industries as intermediates for the production of pesticides, rubber chemicals, dyes, pigments and pharmaceuticals;

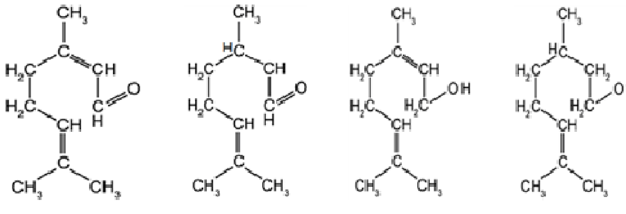
c) Category three nitrogroup hydrogenations include the selective hydrogenation of nitroaromatic compounds to anilines without hydrogenation of other functional groups present in the aromatic system [77].

Aniline is an important raw material and intermediate for the production of dyes, medicine, agriculture pesticides, antioxidants and vulcanisation accelerators. It is usually manufactured by the reduction of

$$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O \qquad (2)$$

Copper chromite is known for its ability to hydrogenate functional groups in aromatic compounds selectively without affecting the benzene nucleus [79]. Fang et al. concluded that hydrogenation of nitrobenzene is enhanced by addition of Cr-Cu/SiO_2 catalysts [80]. Keki et al. [81] found that the unreduced copper chromite is the stable active catalyst for hydrogenation of nitrobenzene.

The hydrogenation of nitrobenzene to aniline over reduced $Cu(Fe_xCr_{2-x})O_4$ series of catalysts (where x=0, 0.2, 0.4, 0.6, 0.8 and 1.0) has been studied by Jebarathinam et al. [82] at 250 ^{0}C in a fixed bed flow type reactor. The conversion of nitrobenzene to aniline is optimum over the catalysts with composition x=0.4. They compared the results of reversible and irreversible adsorption of carbon monoxide with hydrogenation activity and concluded that univalent copper at octahedral sites is more active for hydrogenation than metallic copper. The second cations [Cr(III) or Fe(III)] develop their catalytic activity by sharing anionic vacancies.



I **II** **III** **IV**

Fig.1. Hydrogenation of citral at atmospheric pressure [20]

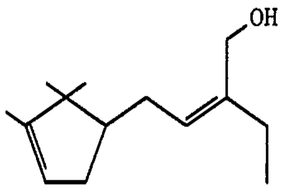


Fig. 2. 2-campholenylidenbutanol [83]

2.1.1.3 Perfumery and synthesis of fragrances

There is a continuing search for synthetic materials having desirable fragrance properties. Such materials are used either to replace costly natural materials or to provide new fragrances of perfume types which have not theretofore been available. For perfumery and synthesis of fragrances semihydrogenation is often needed, which require the selective formation of allylic alcohols [20]. During citral (I) hydrogenation at atmospheric pressure, citronellal (II) nerol (III) appears simultaneously at the initial stage of the reaction (Fig. 1). The ratio of the amounts of these two primary products is about 5 in favour of the saturated aldehyde (II). Citronellol (IV), the saturated alcohol appears before complete consumption of the starting material but remains a secondary product [46]. The higher amounts of both primary products (II) and (III) are reached for the same conversion value which roughly corresponds almost to the total disappearance of citral.

Furfuryl alcohol is an important compound in the fragrance industry. The hydrogenation of furfural with copper chromite is the industrial means of producing furfuryl alcohol given by the eqn. (3) [45].

$$C_4H_3OCHO + H_2 \rightarrow C_4H_3OCH_2OH \qquad (3)$$

It is well known, a need exists for synthetic substances which are precious, in demand and having limited supply such as sandalwood substitute or extenders. It would be most desirable to be able to synthetically provide the major odorant compound of such natural sandalwood oils such as, α-santalol and ß-santalol. Weigers et al. [83] described an economical and novel process for preparing a mixture containing 2-campholenylidenbutanol

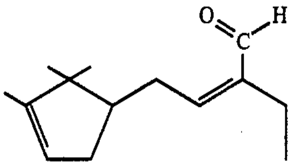


Fig. 3. Compound formed by hydrogenation of 2-campholenylidenbutanol [83]

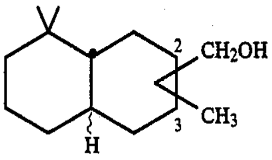


Fig. 4. Bicyclic alcohol [84]

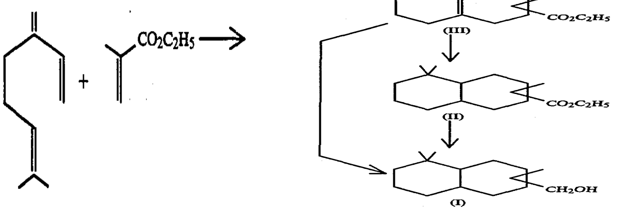


Fig. 5. Preparation of bicyclic aliphatic alcohols [84]

having the structure shown in Fig. 2, by hydrogenating the compound having structure given in Fig. 3, in the presence of copper chromite catalyst. Such mixtures are used in augmenting or enhancing the aroma of perfume compositions, colognes and perfumed articles including fabric softener compositions, cosmetic powders and solid or liquid anionic, cationic, non-ionic and zwitteronic detergents.

Giersch and Ohloff [84] discovered the bicyclic alcohol of formula as shown in the Fig. 4. The alcohol possesses a natural woody odour with an ambary character. The woody note is reminiscent in particular of cedar wood without however possessing the "sawdust" character of latter. The ambary note, on the other hand, is reminiscent of certain aspects presented by precious materials such as grey amber. Owing to their odour properties, the alcohols find an utilisation of wide scope, both in alcoholic perfumery and in technical applications such as, in the perfuming of soaps, powder or liquid detergents, fabric softeners, household materials, cosmetics, shampoos, beauty creams, body deodorizers or air fresheners.

A process for the preparation of bicyclic aliphatic alcohols comprises the following reaction steps shown in Fig. 5 [84]:

a) the addition of ethyl methacrylate to mycrene under the conditions of a Diels-Alder type reaction and the treatment of the resulting reaction mixture with an acidic cyclization catalyst;
b) the reduction of the obtained ester by Ni-$CuCr_2O4$ hydrogenation, and
c) the reduction of the resulting by means of a usual reduction reagent of the ester formation.

2.1.1.4 Hydrogenation of Alcohols

Long-chain alcohols can be converted directly to N,N-dimethylalkylamines by the reaction with dimethylamine at 36 ^0C in the presence of of Cu-Cr catalyst and hydrogen at elevated temperatures and pressure as shown by eqn. (4) [85,86].

$$RCH_2OH + HN(CH_3)_2 \xrightarrow[H_2]{Cu\text{-}Cr} RCH_2N(CH_3)_2 + H_2O \qquad (4)$$

Ethoxylated tertiary amines can be produced by the reaction of primary or secondary amines with ethylene oxide. The asymmetrical tertiary amines are used exclusively as starting materials for the manufacture of quaternary ammonium compounds, cationic and amphoteric surfactants, and amine oxides. Quaternary ammonium compounds used as bactericides and algaecides are produced by the reaction of tertiary amines with benzyl chloride, methyl chloride, or dimethyl sulphate. Of these, the benzyl ammonium chloride salt is the most widely used [87].

2.1.1.5 Hydrogenation of aldehydes

Copper-chromium oxide catalyst is effective for the hydrogenation of aldehydes [88] at a temperature of 125-150 ^0C. The hydrogenation of benzaldehyde over copper-chromium gives a high yield of benzyl alcohol even at 180 ^0C without hydrogenolysis [44] to give toluene (eqn. 5).

$$C_6H_5CHO + H_2 \rightarrow C_6H_5CH_2OH \qquad (5)$$

Vapour-phase hydrogenation of furfural over copper chromite catalyst is perhaps the best method of producing furfuryl alcohol [1,89]. Furfuryl alcohol is an important fine chemical for polymer industry. It is widely used in production of various synthetic fibres, rubbers, resins, e.g., dark thermostatic resins resistant to acids, bases and resins used for strengthening ceramics. It is also used as solvent for furan resin, pigment, varnish and as rocket fuel. Pramottana et al. [39] observed Cu^0 as the active phase in the copper chromite particles for the selective hydrogenation of furfural to furfuryl alcohol.

2.1.1.6 Hydrogenation of ketone

Copper-chromite catalyst is also effective for the hydrogenation of ketones to corresponding alcohols. Yurieva [90], reported maximum yield of isopropanol on hydrogenation of acetone (eqn. 6) over copper chromite catalyst at 300-350 ^{0}C, prepared by thermal decomposition of basic copper ammonium chromate at 900 ^{0}C.

$$CH_3COCH_3 + H_2 \leftrightarrow C_3H_7OH \qquad (6)$$

Kang et al. [91] carried out hydrogenation of methyl dodecanoate for the synthesis of 1-dodecanol in the presence of a copper chromite catalyst. The catalysts used were synthesized by ceramic method, co-precipitation, and improved co-precipitation method. The highest yield of dodecanol in the hydrogenation reaction was 95.5% when copper chromite synthesized in the PEG solution was used as a catalyst in the optimized reaction condition. 1-dodecanol is also known as lauryl alcohol ($C_{12}H_{25}OH$), is a fatty alcohol. It has a floral odour. Dodecanol is used to make surfactants, lubricating oils, and pharmaceuticals. In cosmetics, dodecanol is used as an emollient.

2.1.2 Dehydrogenation of alcohols

The dehydrogenation of alcohols to aldehydes or ketones is a well-known industrial process, and these reactions are primarily carried out on copper catalysts because of their high selectivity to the dehydrogenation product [27]. Catalytic dehydrogenation of alcohols plays a key role in the chemical industry particularly in the synthesis of various pharmaceuticals and fine chemicals apart from bulk chemicals. The reaction can generally be described by the eqn. 7:

$$R_1\text{–}CHOH\text{–}R_2 \rightarrow R_1\text{–}CO\text{–}R_2 + H_2 \qquad (7)$$

where, R_2 = H for primary alcohols or an alkyl or aryl group for secondary alcohols.

Methanol dehydrogenation to formaldehyde [92] or methyl formate over copper chromite catalysts proceeds via successive reactions (eqn. 8 and 9) [93]:

$$CH_3OH \leftrightarrow HCOH + H_2 \qquad (8)$$
$$HCOH + CH_3OH \leftrightarrow HCOOCH_3 + 2H_2 \qquad (9)$$

Unlike other primary alcohols which are dehydrogenated to aldehydes, the dehydrogenation of methanol forms methyl formate over copper chromite catalysts [94,95]. Methyl formate is used as larvicide and fumigant. It is a starting material in the synthesis of formic acid, acetic acid, N, N dimethylformamide, formamide, hydrogen cynide, methyl cellulose and high purity carbon monoxide [96].

Ethanol dehydrogenation to acetaldehyde over copper chromite catalysts [97,2,98] is highly selective (selectivity > 95%) represented by the eqn. 10:

$$C_2H_5OH \leftrightarrow CH_3CHO + H_2 \quad \Delta H^0 = 12.51 \text{ Kcal/mole} \qquad (10)$$

Acetaldehyde is an important intermediate for the production of a number of industrial chemicals such as acetic acid, acetic anhydride, n-butanol, pentaerythritol, pyridines, peracetic acid, ethyl acetate, 2-ethylhexanol, aldol, chloral, 1,3-butylene glycol, trimethylolpropane, vinyl acetate, perfumes, aniline dyes, plastics and synthetic rubber [99]. It is used in silvering mirrors and in hardening gelatin fibers. It is also a starting material for the polymer paraldehyde, phenol, aldehyde condensation products, dyes, synthetic flavouring substance and finds its use as a hardener in photography.

Isopropyl alcohol dehydrogenation to acetone involves a secondary alcohol, whereas both R1 and R2 are methyl groups in eqn. (7). Copper chromite catalysts possess high selectivity and satisfactory activity [27,100] for isopropyl alcohol dehydrogenation (eqn. 11):

$$\text{Iso-propanol: } C_3H_7OH \leftrightarrow CH_3COCH_3 + H_2 \qquad (11)$$

Acetone is an excellent solvent for a wide range of gums, waxes, resins, fats, greases, oils, dyestuffs, and cellulosics. It is used as a carrier for acetylene, in the manufacture of a variety of coatings and plastics, and as a raw material for the chemical synthesis of a wide range of products [101] such as ketene, methyl methacrylate, bisphenol A, diacetone alcohol, methyl isobutyl ketone, hexylene glycol (2- methyl-2,4-pentanediol), and isophorone.

The use of dehydrogenation for obtaining butyraldehyde from 1-butanol is of interest because it does not allow any side reaction and yields pure hydrogen as a by-product. The stoichiometric equation for the dehydrogenation of 1-butanol is given by eqn. 12 [102]:

$$C_4H_9OH \rightarrow C_3H_7CHO + H_2 \qquad (12)$$

According to Rao [1], 90% copper, 8% chromia, and 2% carbon supported on pumice was best catalyst for dehydrogenation of 1-butanol to butyraldehyde, with high activity and selectivity. The Cu-ZnO-Cr_2O_3/SiO_2 catalysts prepared by impregnation method, exhibits high activity for the dehydrogenation of 2-butanol to 2-butanone [103]. A copper catalyst with chromium addition, prepared by the electroless plating method, was investigated by Shiau et al. [104] for dehydrogenation of 1-butanol.

Butyraldehyde is used in organic synthesis, mainly in the manufacture of rubber accelerators, and as a synthetic flavouring agent in foods. Isobutyraldehyde is an intermediate for rubber antioxidants and accelerators. It is used in the synthesis of amino acids and in the manufacture of perfumes, flavourings, plasticizers and gasoline additives.

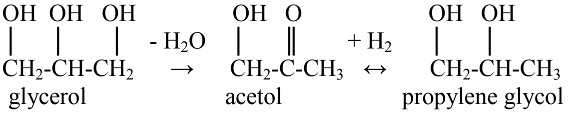
Crivello et al. [105] prepared hydrotalcite-like materials containing Cu^{2+}, Mg^{2+} and Cr^{3+} cations in the layers and carbonate in the interlayer by the co-precipitation method with different Cu/Cr/Mg molar ratios. The synthesized catalysts with 40% of Cu show a high conversion of isoamylic alcohol and selectivity to isovaleraldehyde. The authors proposed that the presence of small percentages of magnesium contributes in a significant extent to the dispersion of entities of oxidized copper on the surface of the calcined samples. Isovaleraldehyde is an important industrial intermediary in the manufacturing of synthetic resins, special chemicals and isovaleric acid which is widely used in the medical industry.

2.1.3 Hydrogenolysis of glycerol to propylene glycol

Glycerol is a by-product from bio-diesel industry. As the bio-diesel production is increasing exponentially, the crude glycerol generated from the trans-esterification of vegetables oils has also been generated in a large quantity. For every 9 kg of biodiesel produced, about 1 kg of a crude glycerol by-product is formed [106]. The rapidly increased production of biodiesel has led to a drastic surplus of glycerol in the chemical markets. For this reason, many catalytic processes had been reported to convert glycerol into value-added chemicals [107-109] by means of oxidation, hydrogenolysis, dehydration, esterification, carboxylation and gasification. Among those routes, selective hydrogenolysis of glycerol to propylene glycol (PG) is a promising route to increase the profitability of biodiesel plant. PG is an important chemical used to make unsaturated polyester resins, functional fluids (antifreeze, de-icing, and heat transfer), personal care, paints, animal feed, food industry coolants, non-ionic detergents, pharmaceuticals, cosmetics, flavours and fragrances, plasticisers and hydraulic brake fluids [107,109]. It is also an excellent solvent and extractant, and used as a tobacco humectant. Dasari et al. [110] reported the efficiency of pre-reduced copper chromite catalysts for the hydrogenolysis of glycerol to PG (85.0% selectivity, 54.8% conversion and 73% yield) at 473 K and 1.4 MPa (a mild hydrogen pressure).

The reduced Cu-Cr catalysts show significant catalytic activity and selectivity in glycerol hydrogenolysis, i.e. above 51% conversion of glycerol and above 96% selectivity to 1,2-propanediol in 4.15 MPa H_2 at 210 ^{0}C. The Cu-Cr catalysts with low Cu/Cr molar ratio present high conversion of glycerol, which is different from the conventional copper-chromite catalyst [107].

Chiu et al. [111,112] performed dehydration of glycerol in the presence of copper-chromite catalyst to obtain acetol in a single stage semi-batch reactive distillation unit under mild conditions. The acetol from this reaction readily hydrogenates to form propylene glycol providing an alternative route for converting glycerol to propylene glycol. They achieved high acetol selectivity levels (>90%) using copper-chromite catalyst. The conversion of glycerol to propylene glycol is achieved through a reactive intermediate (acetol). First, glycerol is dehydrated to form acetol, and then, this acetol is hydrogenated in a further reaction step to produce propylene glycol as illustrated by reaction eqn. 13.



$$\underset{\text{glycerol}}{\overset{\text{OH}\;\;\text{OH}\;\;\text{OH}}{CH_2\text{-}CH\text{-}CH_2}} \xrightarrow{-H_2O} \underset{\text{acetol}}{\overset{\text{OH}\;\;\text{O}}{CH_2\text{-}C\text{-}CH_3}} \overset{+H_2}{\leftrightarrow} \underset{\text{propylene glycol}}{\overset{\text{OH}\;\;\text{OH}}{CH_2\text{-}CH\text{-}CH_3}} \qquad (13)$$

Kim et al. prepared copper chromite catalysts using methods involving impregnation and precipitation, and evaluated for the hydrogenolysis of glycerol [28]. Catalyst (10I and 50I) prepared by the impregnation method contained a mixed phase of both individual copper and chromium oxide structures, while the catalyst (50P) prepared by precipitation showed a single phase, with a copper chromite spinel structure ($CuCr_2O4$). XPS data indicated that, after the reduction step, the copper species in the impregnated catalyst was reduced to Cu^0, but the catalyst prepared by the precipitation method retained a spinel structure evidenced by the large amount of Cu^{2+} species. In hydrogenolysis reactions, the precipitated catalyst showed a higher catalytic activity than the impregnated catalyst. Thus, the reduced copper chromite spinel structure, which constitutes a single phase, appears to be responsible for the high catalytic activity in the hydrogenolysis of glycerol to propylene glycol.

Copper chromite catalysts are useful for a variety of chemical reactions in the processing of oleo-chemical feedstocks. Major oleo-chemical applications include hydrogenolysis of fatty esters to fatty alcohols including both methyl ester and wax ester processes, alkylation of alcohols with amines and amination of fatty alcohols. The catalysts have unique performance for selective hydrogenation of vegetable oils and can be used in the conversion of bio-renewable feedstocks into industrial chemicals. Dovell and Greenfield [113] used copper chromite as a catalyst for the preparation of alkylaryl secondary amines by the reductive alkylation of a primary aromatic amine with an aliphatic ketone in the presence of hydrogen (eqn. 14).

$$ArNH_2 + ORCR' + H_2 \rightarrow ArNHRCHR' + H_2O \quad (14)$$

The noble metals cause both nuclear hydrogenation and formation of alkylamines [114] by hydrogenolysis of the carbon-nitrogen bond between the alkyl group and the nitrogen atom in the secondary amine i.e.: $ArNHR + H_2 \rightarrow ArH + RNH_2$. Copper chromite catalysts avoid these undesirable side reactions, but a large amount of ketone is reduced to the corresponding alcohol.

Fatty alcohols are an important raw material for surfactants as well as constitute one of the largest groups within the oleochemicals. The fraction of natural fatty alcohols, i.e. fatty alcohols based on natural fats and oils, is steadily growing [115]. The fatty alcohols can be produced by hydrogenation of fatty acid methyl esters, a product from natural abundant coconut and palm kernel oils, to form high alcohol in the presence of a $CuCr_2O_4$ catalyst [116]. The hydrogenation of methyl esters and of fatty acids to form fatty alcohols is given by the following general eqns. (15) and (16) respectively:

$$\underset{\text{Methyl ester}}{RCOOCH} + 2H_2 \overset{CuCr}{\leftrightarrow} \underset{\text{Fatty alcohol}}{RCH_2OH} + CH_3OH \quad (15)$$

$$\underset{\text{Fatty acid}}{RCOOH} + 2H_2 \overset{CuCr}{\leftrightarrow} \underset{\text{Fatty alcohol}}{RCH_2OH} + H_2O \quad (16)$$

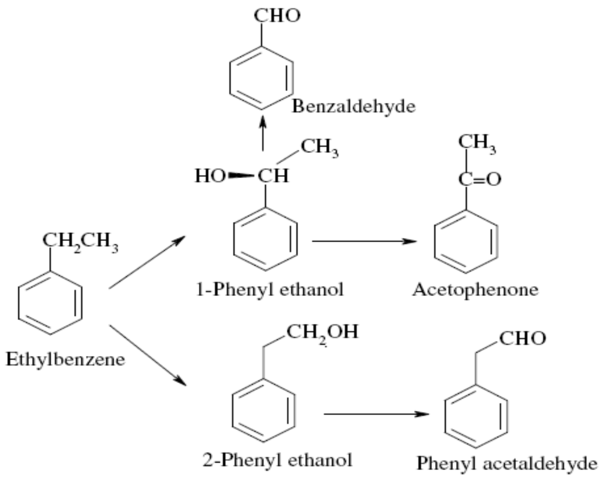


Fig. 6. Reaction scheme of ethylbenzene oxidation [117].

Copper chromite catalyst also converts any unsaturated carbon double bonds so that only saturated fatty alcohols are formed [87]. The hydrogenation process is carried out at 25-30 MPa and a temperature of 250-300 ^{0}C in a tubular column.

2.1.4 Oxidation reactions

Oxidation of ethylbenzene (liquid phase) with t-butyl hydroperoxide (TBHP) as an oxidant is feasible over nickel substituted copper chromite catalysts [4]. Effective utilization of ethylbenzene, available in the xylene stream of the petrochemical industry, for more value-added products is an interesting option. Oxidation of ethylbenzene is of much importance for the production of the aromatic ketone, acetophenone, one of the key products in the industries. It is used as a component of perfumes and as an intermediate for the manufacture of pharmaceuticals, resins, alcohols and tear gas. The oxidation pathways of ethylbenzene are presented in fig. 6.

Benzaldehyde is used in perfumery and pharmaceutical industries. Choudhary et al [117] prepared benzaldehyde in liquid phase oxidation of benzyl alcohol by tert-butyl hydroperoxide using Cu-Cr containing layered double hydroxides and/or mixed hydroxides selectively. The reaction is given by eqn. (17):

$$C_6H_5CH_2OH + (CH_3)_3COOH \rightarrow C_6H_5CHO + (CH_3)C\text{-}OH + H_2O \quad (17)$$

George and Sugunan [118] prepared spinel system with the composition of $[Cu_{1-x}Zn_xCr_2O_4]$ by co-precipitation method and reported cyclohexane oxidation at 273 K using TBHP as oxidant. 69.2% selectivity to cyclohexanol and cyclohexanone at 23% conversion of cyclohexane. Oxidation of cyclohexane is one of the important bulk processes for the production of polyamide fibres and plastics, such as nylon-6 and nylon-6,6.

2.1.5 Alkylation

Alkylation reactions are of great interest in the petrochemical industry as they lead to several commercially important alkyl aromatics. Cumene is one such alkyl aromatic produced by isopropylation of benzene. The commercial importance of cumene is felt by the world's growing phenol demand, 90% of which is met through cumene. In the cumene route for the production of phenol, acetone is produced as a low value by product. Barman et al. [119] synthesised cumene with 100% selectivity, by reductive alkylation of benzene with acetone in the presence of a bifunctional catalyst system comprising a solid acid material, H-mordenite (HM), as alkylation functional and nano-copper chromite as hydrogenation functional, eqn. (18).

$$C_6H_6 + CH_3COCH_3 + H_2 \rightarrow C_6H_5CH(CH_3)_2 + H_2O \quad (18)$$

Copper chromite has been reported as a catalyst for the reductive N-alkylation of aniline with acetone [120,100]. Pillai [121] prepared different aliphatic secondary amines by reductive alkylation of methylamine and ethanolamine with carbonyl compounds over copper chromite catalyst. Almost 100% selectivity was observed in all cases. Under optimum conditions of reaction the yield of N-isopropylaniline was 91% and that of N-benzyl-ethanolamine was 94%.

2.1.6 Cyclization

Nitrogen-containing heterocyclic compounds are pharmaceutically important [122,123]. Intensive attention was concentrated on the manufacture of this type of compounds over a half century. Bai et al. [124] employed Cu-Cr-Fe/γ-Al_2O_3 catalysts for the intramolecular cyclization of N-(2-hydroxyethyl)-ethylenediamine to piperazine which showed excellent activity, selectivity and long service life under the optimum reaction conditions (eqn. 19). Further they reported that satisfactory results were obtained for cyclizations of other alkanolamines, such as N-(2-hydroxyethyl) -1,2-diaminopropane and 5-amino-1-pentanol.

$$2C_2H_2(NH_2)_2 \rightarrow C_4H_4(NH)_2 \quad (19)$$

Ethylene diamine Piperazine

Moss and Bell [125] used Ni-Cu-Cr-oxide for the amination of ethanolamine to a mixture of ethylenediamine and cyclic product, piperazine. They found that addition of water increased the selectivity of a Ni-Cu-Cr-oxide catalyst to the cyclic product. Wang et al. [6] found that the Cu-Cr-Ba-Al_2O_3 catalyst was suitable for highly selective synthesis of homopiperazine. Cu^0 is believed to be the active site of the catalyst and the addition of Ba to the Cu-based catalyst improves the dispersion of copper and prevents it from sintering. The cyclization of N-ß-hydroxyethyl-1,3-propanediamine to homopiperazine proceeded with more than a 90% yield under optimum reaction conditions.

2.2 Hydrogen production

Hydrogen is used in massive quantities in the petroleum and chemical industries [126]. In a petrochemical plant, hydrogen is used for hydrodealkylation, hydrodesulfurization, and hydrocracking, all methods of refining crude oil for wider use. Ammonia synthesis plants accounted for 40% of the world's consumption of H2 in making fertilizer. In the food industry, hydrogen is used to hydrogenate oils or fats, which permits the production of margarine from liquid vegetable oil. Hydrogen is used to produce methanol and hydrochloric acid, as well as being used as a reducing agent for metal ores. Since H2 is the least dense of gases, meteorologists use hydrogen to fill their weather balloons. The balloons carrying a load of instruments float up into the atmosphere, for recording information about atmospheric conditions.

Hydrogen has the highest combustion energy release per unit of weight of any commonly occurring material (eqn. 20).

$$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l) \quad \Delta H^0 = 286 \text{ kJ/mol} \quad (20)$$

This property makes it the fuel of choice for upper stages of multi-stage rockets. Much has been said about hydrogen being the "energy carrier of the future" due to its abundance and its non-polluting combustion products. When it is combusted, heat and water are the only products. The use of hydrogen as a fuel for fuel cell-powered vehicles can greatly reduce green house gas emissions from internal combustion engines. Moreover, development of affordable hydrogen fuel cells will help reduce the nation's dependence on foreign oil, leading to an increased national energy security. Thus, hydrogen offers a potentially non-polluting, inexhaustible, efficient, and cost attractive cleanest fuel for today's rising energy demands [127].

Hydrogen is not found in free state but it is abundantly available in nature as compounds of oxygen (water) or carbon (alcohols, hydrocarbons, carbohydrates, etc.). Energy must be supplied to generate hydrogen from either water or carbonaceous materials. Thus, note that hydrogen is not an energy source, as energy is needed to produce it (21). As an energy carrier, hydrogen is the most attractive option with many ways to produce and utilize it [128].

$$H_2O + \text{energy} \rightarrow H_2 + 0.5O_2 \qquad (21)$$

Processes using copper chromite as catalysts for the production of hydrogen are as follows:

a). From water splitting
  - Photo-electrolysis of water
  - Sulphur based thermo-chemical water splitting cycles

b). Catalytic conversion of alcohols
  - Dehydrogenation of alcohols
  - Decomposition of methanol
  - Reforming of alcohols
    - Methanol reforming
    - Ethanol reforming

c). Water gas shift reaction

2.2.1 From water splitting

2.2.1.1 Photo-electrolysis of water

In the past two decades, the photo-electrochemical (PEC) processes at semiconductor (SC)/electrolyte junctions have been intensively investigated [11]. The search of new materials to achieve the photo-chemical conversion has led to a great deal of work on $CuCr_2O_4$ [11-13,129-130] and remains the best possible way of solar energy storage in hydrogen form. Photochemical H_2 evolution based on a dispersion of $CuCrO_2$ powder in aqueous electrolytes containing various reducing agents (S_2, SO_2^{-3} and $S_2O_2^{-3}$) has been studied by Saadi [129]. The powder dispersion has the advantage of a liquid-junction solar-cell where the two half reactions take place simultaneously on the same particle that behaves like a micro-photo-electrochemical cell and it is cost effective too. It has a long lifetime, a pH insensitive energetic and absorbs a large part of the sun spectrum. Schematic photocatalytic evolution of H_2 is illustrated in Fig. 7.

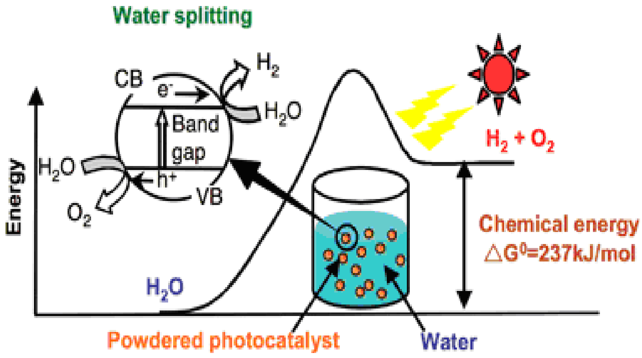


Fig. 7. Schematic illustration of photocatalytic evolution of hydrogen

Yan et al. [12] synthesized $CuCr_2O_4/TiO_2$ hetero-junction via a facile citric acid assisted sol-gel method for photocatalytic H_2 evolution. The nano-composite of $CuCr_2O_4/TiO_2$ is more efficient than their single part of $CuCr_2O_4$ or TiO_2 in producing hydrogen. $CuCr_2O_4$ is a p-type semiconductor with a small band gap [129]. A possible reaction model (eqns. 22,23,24) of the $CuCr_2O_4/TiO_2$ hetero-junction is proposed by Yan, et al. [12]. For both pure $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ hetero-junction, mainly $CuCr_2O_4$ can be activated under simulated sunlight irradiation:

$$CuCr_2O_4 + hv \rightarrow CuCr_2O_4\,(e^-, h^+) \qquad (22)$$

The photo-generated electrons and holes migrate in opposite directions according to the p-type conductivity of $CuCr_2O_4$, i.e. the electrons migrate in the direction of the illuminated side of the particle to react with adsorbed water and produce H_2. Meanwhile holes move in the opposite direction (the particles dark side) to oxidize adsorbed oxalic acid. Because of the Schottky barrier formed between the interface of $CuCr_2O_4$ and TiO_2, the hetero-junction can improve the separation of the photo-generated electrons and holes. When coupled with TiO_2, the photo-generated electrons are injected from excited $CuCr_2O_4$ into the conduction band of TiO_2 and reduce adsorbed water into H_2:

$$CuCr_2O_4\,(e^-) + TiO_2 \rightarrow CuCr_2O_4 + TiO_2\,(e^-) \qquad (23)$$
$$CuCr_2O_4\,(e^-, h^+) + TiO_2 \rightarrow CuCr_2O_4\,(h^+) + TiO_2\,(e^-) \qquad (24)$$

As a result, $CuCr_2O_4/TiO_2$ hetero-junction with appropriate $CuCr_2O_4/TiO_2$ ratio can enhance the separation of the photo-generated electrons and holes, and therefore improve the H_2 photo-catalytic activity [130]. Boumaza et al. [13] reported that the best catalytic performance over $CuCr_2O_4$ for H_2 -photoproduction was obtained in (NaOH 0.5 M, $Na_2S_2O_3$ 0.025 M) with an average rate of 0.013 cm^3 h^{-1}/mg catalyst and a quantum efficiency of 0.2% under polychromatic light.

2.2.1.2 Sulphur based thermo-chemical water splitting cycles

Thermochemical water-splitting cycle is a promising process to produce hydrogen using solar or nuclear energy [131]. Ginosar et al. [16] evaluated the activity and stability of several complex metal oxides: two ABO_3 structures ($FeTiO_3$ and $MnTiO_3$) and three AB_2O_4 structures ($NiFe_2O_4$, $CuFe_2O_4$, and $NiCr_2O_4$) and copper chromite (i.e., $2CuO.Cr_2O_3$) (was also selected due to the high activities of Cr_2O_3 and CuO [132]) for the atmospheric decomposition of concentrated sulfuric acid in sulfur-based thermochemical water splitting cycles. Catalyst activity was determined at temperatures from 725 to 900 ^{0}C. Catalytic stability was examined at 850 ^{0}C for up to 1 week of continuous operation. The results were compared to a 1.0 wt% Pt/TiO_2 catalyst. Over the temperature range, the catalyst activity of the complex oxides followed the general trend: $2CuO.Cr_2O_3$ > $CuFe_2O_4$ > $NiCr_2O_4.NiFe_2O_4$ > MnTiO3. FeTiO3. Tagawa and Endo [132] observed the order of the activities for the decomposition of sulfuric acid in thermochemical water splitting process at the initial concentration of SO_3 of 4.0 mol% as follows: Pt ≈ Cr_2O_3 > Fe_2O_3 > (CuO) > CeO_2 > NiO > Al_2O_3. The activity of Cr_2O_3 above 700°C was nearly the same as the Pt catalyst.

2.2.2 Catalytic conversion of alcohols

In recent years, the catalytic decomposition/ reforming of alcohols has gained particular interest due to growing environmental, economic, and political concerns regarding energy production [133]. Safe and efficient in situ hydrogen generation from alcohols (i.e. methanol, ethanol, propanol, butanol) can promote the use of fuel cells and other clean technologies as a source of energy for mobile applications. Alcohols can serve as H_2 carriers that are compatible with current infrastructures for liquid fuels and can be catalytically converted on-site in order to minimize energy input requirements and operating temperatures [134]. Methanol and ethanol have the highest H/C ratios among the alcohols and gasoline-range alkanes (e.g., heptane). That is, more hydrogen can be extracted from their molecular frameworks [135]. Production of hydrogen from alcohols can be accomplished by their dehydrogenation and reforming processes.

2.2.2.1 Dehydrogenation of alcohols

Hydrogen as by-product is obtained from dehydrogenation of alcohols over copper chromite catalysts as discussed in section (2.1.2). The dehydrogenation of alcohols is a reversible and an endothermic process which implies that heat must be supplied to the system. Of course very pure hydrogen is obtained on dehydrogenation of ethanol over copper chromite catalyst [136].

2.2.2.2 Decomposition of methanol

Methanol is easy to transport over long distances and to store. The catalytic decomposition of methanol to CO and H_2 can provide a clean and efficient fuel (eqn. 25):

$$CH_3OH \leftrightarrow CO + 2H_2 \quad \Delta H = 90.2 \text{ kJ/mol} \qquad (25)$$

For example, methanol decomposition on board of a vehicle (Fig. 8) provide a fuel which is cleaner and 60% more efficient than gasoline and up to 34% better than undecomposed methanol [137-139]. Methanol decomposition is an endothermic reaction. The reaction heat can be provided by the engine coolant and exhaust gas. This recovers the waste heat and increases the heating value of the fuel. The decomposed methanol may also be used as a clean fuel for gas turbines at times of peak demand of electricity [137-140]. Lean and complete

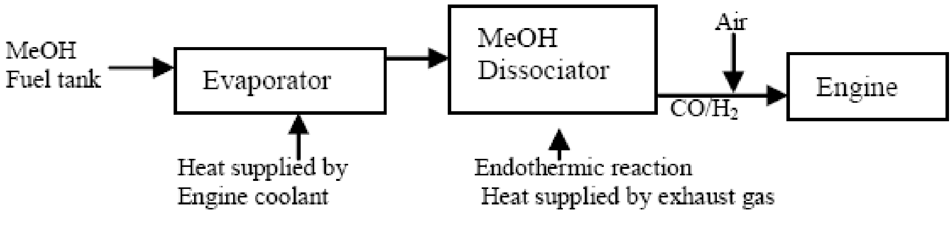


Fig. 8. Methanol decomposition on board a vehicle

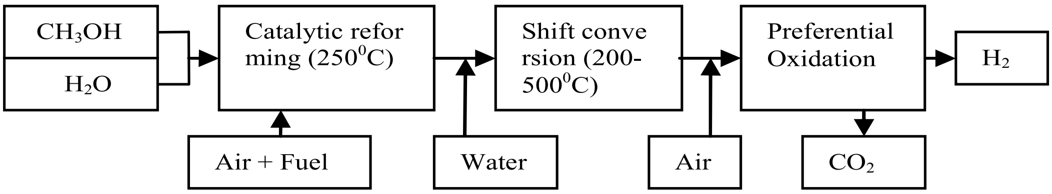


Fig. 9. Flow-sheet for a conventional SRM process

combustion will ensure low CO and formaldehyde emissions. NOx emission will be greatly reduced because of lower combustion temperatures.

Although the potential gain from implementation of methanol decomposition related technology is evident, successful development of efficient catalysts and reaction processes is crucial for the implementation of the technology. Cu-based catalysts such as Cu/Cr/Mn are active catalysts in the decomposition of methanol to CO and H_2. Cheng et al. [138] concluded that Cu/Cr-based catalysts are much more active than the conventional Cu/Zn catalysts in methanol decomposition. The acidic nature of the Cu/Cr-based catalysts, which leads to the decreased selectivity, can be greatly reduced by passivating the catalysts with alkali metal ions such as potassium.

2.2.2.3 Reforming of alcohols

Alcohols and more specifically methanol are convenient storage systems for hydrogen [141]. These liquids can easily be transported through the existing infrastructure and have lesser constraints concerning safety than for instance gaseous hydrogen storage. Alcohols transformation into gaseous mixtures enriched with hydrogen can be achieved by several reactions such as steam reforming (SR) [142,20], partial oxidation (PO) [135] and oxidative steam reforming (OSR) [143].

A. Methanol reforming

Catalytic reforming of methanol is a well-established technology, mainly used for small hydrogen plants. This technology is promising for energy feeding in portable electronic devices, for decentralized refuelling units for hydrogen-based automobiles or as on-board generation systems for hydrogen-based internal combustion engines or PEM fuel cells [144]. Methanol is considered as an appropriate source of hydrogen due its safe handling, low cost and high storage density. Moreover, it can be produced from renewable and fossil fuels [14].

The steam reforming (SRM) of methanol can be modelled as occurring in two stages by two different pathways, the first one involves the decomposition of methanol into CO and hydrogen (eqn. 26):

$$CH_3OH \leftrightarrow CO + 2H_2 \qquad (26)$$

Followed by a water gas shift reaction (eqn. 27):

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (\Delta H^0 = \pm 41.2\ kJmol^{-1}) \qquad (27)$$

The second mechanism for methanol steam reforming consists of the reaction of water and methanol to CO_2 and hydrogen (eqn. 28):

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \quad (\Delta H^0 = \pm 49\ kJmol\text{-}1) \qquad (28)$$

which can be followed by a reverse shift reaction to establish the thermodynamic equilibrium (eqn. 29):

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad (29)$$

The advantage of SRM process is the amount of CO generated along CO_2 is low. This is important since it acts as a poison for fuel cells. The accepted levels of CO are between 10 and 100 ppm [134]. The main disadvantage of SR is its endothermicity requiring external heating, which makes short start-up and fast transient behaviour difficult to achieve [143]. The schematic flow sheet for a conventional SRM process is shown in Fig. 9.

Copper-based catalysts ($CuMn_2O_4$ and $CuCr_2O_4$ spinels or CuO/CeO_2 and CuO/ZnO) exhibit a high activity and selectivity for the steam reforming process. Small amounts of Cr_2O_3 in skeletal copper catalysts significantly enhance the copper surface area and thus promoted the activities for SRM [142,145]. Supported Cu-Cr on yttria-doped ceria (YDC)/Al_2O_3 showed the most pronounced enhancement of the catalyst activity in the SRM at reaction temperatures of 200-250 ^{0}C, the CO concentration in the products was smaller than 0.1% [146]. Valde´s-Solı´s et al. [14] prepared nano-sized $CuCr_2O_4$ catalysts by nano-casting techniques for the production of hydrogen by

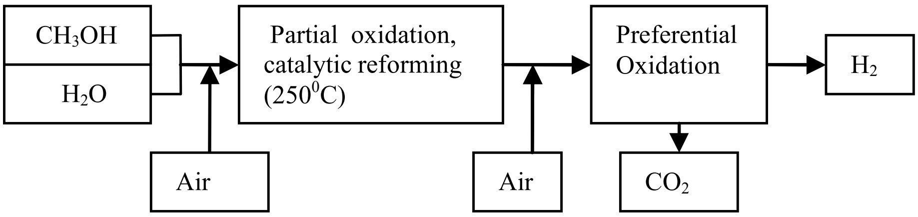


Fig. 10. Flow-sheet for a conventional OSRM process

methanol steam reforming. They observed that the activity values of the catalysts are similar to or greater than those found in the literature for common methanol steam reforming catalysts including noble metal-based catalysts. Deactivation of the catalysts seems to be independent of the preparation method and can be attributed to the concomitant effect of coke deposition and sintering.

Partial oxidation of methanol (POM) is an exothermic reaction (eqn. 30) and can be used for fast dynamic in methanol reforming [147].

$$CH_3OH + 0.5O_2 = CO_2 + 2H_2 \quad \Delta H^0 = -192 \text{ kJ mol}^{-1} \qquad (30)$$

But the formation of hot-spots in the catalytic bed is the main drawback, leading to catalyst sintering resulting in the activity loss [148]. Cu-based catalysts have been the most generally studied catalysts for partial oxidation of methanol [149]. Wang et al. [150] showed that $Cu_{60}Cr_{40}$ catalyst exhibits high CH_3OH conversion and H_2 selectivity as compared with other binary catalysts and the introduction of Zn promoter not only helps to increase the activity of the catalyst but also improves the stability of the catalyst, the highest of the activity of the ternary Cu/Cr/Zn is obtained with a relative composition of Cu/Cr (6:4)/Zn (10%).

Oxidative steam reforming of methanol (OSRM) combined SRM and POM which gives fast dynamics and generates high hydrogen concentrations (eqn. 31).

$$CH_3OH + 0.75\ H_2O + 0.125\ O_2 \rightarrow CO_2 + 2.75\ H_2 \quad \Delta H^0 = 0 \text{ kJ mol}^{-1} \qquad (31)$$

Reactors for this process operate autothermally, i.e. it does not require any external heating or cooling once the operational temperature is reached. For fast transient response, the methanol/oxygen ratio can be varied as in the case of the Hot-Spot reformer [151]. OSRM is combination of steam reforming and partial oxidation processes. Reactions are balanced in such a way that net energy requirement is zero ($\Delta H^0=0$). The schematic flow sheet for a conventional OSRM process is shown in Fig. 10.

Horny et al. [151] developed a compact micro-structured string reactor with catalytic brass wires for OSRM to produce hydrogen in auto-thermal mode for fuel cells. $CuCr_2O_4$ catalyst used in OSRM showed high activity, and selectivity to carbon dioxide and hydrogen. The selectivity towards carbon dioxide was 98% for a methanol conversion of 91.5% being higher than predicted for the water-gas shift equilibrium. The string reactor presents nearly isothermal profile. The reactor presents a short start-up and a fast transient behaviour showing a rapid temperature change when adjusting the oxygen amount introduced into the reactor.

B. Ethanol reforming

Hydrogen is essentially produced by steam reforming (SR) of hydrocarbon fractions (natural gas, naphtha,) on an industrial scale. Replacing fossil fuels by biofuels for H_2 production has attracted much attention with an increased interest for bioethanol reforming [152]. Reforming of ethanol is a potential way to generate renewable hydrogen. Bioethanol can be easily produced in renewable form from several biomass sources, including plants, waste materials from agro-industries (molasses, corn, bole, etc.) or forest residue materials [153]. Moreover, a bioethanol-to-H2 system has the advantage of being CO_2 neutral [154]. Steam reforming, partial oxidation and auto-thermal reforming of ethanol can be illustrated by eqns. 32, 33 and 35 respectively.

Steam reforming is an endothermic process and requires energy input to initiate reactions [155]:

$$C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2 \quad \Delta H^0 = 174 \text{ kJ mol}^{-1} \qquad (32)$$

Alternatively, hydrogen can be obtained by partial oxidation of ethanol at a temperature of about 500

^{0}C according to the following reaction [156]:

$$C_2H_5OH + 1.5O_2 = 2CO_2 + 3H_2 \quad \Delta H^0 = -552 \text{ kJ mol}^{-1} \qquad (33)$$

However, hydrogen selectivity of ethanol partial oxidation is generally low. In order to enhance hydrogen production, autothermal reforming can be applied. Autothermal reforming, also called oxidative steam reforming, is a combination of ethanol oxidation and steam reforming. The total reaction of autothermal reforming of ethanol can be written as eqn. 34 [157,158]:

$$C_2H_5OH + 2.25\, H_2O + 0.375\, O_2 = 2CO_2 + 5.25\, H_2 \quad \Delta H^0 = -30 \text{ kJ mol}^{-1} \qquad (34)$$

This reaction indicates that the autothermal reforming not only attains thermally sustained operation, but also maximizes hydrogen production.

Dolgykh et al. [159] investigated the catalytic activity of copper chromite catalysts in the process of ethanol steam reforming at low temperatures using 12 wt.% C_2H_5OH in water mixtures. They found that without catalyst appreciable hydrogen production starts at the temperatures above 300 ^{0}C and reaches hydrogen yield 0.3 g H_2 (kg cat)$^{-1}$ (h)$^{-1}$ at 400 ^{0}C. Use of catalysts allows reaching the hydrogen productivity 9-25 g H_2/(kg cat.)/(h) at 250-300 ^{0}C.

2.2.3 Water gas shift reaction

The production of hydrogen mainly relies on the liquid fuels reforming processes. Reformate gas (CO/H2 mixture) contains significant amount of CO (10-15%) [160-162]. Water gas shift (WGS) reaction (eqn. 35) is used to enrich hydrogen in the reformate stream and decrease the CO content. The water gas shift reaction is presented by:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41.1 \text{ kJ/mol} \qquad (35)$$

is mildly exothermic, with an adiabatic temperature rise of 8-10 ^{0}C per percent (wet gas) CO converted to CO_2 and H_2. Industrial WGS reaction is carried out using two different catalysts in two stages (high temperature WGS and low temperature WGS) with inter-bed cooling [162] as shown in Fig. 11.

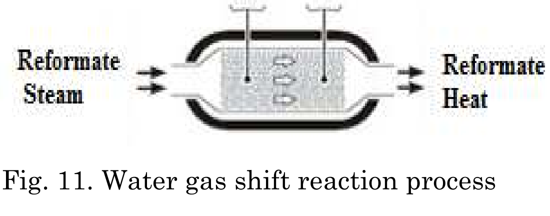


Fig. 11. Water gas shift reaction process

Recently, low-temperature WGS reaction has attracted renewed interest due to the increasing demands for high-purity hydrogen for application in fuel-cell systems [162]. Cu-based spinel-type oxides [163,14-15] have received much attention in the last years owing to their high catalytic activity and durability at low temperatures to that of conventional, $Cu/ZnO/Al_2O_3$ for WGS reaction. Boumaza et al. [15] prepared a series of AB_2O_4 spinel catalysts by the co-precipitation method where B is commonly Al, Zn, Mn, Co, Cr and Fe. The catalysts were tested in the water gas shift reaction at atmospheric pressure. They ranked the oxide systems in the following order follows: Cu-Cr>Cu-Fe>>Zn-Al>Cu-Co at 250 ^{0}C. Significant improvements to the activity of skeletal copper catalysts for the water gas shift reaction were achieved by adding small amounts of Cr_2O_3 to the surface of copper [145].

2.3 Clean energy production

In the last few years new extremely stringent standards in emission legislation have required the development of new technologies for both clean energy production and emission control, either for industrial or for household appliances. Among the processes of energy production, high temperature combustion of fossil fuels is the most conventionally used [164-165]. During combustion, the formation of pollutants, in particular NO_x, is favoured due to the high temperatures attained [164,166]. Catalysis can offer the possibility to realize clean combustion in an interval of temperature in which the formation of given pollutants, e.g. NO_x, is depressed [164,165,167]. The choice of the appropriate catalyst is a fundamental step for improving the combustion, in terms of both activity and selectivity, limiting the formation of hazardous by-products [164,165].

The performances of Pt or Pd with respect to hydrocarbons combustion, in particular methane, have been largely studied by many authors [168,169]. The use of noble metals has stringent effects on the commercial cost of the whole catalyst, so that a great interest has turned to oxide-based catalysts [170]. Various oxides containing Co, Cr, Mn, Fe, Cu, and Ni are potentially interesting for catalytic combustion appliances [171]. Mixed oxide compositions show better activity than the single oxide ones [164]. The copper chromite catalyst offered interesting performances for CH_4 combustion [170] in view of such application. Comino et al. [170] studied complete oxidation of methane over two unsupported over copper chromite ($CuO-Cr_2O_3$) and alumina-supported one ($CuO-Cr_2O_3/Al_2O_3$). The unsupported catalyst showed better activity while supported one was very stable. Kinetic study provided a value of the activation energy about110 kJ/mol.

To increase the combustion efficiency of gasoline, several additives such as antioxidants, oxygenates and other functionalities are added. Most prominent additives among them are oxygenates, which are a class of oxygen containing compounds used as blending components to improve the combustion efficiency of the fuel [172]. Blending of oxygenates with the gasoline results in complete combustion, thereby reducing the CO and hydrocarbon (HC) emissions to a large extent under full load operating conditions [172]. Alcohols such as ethanol and methanol were recognized as octane boosters in 1920. Tertiary alkyl ether based oxygenates such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl ethyl ether (TAEE), tertiary amyl methyl ether (TAME), isopropyl tertiary butyl ether (IPTBE) and diisopropyl ether (DIPE) are other possible candidates for gasoline blending [173].

Methyl-tertbutyl-ether or isooctane (MTBE) is a clean energy resource and an alternative fuel. The selective synthesis of isobutyl alcohol (iBuOH) has recently gained an increasing interest because this substrate is a potential precursor of gasoline additives such as methyl-tertbutyl-ether or isooctane. iBuOH may be directly synthesized from syngas through the higher-molecular-weight alcohols synthesis carried out at high temperature and pressure over copper chromite catalysts [174].

Another most promising clean energy source is methanol. Methanol decomposition or reforming can provide clean fuel for fuel cells, automobiles, power generation, chemical processes and material processing (see section 2.3.1 and 2.3.3.1). The use of methanol as a fuel additive and in MTBE production has renewed interest in the search for improved methanol processes.

2.3.1 Methanol synthesis

Commercially methanol is synthesized from synthesis-gas using $Cu/ZnO/Al_2O_3$ catalysts (eqn. 36) [164]:

$$CO + 2H_2 \rightarrow CH_3OH \qquad (36)$$

The stability of Cu/ZnO catalysts has been discussed in view of the sintering of Cu via brass formation [175-178]. It is suggested that the sintering of Cu via brass formation could be prevented in $Cu-ZnO-Cr_2O_3$ catalysts obtained from Cu-Zn-Cr hydrotalcite-like precursor [179]. Venugopal et al. [180] synthesized a series of $Cu-ZnO-Cr_2O_3-Al_2O_3$ (Zn/Cr = 1.2-6.8) catalysts using hydrotalcite like layered double hydroxide precursors for conversions of synthesis gas to dimethyl ether in a single step process. Single step dimethyl ether (DME) synthesis from syngas has technological advantages over the two step process of methanol synthesis (eqn. 37) and dehydration of the methanol (eqn. 37).

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad (37)$$

The advantages being high one-through conversion in thermodynamic point of view [181] and low operating cost in the economic point of view [182]. Venugopal et al. [180] concluded that the high syngas conversion over Cu:Zn:Cr = 7:6:1.88 (mol ratios) catalyst was attributed to the high copper metal surface area as compared to the other catalysts and higher yields of DME was obtained in single step over a Cu-Zn-Cr (Zn/Cr = 3.3) with γ-Al_2O_3.

Ohyama and Kishida [183] prepared slurry-phase methanol via methyl formate at 100 0C and an initial pressure of 5 MPa using alkoxide and a physical mixture of CuO and Cr_2O_3 as a catalyst. Methanol synthesis is a highly exothermic reaction and thermodynamically favourable at lower temperatures. Thus, if a catalyst which is highly active at low temperatures is available and the heat of reaction is efficiently removed, methanol production with high per-pass conversion could be achieved. Slurry-phase methanol synthesis using alkali metal alkoxide and copper-based compound as a catalyst has been investigated by several researchers [184-188]. In this system, methanol is considered to be formed through the formation of methyl formate by the following two reactions (eqns. 38 and 39) which occur concurrently:

$$CH_3OH + CO \rightarrow HCOOCH_3 \qquad (38)$$
$$HCOOCH_3 + 2H_2 \rightarrow 2CH_3OH \qquad (39)$$

Here, the alkali metal alkoxide is a well-known catalyst for carbonylation of methanol to methyl formate (reaction 3.2) [189-190], whereas copper-based materials such as copper chromite reported to function as catalysts in the hydrogenolysis of methyl formate to methanol (reaction 3.3). Therefore, employing a mixture of both catalysts, methanol can be produced in a single reactor from H_2 and CO according to the above sequence of reactions [190-195]. Ohyama [196] reported excellent activities of copper chromite catalyst for the production of methanol in liquid phase in presence of potassium methoxide, which involves carbonylation of methanol to methyl formate and consecutive hydrogenation of methyl formate to methanol. The effects of reaction variables on the catalytic performance are investigated under the conditions of 373-423K temperature and 1.5-5.0Mpa pressure. Huang and Wainwright [145] observed significant improvements to the activity of skeletal copper catalysts for the methanol synthesis achieved by adding small amounts of Cr_2O_3 to the surface of copper. Slurry phase concurrent synthesis of methanol has also been described by Palekar [192] using a potassium methoxide/copper chromite mixed catalyst which operates under relatively mild conditions (100-180 ^{0}C, 30-65 atm).

2.3.2 Fast pyrolysis of biomass

Biomass, a form of renewable sources, can be transformed via thermochemical processing such as fast pyrolysis into liquid bio-oil, which is a storable and transportable fuel as well as a potential source of a number of valuable chemicals that offer the attraction of much higher added value than fuels. Bio-oil is successfully used as boiler fuel and also showed promise in diesel engine and gas turbine applications. Upgrading bio-oil to a quality of transport liquid fuel still poses several technical challenges and is not currently economically attractive. Some chemicals, especially those produced from the whole bio-oil or its major fractions offer more interesting commercial opportunities. The main properties and applications of bio-oil have been reviewed by Czernik and Bridgwater [197].

Bio-oils are complex hydrocarbon mixtures known to contain significant amount of oxygenated compounds including lignin derivates which ultimately lead to low heating values, low stabilities, high viscosity, low volatility and low pH. Therefore, in order to improve the quality of the bio-oils in terms of heating values, viscosity and storage stability, the oxygenates and the large molecules derived from lignin need to be reformed into more useful products. Catalytic pyrolysis is a promising approach for upgrading bio-oil involves direct catalytic conversion in the vapour phase at low pressure via vapour cracking and reforming. Incorporating a catalyst into the pyrolysis unit is expected to enhance deoxygenation, cracking and reforming reactions. The selection of appropriate catalysts plays a vital part in bio-oil upgrading. The severity of these catalytic reactions often influences the liquid product distribution and depends largely on types of catalyst and other processing parameters. Pattiya et al. [198] used copper chromite catalyst for cassava rhizome as the biomass feedstock for upgrading bio-oil. They observed that the copper chromite was selective to the reduction of most oxygenated lignin derivatives.

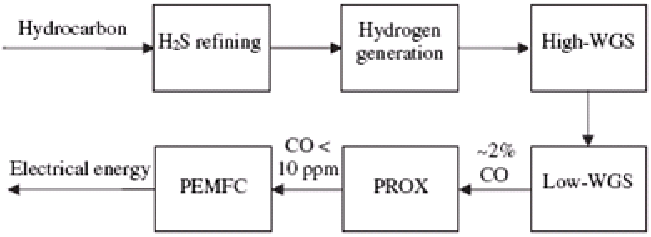


Fig.12. Flow diagram of H_2 purification by CO-PROX

2.3.3 Preferential oxidation of CO

The preferential oxidation (PROX) process is one of the most effective methods for the removal of CO trace from the reformate stream. PROX of CO is a reaction to convert CO in a H_2-rich gas mixture to CO_2 with minimal H_2 consumption. Therefore, preferential oxidation process is an indispensable step to reduce the concentration of CO to 10 ppm level in a H_2 generation process [199]. The flow diagram of hydrogen purification by CO-PROX is shown in Fig. 12.

The following reactions (eqns. 40 and 41) can occur in the PROX system.

$$CO + \frac{1}{2} O_2 \rightarrow CO_2 \quad \Delta H^0 = -282.98 \text{ kJ/mol} \qquad (40)$$

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \quad \Delta H0 = -241.82 \text{ kJ/mol} \qquad (41)$$

CO is a typical by-product in the production of hydrogen by reforming of alcohols or hydrocarbons and must be reduced down to ppm levels in order to be used as feed for proton-exchange membrane fuel cells. Up to date, several options for CO removal have been studied and the selective oxidation (CO-PROX) is considered one of the most straightforward and cost-effective methods to achieve acceptable CO concentrations (eqn. 42).

$$H_2 + CO + O_2\,(air) \rightarrow CO_2 + H_2 \qquad (42)$$

Many industrial applications using H_2 as a feedstock require a H_2 stream containing a little CO. These include ammonium synthesis, fuel cell and semiconductor processing etc. because CO is a poison in these processes. Cu/Cr/Ba based catalysts were found to be non-precious metal catalysts that can selectively oxidize CO in a H_2-containing stream [200].

2.4 Vehicular Pollution control

Vehicles play a very important role in the development of a nation since they are widely used to transport goods, services and people. But there is a major negative effect of the emissions of pollutants from the exhaust of the vehicle engines [201]. The complex reactions occurring in the internal combustion engine can be represented by eqn. 43:

$$Fuel\,(HC) + Air\,(O_2{+}N_2) \rightarrow CO_2 + H_2O + N_2 + O_2 + CO + HC_{(unburned)} + NO_x \qquad (43)$$

Engine exhausts consist of a complex mixture, the composition depending on a variety of factors such as: type of engine (two- or four-stroke, spark- or compression -ignited), driving conditions, e.g. urban or extra-urban, vehicle speed, acceleration/ deceleration, etc. Table 1 reports typical compositions of exhaust gases for some common engine types [202].

It is clear from the table 1 that there are three main primary pollutants, CO, HC and NO_x from the spark ignited engines while NO_x and particulate matter (PM) are the major composition of the diesel engine exhausts. Because of the large vehicle population, significant amounts of HC, CO, NO_x and PM are emitted in the atmosphere. These pollutants have harmful effects [203-205] on living beings, materials, environment and climate change. Morover once emitted into the atmosphere, primary pollutants could be the precursors for the formation of more dangerous secondary pollutants such as smog, aerosol, ground level ozone, peroxy-acetyl-nitrate (PAN), polycyclic aromatic hydrocarbon (PAH) etc. by photochemical reactions [206].

The catalytic control of these pollutants has been proposed as an end of the pipe treatment technology. The benefits of catalytic purification of primary pollutants to atmospheric gases (CO_2, N_2, O_2 and H_2O) using three way catalyst (TWC) for spark ignited engine [207] and catalytic filter for diesel engine [41] exhaust have been documented.

2.4.1 Purification of spark ignited engine exhaust

Automotive catalytic converters having TWCs consisting of noble metals (Pt, Pd, Rh) are used for purification of exhaust gases of gasoline driven vehicles [208]. Catalysts simultaneous carry out both reduction and oxidation reactions that convert exhaust pollutant to normal atmospheric gases. The reactions can be presented by following eqns. 44, 45 and 46:

The oxidation of CO and HC :

$$2CO + O_2 \rightarrow 2CO_2 \qquad (44)$$

$$HC + O_2 \rightarrow CO_2 + H_2O \qquad (45)$$

The reduction of NOx with CO :

$$NO_x + xCO \rightarrow 1/2N_2 + xCO_2 \qquad (46)$$

Because of the abatement of all the three primary pollutants catalyst used is known as TWC. Although noble metal-based catalysts have dominated this area, efforts were always put in towards development of low cost non-noble metal-based catalysts [209] and modification of TWC to decrease precious metal percentages by means of nanotechnologies [210] and in combination with base metals [211]. Among such catalysts copper chromite has been observed to be an attractive alternative to presently used noble metals in view of availability, lower cost and comparable activity [212-216,9] for purification of vehicular exhaust.

Cu-Cr catalyst system has been studied extensively for reactions such as the oxidation of CO [217], hydrocarbons [213], alcohols and aldehydes [218], sulfurated hydrocarbons [219], and chlorinated hydrocarbons [220] as well as NO reduction [214]. Kapteijn et al. [214] reported that Cu-Cr catalysts showed higher CO oxidation and NO reduction activity than single oxide catalysts based on Cu, Ni, Co, Fe, Mn, Cr. Stegenga et al. [212] have found that a monolith-supported 10 wt% $Cu.Cr/Al_2O_3$ catalyst showed a three-way catalytic activity comparable to that of noble metal catalysts operated under the same conditions.

2.4.1.1 Oxidation of carbon monoxide

Carbon monoxide (CO) can prove perilous without giving any physical indication because it is a colorless, tasteless and odourless gas. It is chemically inert under normal conditions with estimated atmospheric mean life of about 2.5 months [221]. This, poisonous gas can seriously

Table 1. Example of exhaust conditions for two- and four-stroke, diesel and lean-four-stroke engines [202]

Exhaust components and conditions[a]	Diesel engine	Four-stroke spark ignited-engine	Four-stroke lean-burn spark ignited-engine	Two-stroke spark ignited-engine
NO_x	350-1000 ppm	100-4000 ppm	≈1200 ppm	100-200 ppm
HC	50-330 ppmC	500-5000 ppmC	≈1300 ppm C	20,000-30,000 ppmC
CO	300-1200 ppm	0.1-6%	≈1300 ppm	1-3%
O_2	10-15%	0.2-2%	4-12%	0.2-2%
H_2O	1.4-7%	10-12%	12%	10-12%
CO_2	7%	10-13.5%	11%	10-13%
SO_x	10–100 ppm[b]	15-60 ppm	20 ppm	≈20 ppm
PM	65 mg/m^3			
Temperatures (test cycle)	r.t.-650 ^{0}C(r.t.–420 ^{0}C)	r.t.-1100 ^{0}C [c]	r.t.-850 ^{0}C	r.t.-1000 ^{0}C
GHSV (h^{-1})	30,000–100,000	30,000–100,000	30,000–100,000	30,000–100,000
λ (A/F)[d]	≈1.8 (26)	≈1 (14.7)	≈1.16 (17)	≈1 (14.7)[e]

[a] N_2 is remainder.
[b] For comparison: diesel fuels with 500 ppm of sulphur produce about 20 ppm of SO_2.
[c] Close-coupled catalyst.
[d] λ defined as ratio of actual A/F to stoichiometric A/F, $\lambda = 1$ at stoichiometry (A/F = 14.7).
[e] Part of the fuel is employed for scavenging of the exhaust, which does not allow to define a precise definition of the A/F.

affect human aerobic metabolism because of its affinity to haemoglobin being 210 times greater than that of oxygen and so, if its concentration becomes higher than 0.0998% by volume in atmosphere, it can lead to the failure of the process of combination of oxygen with the haemoglobin resulting ultimately in respiratory failure and consequent death. It forms a very stable compound called carboxyhaemoglobin (COHb) in blood whose 1-2% concentration can cause headache, fatigue, drowsiness and may have effect on human behavioural performance, 2-5% concentration may cause impairment of time interval discrimination, visual acuity, brightness discrimination and certain other psychomotor functions which may lead to accident on roads. 5-10% concentration can lead to changes in cardiac and pulmonary functions and 10-80% can cause coma, respiratory failure and death [222]. It not only affects human beings but also vegetations by interfering with plant respiration and nitrogen fixation. The vehicle emission is the major source of CO in urban air, accounting for slightly over half of all the anthropogenic air pollutants.

The catalytic oxidation of carbon monoxide with the object of reducing air pollution is actually an important consideration when one thinks in terms of automobile emission control [223]. Copper chromite is found to be most promising among non-noble metal catalysts and exhibits comparable activity for CO oxidation to that of precious metals based auto exhaust purification catalyst [224]. The catalyst converts CO to harmless product CO_2, found in the atmosphere which is useful to the plants. Copper chromite catalysts have been studied in detail for CO oxidation. The studies have been attributed to the catalytic activity and stability tests [225,226], postulating mechanisms [227], characterization of catalysts [228,229], rapid evaluation of the catalysts [230], search for the active sites on the catalysts [231,232], kinetics of the reaction [228,233], catalysts deactivation [229,234], etc. Pantaleo et al. [235] reported the catalytic tests in CO oxidation indicated a synergetic effect between copper and chromium in the mixed oxides supported on silica and calcined at 500 ^{0}C. Xavier et al [236] found that Cu-Cr based catalysts are effective for CO oxidation at lower temperatures. Park and Ledford [228] reported that the Cu/Cr/Al_2O_3 catalyst of Cr/Al = 0.054 showed the highest CO oxidation activity due to the formation of $CuCr_2O_4$ which was more active than the CuO phase. Higher loadings yielded higher activities per amount of catalyst, but above 10 wt.% Cu+Cr the intrinsic activity per metal atom decreased. Li et al. [229] synthesized monodispersed spherical $CuCr_2O_4.CuO$

encapsulated Bi_2O_3 nanoparticles with a homogeneous core/shell structure by using monodispersed Bi_2O_3 nanospheres as templates with a pre-coating of NH_4^+ on the surfaces of Bi_2O_3 nanoparticles. The prepared core/shell nanoparticles exhibit promising catalytic activities towards the oxidation of CO. Therefore, the Bi_2O_3/$CuCr_2O_4$-CuO core/shell nanomaterials provide promising for pollution treatment in car exhaust purification.

Pre-reduced copper chromite catalysts have been shown to be more active than unreduced ones [232]. Pre-reduction with H_2 produced higher activity than prereduction with CO, which can be attributed to a higher surface concentration of active species after the former treatment. Activity results, together with TPR and XPS characterization point out that both Cu^0 and Cu^+ species are the primary active sites of CO oxidation while surrounding Cr_2O_3 phase can prevent Cu^0 and Cu^+ from being oxidized to Cu(II), which will limit the catalytic activity. The activated carbon impregnated with Cu/Cr/Ag is a good catalyst for CO oxidation at low temperature (<70 ^{0}C) [234]. Stegenga et al. [235] reported that Cu-Cr oxide based converters are superior to precious metal based device for CO oxidation.

Hertl and Farrauto [227] employing infrared spectroscopic, gravimetric, and kinetic techniques studied the mechanism of oxidation of CO on a copper chromite catalyst. They showed that surface species involved in reaction are either a copper carbonyl, at temperatures above 80 ^{0}C or a carbonate associated with chromium at higher temperatures above 200 ^{0}C. A thorough kinetic study [228] of the two reactions, including the phenomena of N_2O formation and the reduction of N_2O with CO, provided a kinetic model that accounts for the observed reaction behaviour of the catalyst, and which can serve to model a converter based on the Cu/Cr catalyst. The experimental results indicate that these oxidic Cu/Cr catalysts have a three way performance and that they may find application in the purification of exhaust gases of low sulphur contents. Prasad and Rattan [233] studied kinetics of oxidation of CO over a novel copper chromite catalyst in a compact bench scale reactor. Preparation details of the catalyst are given elsewhere [232]. On the basis of the experimental findings they proposed the following empirical rate expression (eqn. 47):

$$\text{Rate} = 2.02\text{x}10^4 \exp(-12290/RT)(C_{CO})^{0.7} \qquad (47)$$

Phosphorous and sulphor originating from fuel and engine oil may lead to degradation of automotive exhaust purification catalysts. Shelef et al. [236] have documented the effects of various poisons on the durability of various catalysts. Mechanisms of catalyst deactivation have been reviewed by Bartholomew [237]. SO_2 can be severe inhibitor for the oxidation of CO and hydrocarbons [238] in the temperature range (400-600 ^{0}C) of use of base metal catalysts in automobiles. Kim et al. [239] studied the deactivation of supported copper chromite catalyst by SO_2 and water vapour and found that the degree of deactivation of the catalyst due to SO_2 was more severe than water vapour. Lauder [240] reported that small amounts of noble metals present in base metal perovskites significantly improve their resistance to poison.

General Motors company preferred copper chromite catalyst for exhaust emission control in the beginning due to its much lower cost in comparision to platinum [208]. It was later shown to have inferior activity and was susceptible poisoning by sulphur present in the fuel. By the time catalysts were introduced in 1974, all car companies had adopted platinum based systems for emission control.

The main reason for withdrawal of base metals from catalytic converter formulations was their undesirable behavior in cycled transient conditions and their high susceptibility to deactivation by lead, sulphur and water [207]. The huge decrease in sulphur content in the lead free fuels and progress in oxide catalyst synthesis, have allowed copper chromite to be reconsidered for practical applications [241] in the catalytic converter.

2.4.1.2 Oxidation of hydrocarbon

Hydrocarbons such as benzene, formaldehyde, hazardous polycyclic aromatic hydrocarbons (PAHs), and nitropolycyclic aromatic hydrocarbons (NPAHs), methane, butane, hexane, soot, propene, decane, toluene etc. are mainly originated from imperfect combustion of fossil fuels such as petroleum and coal [242]. (PAHs) and (NPAHs) have been identified as potent mutagens and possible carcinogens. Both PAHs having 4 rings or more and NPAHs are detected in particulates exhausted from diesel and gasoline-engine vehicles, while PAHs of lower molecular weights (3 rings or below) were detected in the gaseous phase in the atmosphere and unburned diesel fuel [243-245]. Copper chrmomite is the active catalyst for the pyridine oxidation and NO_x control [246].

Methane is a potent greenhouse gas. It has a global warming potential (GWP) 23 times greater than carbon dioxide. Reducing methane emissions would lead to substantial economic and environmental benefits. Methane is emitted from a variety of anthropogenic activities, such as fossil fuel production, biomass combustion, operation of natural gas vehicles (NGVs), and waste management [247]. For example, in mine ventilation air, the methane concentration is 0.1-1vol% [248]. In natural-gas-fuelled vehicles, which are increasingly popular in some countries because of their low emissions of NO_x and particulates [249 -251], the unburned methane concentration in the exhaust is around 0.3 vol.% [252]. It is estimated that 60% of global methane emissions are related to human-related activities [253]. Catalytic combustion (eqn. 48) is considered to be an effective approach to methane emissions abatement [254].

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (48)$$

Hui et al. [255] showed that multi-transition-metal-(Cu, Cr, Ni, and Co)-ion-exchanged zeolite 13X catalysts outperformed single-ion-exchanged and acidified 13X catalysts and that lengthening the residence time led up to 100% conversion at a relatively low temperature of 500 ^{0}C. The enhanced catalytic activity in the multi-ion-exchanged catalysts was attributed to the presence of exchanged transition ions instead of acid sites in the catalyst.

Comino et al. [170] found higher activity of $CuCr_2O_4$ for CH_4 combustion in the temperature range 300-700 ^{0}C at constant CH_4/air ratio of 1:30 and constant methane content, 1.2%. Ismagilov et al. [256] reported higher catalytic activity of Cu-Cr-O catalyst for complete oxidation of n-butane in a micro-channel reactor. According to Solovev [41] the catalysts for n-hexane conversion are arranged in the order of activities are expressed as follows: $CuCr_2O_4 > CuCo_3O_5 > CuMnO_3 > Co_3MnO_6$. Chien et al. [213] repoted that the Cu-Cr/γ-Al_2O_3 catalyst is highly active for oxidation of CO as well as for propene also (eqn. 49).

$$2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O \qquad (49)$$

The activity of propene oxidation over Cu-Cr/γ-Al_2O_3 catalysts increases with increasing heat-treatment temperature in an oxidizing atmosphere. The activity of propene oxidation on the CuO catalyst reaches a maximum at a copper content of about 10 wt.-% and that on the Cr_2O_3 catalyst reaches a maximum at a chromium content of about 25 wt.-%. Harrison et al [257] studied the preparation, characterization, and catalytic activity of Cr(VI)-and Cu(II)-doped tin(IV) oxide catalysts. The catalysts, particularly the mixed Sn-Cu-Cr-O catalysts, exhibit comparable activity to conventional platinum catalysts for CO and hydrocarbon oxidation.

2.4.1.3 NO_X abatement

Oxides of nitrogen (NO_x) consist of N_2O, NO and NO_2 pollutants which are emitted from both natural and anthropogenic sources in large quantities. Enormous concern over the role of NO_x, as one of the primary pollutants for the green house effect, on ozone formation and depletion in stratosphere, on formation of photochemical smog, and acidic precipitation has received increasing attention since 1970s because of its detrimental effect on life on earth in general [258]. If NO_x is prevented from entering the atmosphere, most of the down-stream effects of pollution can be eliminated. Copper chromite has been recognised as the active catalyst for the NO_x pollution control [259,260].

Nitrous oxide (N_2O) is a compound that during the last decade has been recognized as a potential contributor to the destruction of the ozone in the stratosphere and acknowledged as a relatively strong greenhouse gas [261,262]. The continuous increase of its concentration, both due to natural and anthropogenic sources (adipic acid production, nitric acid production, fossil fuels, biomass burning) and longer atmospheric residence time (150 years), entails the need of developing efficient catalysts for its decomposition (into nitrogen and oxygen). In recent years, spinel-type oxides such as $CuCr_2O_4$ have been the subject of increasing fundamental and applied research because of their good stability and intrinsic catalytic activity [259]. The two most toxic oxide gases of nitrogen are NO and NO_2 of which NO_2 is known to be more toxic. NO_x are These oxides produced by the high temperature combustion of fuels that use air as an oxidant, through endothermic oxidation of N_2 by O_2. Automotive vehicles as well as industries are also the major sources of NO_x emission [263,264].

NO plays a major role in the photochemistry of the troposphere and the stratosphere [265]. The photochemical complex HC-NO_x-O_x is formed during the HC interactions in the photolytic cycle of NO; the mixture of products generated is called "photochemical smog" and contains O_3, CO, peroxyacetyl nitrates (PAN), alkyl nitrates, ketones, etc [265]. The chemical depletion of ozone, in an important part due to nitrogen oxide species, is a prolonged phenomenon [266]. Carcinogenic products are also formed during these reactions. NO_2 is linked to causing bronchitis, pneumonia, susceptibility to viral infection, and alterations to the immune system [267]. It also contributes to acid rain, urban smog, and ozone [268]. Therefore, it is important to control the emission of such gases to comply with stringent emission standards. The three way catalytic (TWC) reduction of NO in the presence of CO, HC and/or hydrogen is typical of automotive pollution control [265]. Shelef and Gandhi [269] first investigated the reduction of NO with hydrogen on copper chromite catalysts. NO reduction by CO has been examined over supported Cu-Cr systems by sevaral workers [209,235,270]. Lee at al. [271] observed maximum activity for NO decomposition over co-impregnated copper chromite on mordenites at 450 ^{0}C. For the NO + CO reaction, the catalytic performance of copper-supported catalyst was significantly affected by the addition of Cr. The Cu-Cr system exhibited an overall better performance than the single metal catalytic system (Cu, Co, and Ni) and three-way catalytic converter [209,235]. The characteristics of CO and NO molecules at Cu^{2+} and Cr^{3+} ion sites on the $CuCr_2O_4$ (100) surface have been studied by Xu et al. [272]. They found that CO/NO mixture adsorb selectively at the Cu^{2+} ion site and simultaneously at the Cr^{3+} ion site, respectively. Stegenga et al. [235] investigated a Zr -stabilized Degussa monolith prepared by using washcoats corresponding to 10 wt% Cu-Cr loading on Al_2O_3 or 2.5 wt% La-stabilized Al_2O_3. These monoliths had behaviour typical of three-way catalysts.

2.4.1.4 Volatile organic compounds abatement

Volatile organic compounds (VOCs) are the carbon containing compounds which have significant vaporization due to high vapour pressure at ambient conditions [273]. Being volatile they enter the atmosphere and are harmful to human beings and environment because of their toxicity and malodorous nature. These are emitted from many industrial processes, transportation and house-hold activities and are considered as an important class of air pollutants [274]. Many VOCs have been proved to be carcinogenic and mutagenic and contribute to stratospheric ozone depletion [275]. Moreover, once emitted into the atmosphere, VOCs could be the precursors for the formation of secondary pollutants such as smog, aerosol, ground level ozone, peroxy-acetyl-nitrate (PAN), and polycyclic aromatic hydrocarbon (PAH) etc. by photochemical reaction [276]. Because of these negative effects, legislation has been introduced in many countries setting very low emission limits for VOCs in process exhaust e.g. Occupational Safety and Health Administration Permissible Exposure Level (OSHA PEL) for toluene is 100 ppm in the workplace [277]. Therefore, the proper control, removal, and reduction of the emission of VOCs are the crucial tasks for the protection of the environment.

Catalytic combustion is a promising way to control the emissions of the VOCs [278]. Catalytic combustion processes (Fig.13), typically achieve complete destruction at temperatures around 350-500 ^{0}C, which are much lower than those used in thermal combustion (800-1200 ^{0}C) [279]. The lowering of reaction temperatures leads to several advantages in terms of environmental impact as well as energy saving: very low production of secondary pollutants (i.e., NO_x and micropollutants such as dioxins from chlorinated compounds) and reduction of fuel costs [275]. Moreover catalytic combustion exhibits advantages such as high efficiency, ultra low pollutant emissions, stable combustion, and so on [280]. The coupling of a low-temperature oxidation catalyst with an improved combustion technology can lead to further decrease of reaction temperatures at which the complete destruction of VOCs is obtained [280].

Among VOC, ethyl acetate is a key component in ink manufacture. The catalytic combustion of ethyl acetate has been investigated by Mazzocchia and Kaddouri [9] using undoped and Mn- or Ba-doped copper chromite catalysts. Good conversion reported even at low temperatures (180-240 ^{0}C). While in the presence of molecular oxygen the only product observed was CO_2, when the reaction has been carried out in the absence of oxygen (with lattice oxygen alone) noticeable amounts of CO were also detected [281]. The synergic effects of the combustion catalyst Ba-CuO-Cr_2O_3/Al_20_3 and ozone, used as strong oxidant species in the combustion of various VOCs such as, acrylonitrile,

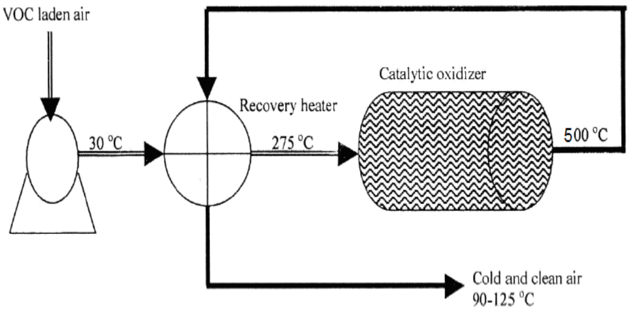


Fig. 13. Schematic drawing of catalytic oxidation of VOCs

methanol, styrene, toluene and 1,2-dichloroethane [278] .

With the Clean Air Act amendments requiring increased use of oxygenated compounds such as alcohols and ethers in motor fuels, the problem of effectively controlling the emissions caused by burning these substances has become a more pressing issue. Alcohols, both ethanol and methanol, are currently in use. Supported catalysts containing mixed oxides of copper and chromium prepared by a wet impregnation technique and supported on γ-alumina shows activity for complete oxidation of ethanol, acetaldehyde, and methanol-ethanol mixture [213].

Driven by the need for decreasing manufacturing cost and increasing resistance to poisoning of commercial catalysts for volatile organic compounds (VOCs) elimination, efforts have been made to develop metal oxide catalysts, which can exhibit activity similar or higher than of noble metal catalysts [281]. Among these catalysts the copper-chromite seems to be promising for the VOCs total combustion and it was also comparatively tested with noble metal catalysts [278,281]. Ismagilov et al. [256] fabricated microreactors with alumina coating impregnated with an aqueous solution of copper dichromate followed by drying and calcination at 450 ^{0}C to produce active copper chromite catalysts. They studied the effect of a copper dichromate concentration, number of impregnation cycles (1 or 2), and different after-treatments on catalytic activity and stability in complete oxidation of n-butane. They observed that even at much lower loadings of active metals, the catalytic activity of the prepared coatings, related to the volume of the alumina layer, is superior to that of pelletized catalysts. They concluded that the microreactors made according to their procedures can be used for a variety of small-scale total oxidation processes involving combustion of toxic and hazardous chemicals.

The industrial formaldehyde production all over the world produce huge amount of dusts and exhaust gases, which contains CO, dimethyl ether and methanol as main components. Therefore, their complete oxidation is of high importance for environmental protection. Cherkezova-Zheleva et al. [282] reported total oxidation of CO, dimethyl ether and methanol over copper chromite catalysts supported on γ-Al_2O_3. Copper chromite catalysts were evaluated by Heyes et al. [214] for the control of organic air pollutants responsible for malodorous process emissions. In laboratory tests, catalyst shows the ability to achieve and maintain high efficiency for the complete oxidation of n-butanal and methyl mercaptan [100 ppm in air]. The life of copper chromite could be extended by washing after partial deactivation by retained sulphur. Odour removal efficiencies (measured by olfactometry in terms of dilution to detection threshold values) at 340-415 ^{0}C was found mostly in the range 98.5-99.5%.

Organic Ion Exchange (IX) resins used to purify primary coolant of nuclear power plants contain high 137 Cesium and 60 Cobalt radioactivities. Direct fixation of spent IX resin wastes in polymer or slag cement matrices leads to increase in waste form volumes. For organic wastes, incineration appears to be most logical route to reduce waste form volumes. Pyrolysis of IX resins leads to release of radioactivity, SO_2, styrene, toluene, ethyl benzene and trimethyl amine to the off gases. The organic matter in off gases could be successfully oxidised by using $CuO.CuCr_2O_4$ catalysts at temperature above 475 ^{0}C and 22500 hr^{-1} space velocity [283].

2.4.2 Diesel exhaust gas purification

It is expected that the world market for diesel engines will grow significantly in the near future because of their superior thermal efficiency, durability, and reliability in comparison to the gasoline-powered engine. Exhausts of gasoline-fueled engines operated near stoichiometric air/fuel ratio have been successfully cleaned up by three-way catalytic systems, while the pollution by diesel -engine exhausts has become more and more serious in the last decade. For diesel emission control, three possibilities, i.e., oxidation, soot trapping and NO_x reduction, have been investigated [284]. Nitrogen oxides (NO_x) and particulate matters (PM) are main objectives to be removed from diesel exhausts. Since concentrations of CO and hydrocarbons are lower and that of O2 is higher in diesel exhausts than in gasoline-engine exhausts, three-way catalysts cannot remove NO_x from the diesel exhausts [285].

The ever-increasingly stringent exhaust emissions legislation requires an ever-increasing degree of efficiency of a catalytic converter. $CuCr_2O_4$ catalysts are found active for simultaneous catalytic removal of NO and diesel soot particulates [286]. Catalytic performance of $CuCr_2O_4$ for the simultaneous NO_x-soot removal reaction was investigated by Teraoka and Kagawa [285]. Selective catalytic reduction of NO_x with hydrocarbons (SCR-HC) has the potential in eliminating NOx emission from the oxygen rich (lean conditions) exhaust. $CuCr_2O_4$ is identified as one such catalyst active for SCR-HC [287]. The conversion of NO over Cu-Cr/γ-Al_2O_3 catalyst in the SCR of NO by NH_3 in the presence of sulfur dioxide was reported to be very high (95-100%) [288].

Recent studies have demonstrated a positive effect on the reduction of diesel emissions by adding oxygenated compounds [289]. Light catalytic gas oil (LCO) hydrotreating was performed by Tailleur and Caris [290] on a laboratory-scale trickle bed reactor to obtain a 15 ppm sulfur fuel. The fuel was then selectively oxidized using a CuCr/IP(4-PVP) catalyst in air at different operating conditions on a laboratory-scale continuously stirred tank reactor. The oxygenated and polyoxygenated compounds formed were measured and fuel stability was also measured. The results show a decrease in emissions by low-sulfur diesel oxidation, as well as the benefits of having a high selectivity toward ketone formation when using a CuCr/IP(4-PVP) catalyst [290].

2.4.2.1 Diesel soot oxidation

The diesel engines find widespread applications as power source in both automotive and stationary applications but their emissions of particulate matter (soot) and NO_x are responsible of severe environmental and health problems. Therefore, special attention has been paid to the reduction of soot particulate emitted from diesel engines. Soot can be effectively trapped by diesel particulate filters [291]. Traditional soot filters are made from metallic wires, ceramic foams, inorganic fibers, etc., which have a number of unsatisfactory features connected, in the first place with the complexity of regenerating the filters. The most effective solution to the problem is the combination in a single element of the functions of the soot filter and soot oxidant [292].

In recent years there have been attempts to develop catalytic coatings for soot filters, capable of improving their effectiveness and of oxidizing carbon particles directly in the soot filters. Solov'ev et al. [41,292] showed that the most reactive catalyst both in the model reaction of oxidising CO and hexane and in the burning of diesel soot present in the gaseous exhaust of internal combustion engines is copper chromite. Further they reported that regeneration of soot filters with catalytic coatings of copper chromite is possible even at the temperatures of exhaust gases from internal combustion engine.

2.5 Desulphurization of hot coal gas

The energy demand of the world, which increases in accordance with the rise in economic development, will have to be met by the prevalent energy sources, such as coal, new sources, as well as improvement of the efficiency of energy production technologies. However, the growth in energy production need not take place to the detriment of the environment, so that strict regulations on pollutant emissions have been imposed around the world. An integrated gasification combined cycle (IGCC) systems are being advanced today, due to their higher thermal efficiency and superior environmental performance and economics, compared to conventional plants [293]. The development of these systems depends on the ability to remove sulphur compounds, mainly H_2S, from the coal gas. During gasification process, about 95% of the sulphur contained in the coal is turned into H_2S and rest of them are converted into SO_2 [294]. The produced H_2S should be lowered from the typical gasifier output of 5000 ppm to the tolerable limit of 150 ppm [295]. H_2S being a very corrosive gas, could be damaging to the mechanical parts and the construction material at high temperatures and pressures under IGCC system conditions.

Although thermal efficiencies of 30-35% are typical for conventional pulverized coal plants, efficiencies of 43-46% may be easily attainable by IGCC with HGC. This improvement in efficiency would represent a significant decrease in the cost of electricity along with a reduction in emissions of sulphur compounds [296]. In addition, the method offers potential improvements for hydrogen fuelled solid oxide fuel cells (SOFC) and molten carbonate fuel cells (MCFC) technologies [297].

In order to have high efficiency in the IGCC system, removal of H_2S without cooling the coal gas is a very important task. These facts emphasises the importance of hot gas desulphurization. Hot gas desulphurization may be accomplished by using sorbents such as metal oxides that forms stable sulphides. Typically, these metal oxides are converted to sulphides during a sulphur-loading stage under reducing hot fuel gas conditions [298]. This reaction is represented generically by the following equation 50:

$$\text{Sulfidation:} \quad MO + H_2S \rightarrow MS + H_2O \qquad (50)$$

The ultimate capability of removing H_2S depends on the thermodynamic properties of the metal oxide. In addition, H_2S capacity, which is defined as grams of sulphur removed by 100 grams of sorbent, is an important parameter. Economic considerations require that the sulphided sorbent be regenerable according to the following generic reaction (eqn. 51):

Regeneration: $MS + 1.5O_2 \rightarrow MO + SO_2$ (51)

SO_2 must be captured and ultimately be converted to elemental sulphur or sulphuric acid. Copper oxide is able to achieve low levels of H2S in the clean fuel gas provided the sorbent is not reduced to elemental copper. This is because copper oxide readily reduces in high temperature reducing atmospheres, and elemental copper is an order of magnitude less active for sulfidation than Cu_2O and CuO [299].

Binary Cu-Cr-O oxides were studied as regenerable sorbents for high temperature fuel gas desulphurization by Li and Stephanopoulos [21]. $CuO\text{-}Cr_2O_3$ sorbents can remove H_2S from simulated coal-derived fuel gas to less than 5-10 ppmv in the temperature range of 650-850 ^{0}C. The presence of stable $CuCr_2O_4$ in $CuO\text{-}Cr_2O_3$ solids retains some copper in the Cu^{+2} or Cu^{+1} oxidation state, which can account for the high H_2S removal efficiency. A regenerable copper chromite sorbent with superior hot fuel gas desulfurization performance has been developed for IGCC applications by Abbasian and Slimane [300] in the temperature range of 550-650 ^{0}C. This sorbent is capable of achieving less than 5 ppmv H_2S concentration in the cleaned fuel gas.

2.6 Mercury capture from hot coal gas

Coal-fired utilities are the largest source of anthropogenic mercury emissions. Because of its high volatility, almost all the mercury present in coal is transformed into gas phase during combustion or gasification of coal. Control of mercury emissions from coal-fired power plants is a difficult task, in part due to its high volatility and its much lower concentration (5-20 μg/m3) in a large volume of flue gas. In addition, depending on the type of coal and combustion conditions, a majority of mercury in the flue gas can exist in the elemental form (Hg^0), which is more difficult to capture than its oxidized (Hg^{2+}) or particulate (Hg_p) forms. Jadhav [301] evaluated Nano Active sorbents ($CuO\text{-}Cr_2O_3$) for Hg capture. He explained the role of Cr, which would suppress the reduction of Cu in the presence of H_2 and would maintain Cu in Cu^{2+} state [4], which would have enhanced reactivity towards Hg. This experimental study has demonstrated that supported forms of binary oxides of Cu and Cr have showed their potential as effective Hg sorbents.

2.7 Removal of aqueous organic waste

The main polluting branches of industry are refineries, coke ovens, organic compounds production plants, pharmaceuticals factories, pulp and paper mills, textile, leather industries, etc. Waste water from these industrial and agricultural activities contains refractory organic pollutants such as plaguicides, organochloride compounds, phenols, detergents, polycyclic aromatic hydrocarbons, etc. that must be treated before discharge to comply with the environmental regulations. Water treatment technologies require revision, modernization and enriching by utilizing more effective methods and catalyst to achieve required standards for drinking water along with keeping in mind the conomic aspects [302]. Therefore, it is important to have efficient catalyst at our disposal for removal and oxidation of pollutants present in wastewater in reduced forms - NO^{2-}, NH^{4+}, phenols etc.

2.7.1 Wet oxidation of phenol

Among the harmful organic compounds in industrial wastewaters, phenol and phenolic substances have deserved more attention in the last two decades, because of their toxicity and the frequency of industrial processes producing waters contaminated by phenol. Moreover, phenol is considered to be an intermediate product in the oxidation pathway of higher molecular weight aromatic hydrocarbons, thus it is usually taken as a model compound for advanced wastewater treatments [303]. The conventional process of biological oxidation fails to destroy toxic and recalcitrant pollutants like phenol. Santos et al. [304] have reported the high detoxification of phenolic wastewater about 77% using a heterogeneous catalyst based on $CuO.Cr_2O_3$ at basic pH, obtained by adding sodium bicarbonate as buffer reactive (pH 8). Further, they observed that the catalyst was chemically and mechanically stable during long periods of time on stream, this point being of great importance for its industrial application. The oxidation of phenol in water over 26% CuO + 74% Cu-Chromite in a batch autoclave was investigated by Akyurtlu et al. [305]. They found copper chromite to be most active catalyst and concluded that depending on the operating conditions, the catalyst can facilitate complete phenol conversion within 90 min.

2.7.2 Ammonia removal

The formation of ammonia is inevitable during industrial-scale wet oxidation of wastewater if nitrogen-containing compounds (like: production of soda, nitric acid, urea; metallurgical industry; coal or biomass gasification) are present. The major source of ammonia emission has been attributed to the intensive farming areas and notably to livestock manure [306]. Ammonia is toxic for fishes and other marine organisms. It causes eutrophication in ponds and lakes. It has been recently studied for its role in the formation of a rural version of urban smog [307]. The ammonia-containing waste produced in industries is usually characterized by high concentration and high temperature, and is not treatable by biological methods directly [308]. Huang et al. [308] suggested wet oxidation as a promising means of pretreating wastewater containing ammonia at concentrations of up to 600 mg/L.

As most of the wet oxidation processes run at elevated pressure and temperature, running the heterogeneously catalysed oxidation of ammonia in the gas phase in a downstream reactor could protect the catalysts mainly from leaching and offers an economic alternative by avoiding loss of unused oxygen after depressurisation. Noble metal -containing catalysts [309] are used for wet oxidation processes, but they are very costly and insufficient stability against hydrothermal impact. Martin et al [310] reported oxidation of ammonia with air in steam atmosphere using Cu,Cr-containing supported and bulk copper chromite catalysts at 235-305 ^{0}C and 30-60 bar. Bulk copper chromite catalyst gave the best performance (86% conversion) at 305 ^{0}C, 45 bar and contact time of 1 second. It shows only slight changes in their structural phase composition, high contents of Cr (III) in a $CuCr_2O_4$ spinel phase and higher stability.

2.7.3 Nitrite Removal

Nitrite is a common pollutant in water whose principal source arises from fertilizers and industrial rejects causing ecological problems [311]. The world health organization guidelines required the levels of NO^{2-} and NO^{3-} in drinking water less than or equal to 3.3 and 44 mg L^{-1} respectively. The nitrite removal from water is a topic of great concern owing to its toxicity to the environment and detrimental to human health. NO^{2-} coming from industrial activities disturbs the ecological system and beyond a threshold concentration, it becomes an increasing problem [312]. High concentrations of nitrates in drinking water are harmful due to their reduction to nitrites (NO^{2-}) that combine with haemoglobin in the human blood to form the toxic compound of methaemoglobin [313]. The photoactive $CuCrO_2$ is low cost, easy to synthesize and exhibits a long term chemical stability in the nitrite conversion almost complete in less than ~5 h [314]. $CuCrO_2$ exhibits a long term chemical stability with a corrosion rate of 0.34 µmol m^{-2} $year^{-1}$ in KCl (0.5 M).

2.8. Burning rate catalyst for solid propellants

In recent years the Cu-Cr-O composites are found great promising in application as burning rate catalysts (ballistic modifier) for solid propellants used in defence (high explosives, ballistic missiles) [315] and space vehicles (rocket propellants) [316-318]. Solid composite propellants are mixtures of prepolymer (binder), aluminum fuel, oxidizer salts (e.g. ammonium perchlorate), and other components, including curatives, plasticizers, bonding agents, stabilizers and catalysts [319]. Even though added at few percent of the propellant binder, the catalysts used to control the burn rate are of high importance, since they allow improving the ballistics of rockets. Combustion of this system involves the decomposition of AP(ammonium perchlorate) and the binder and mixing and oxidation-reduction of the decomposition products.

Rajeev et al. [316] prepared Cu-Cr-O composite oxides via thermal decomposition of copper ammonium chromate and found that the propellant burning rate is enhanced by the addition of Cu-Cr-O composite oxides. Li et al. [10] used Cu-Cr-O nanocomposites as additives for the catalytic combustion of AP-based solid-state propellants, synthesized via a citric acid (CA) complexing approach. They showed that well-crystallized Cu-Cr-O nanocomposites could be produced after the CA-Cu-Cr precursors are calcined at 500 ^{0}C for 3 h. Addition of the as-synthesized Cu-Cr-O nanocomposites as catalysts enhances the burning rate as well as lowers the pressure exponent of the AP-based solid-state propellants considerably. Noticeably, catalyst with a Cu/Cr molar ratio of 0.7 exhibited promising catalytic activity with high burning rate and low pressure exponent at all pressures, due to the effective phase interaction between the spinel $CuCr_2O_4$ and delafossite $CuCrO_2$ contained in the as-synthesized Cu-Cr-O nanocomposites. Patil, et al. [320] synthesized p-type nano-CuO and $CuCr_2O_4$ by an electrochemical method and investigated the catalytic effect on the thermal decomposition behaviour of ammonium perchlorate (AP) as a function of catalyst concentration using differential scanning calorimetry. The nano-copper chromite ($CuCr_2O_4$) showed best catalytic effects as compared to nano-cupric oxide (CuO) in lowering the high temperature decomposition by 118 ^{0}C at 2 wt.%. They observed high heat released of 5.430 and 3.921 kJ g^{-1} in the presence of nano-CuO and $CuCr_2O_4$, respectively. The decrease in the activation energy and the increase in the rate constant for both the oxides confirmed the enhancement in catalytic activity of AP. They proposed a mechanism based on an electron transfer process for AP in the presence of nano-metal oxides.

2.9. Electrodes and Sensors

NO_x, are the primary pollutants produced by the high temperature combustion processes, automotive vehicles as well as industries. There is a need to detect NO_x in the concentration range between 10 and 2000 ppm for a greater control of fuel combustion processes and for monitoring automobile exhaust gases [321]. NO_x electrochemical sensors based on ceramic materials are suitable in high temperature application and in chemically harsh environment since they are mainly based on semi-conducting oxides and solid electrolytes. Xiong et al. [322,323] studied a mixed-potential sensor based on CuO + $CuCr_2O_4$ which exhibited high selectivity and sensitivity toward NO_2. They found the open-circuit electromotive force (EMF) of the NO_2 sensor to be stable, reproducible and, the sensor responded rapidly (t90 < 8 s) to change in the NO_2 concentration between 100 and 500 ppm at 659 ^{0}C [323]. Porous Pt reference electrode was used in the research [321,322]. Recently, the same workers [23] tested a solid-state planar sensor consisting of scandia-stabilised zirconia (8 mol% Sc_2O_3-ZrO_2) solid electrolyte sandwiched between CuO + $CuCr_2O_4$ mixed-oxide and Au foil reference electrodes in NO_2 containing gaseous atmosphere in the range of 100-500 ppm NO_2 at 611 and 658 ^{0}C. They found that the response time of the sensor was less than 6 s and the recovery time was approximately 6 s at 658 ^{0}C, respectively. The response of the sensor was found to be logarithmically dependent on the concentration of NO_2 between 100 and 500 ppm at 611 ^{0}C whereas it was found to vary linearly with the concentration of NO_2 at 658 ^{0}C. The response of the sensor was highly reproducible to change in concentration of NO_2 and also showed negligible cross-sensitivity to O_2, CO and CH_4 in the gas stream.

2.10. Semiconductors

Diluted magnetic semiconductors (DMSs) involve charge and spin degrees of freedom in a single substance and therefore have attracted much interest owing to their unique magnetic, magneto-optical and magneto-electrical effects. Possible spintronic devices are spin-valve transistors, spin light-emitting diodes and nonvolatile logic devices [24]. Generally, oxide semiconductors have wide band gaps, i.e. transparent for visible light. This feature serves an important role as transparent conducting oxides (TCOs) that are used for various applications such as transparent electrodes in flat panel displays and window layers in solar cells. Li et al. [24] successfully prepared Mn-doped $CuCrO_2$ polycrystalline semiconductors by the sol-gel method which exhibit FM transitions at about 120 K.

Among the physical properties of solid materials which have been used as heterogeneous catalysts in a variety of chemical industries, the electrical conductivity and thermoelectric power are of fundamental importance [324]. The electrical transport of catalysts is of basic importance in the determination of the relationship between electronic structures and catalytic properties of semiconductors. The electrical conductivity and thermoelectric power of $CuCr_2O_4$ are reported in the temperature range 295 to 815 K [325].

2.11. Drugs and agrochemicals

Nitrogen-containing heterocyclic compounds, such as quinoline, indoles, pyrroles, pyrrolidines (and their alkylated homologues), piperazine and pyrazine are of high industrial interest, for applications as intermediates to produce pharmaceuticals, agro chemicals (herbicides, fungicides), dyes, etc. [326-328]. Pyrazine is synthesized by passing ethylene-diamine (ED) vapor over a copper oxide/copper chromite catalysts in the temperature range of 340-440 ^{0}C with a very high selectivity (98-100%) [19]. The reaction proceeds by intermolecular deamination and cyclization of ED to form piperazine, which undergoes subsequent dehydrogenation to form pyrazine (Fig. 14).

Propylene glycol (PG) is used in pharmaceuticals, such as: a carrier of active ingredients in vaccines, cough relief syrups or gel capsules to help deliver these substances within the body for treatment and prevention of diseases. It is also used as a solvent in many pharmaceuticals, including oral, injectable and topical formulations. Notably, diazepam, which is insoluble in water, uses PG as its solvent in its clinical, injectable form [329]. PG is synthesized efficiently by hydrogenolysis of glycerol over copper chromite catalysts [110].

A novel environment-friendly vapour phase synthesis of different classes of nitrogen-containing heterocyclic compounds was developed by Campanati et al. [330] using non-hazardous, commercially available and low cost feeds. 2-Methyl-8-ethylquinoline (MEQUI) was synthesized from 2-ethylaniline (2-ETAN) and ethylene glycol (EG) or chloro-ethanol (CE), operating at high temperature in the presence of acid-treated K10 montmorillonite or $ZnCl_2$/K10 montmorillonite. At lower temperatures and using copper chromite catalysts, 7-ethylindole (7-ETI) or 5-ethylindole (5-ETI) were obtained from 2-ETAN or 4-ethylaniline (4-ETAN), respectively, and EG; excess of alkyl-aniline was required to avoid the formation of polyalkylated by-products. Mixing SiO_2 with the best copper chromite, made it possible to operate with higher LHSV values, thus improving the yield in alkylindoles. Finally, N-(2-ethylphenyl) pyrrole (EPP) and N-(2-ethylphenyl) pyrrolidine (EPD) were synthesised using a commercial copper chromite catalyst and feeding 2-ETAN and 2,3-dihydrofuran (DHF), EPP being favoured by high temperatures and absence of water in the feed (Fig. 15).

3. Preparation methods of copper chromite catalyst

Catalysts, when prepared via different routes, would demonstrate different properties, even with the same starting compositions. Crystallinity, surface properties, and specific surface area, three of the most important parameters determining the catalytic activity of the product are highly dependent on the synthesizing routes [14]. Several preparation methods have been established to prepare $CuCr_2O_4$, for instance chromium and copper doubly promoted ceria catalysts have been prepared by Harrison et al. [331] by three routes: (A) coprecipitation from aqueous solutions containing cerium(IV), copper(II), and chromium (III) ions, (B) sequential impregnation of CeO_2 by using an aqueous CrO_3 solution followed by an aqueous solution of copper(II) nitrate, and (C) impregnation of Cu(II)/CeO_2 prepared by coprecipitation by using an aqueous CrO_3 solution. They found that at low processing temperatures, copper is present as (polymeric) $Cu(OH)_2$ in both the Cu/Cr/CeO_2-cop and Cu/Cr/CeO_2-cop/imp materials. Chromium is present as adsorbed ($Cr_2O_7^{2-}$) ions in the Cu/Cr/CeO_2-imp/imp and Cu/Cr/CeO_2-cop/imp materials, but a variety of chromium species in oxidation states +III, +V and +VI are present in the Cu/Cr/CeO_2-cop material.

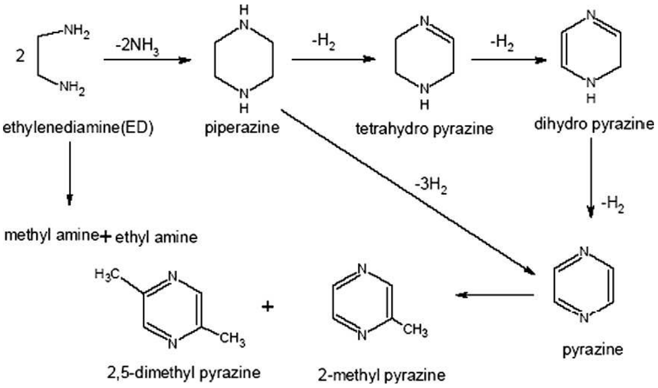


Fig. 14. A generalized reaction pathway for the formation of pyrazine and other products.

Brief descriptions of synthesis principles, typical processes, important aspects that influence the characteristics, specific advantages and some experimental data are presented for the following methods for the preparation of $CuCr_2O_4$ catalysts:

- Co-precipitation method
  - Adkins' method
  - Complexing-coprecipitation method
- Co-impregnation method
- Thermal decomposition (ACOC)
- Thermal decomposition of ammoniacal copper oxalate chromate (ACOC)
- Hydrothermal method
- Non-Casting method: Template technique
- Hydrolysis of some soluble salts
- Microemulsion method

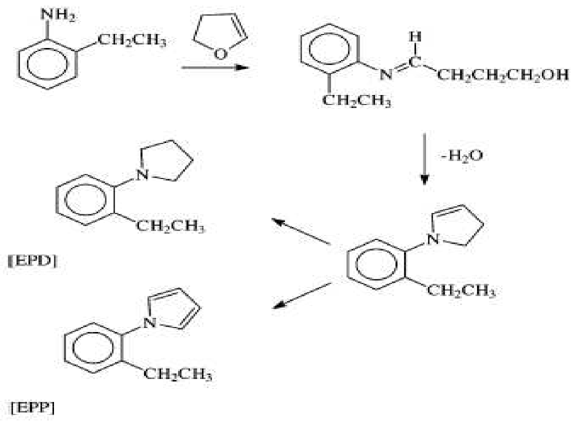


Fig. 15. Reaction pathway for the synthesis of *N*-(2-ethylphenyl) pyrrole (EPP) and *N*-(ethylphenyl) pyrrolidine (EPD) using $CuCr_2O_4$ catalysts [331]

- Combustion synthesis
  - Self-propagating high-temperature synthesis
  - Solution combustion synthesis
- Electroless method
- Sonochemical method
- Metal organic chemical vapour deposition (MOCVD)
- Flame Synthesis of Nanostructured
- Chemical reduction method
- Sol-gel process
  - Citric acid (CA) complexing approach
  - Pechini Method
  - Non-alkoxide sol-gel route

3. 1 Co-precipitation method

3.1.1 Adkins' method

The preparation procedure [44] is as follows: Ammonium hydroxide was added to a solution of 126 g. (0.5 mole) of ammonium dichromate in 500 ml. of water until the colour of the solution changed from orange to yellow. The volume of the solution was now 653 ml. The solution was allowed to come to room temperature and a solution of 241.6 g. (1.0 mole) of cupric nitrate tri-hydrate in 300 ml. of water was added with stirring. The red-brown precipitate of basic copper ammonium chromate (BCAC) was filtered with suction and dried overnight in an oven at 100-110 ^{0}C. It was then finely powdered, transferred to a porcelain casserole, and decomposed by heating the casserole in the flame of a Bunsen burner. After decomposition had begun, the heat of reaction was sufficient almost completely to decompose the chromate. When spontaneous decomposition had ceased, the casserole was heated with the free flame until fumes ceased to be evolved and the contents was black and so finely powdered as to be almost like a liquid. During this heating, care was taken to keep the material well stirred and to rotate the flame in order to avoid local superheating. The product was allowed to cool and then suspended in 200 ml. of a 10% solution of acetic acid. The suspension was filtered with suction, washed thoroughly with water, dried for twelve hours in an oven at 100-110 ^{0}C, and finely powdered. The yield of catalyst was 113 g. The reactions involved can be represented by the following equation 52-55:

$$(NH_4)_2Cr_2O_7 + 2NH_4OH \rightarrow 2(NH_4)_2CrO_4 + H_2O \quad (52)$$

$$(NH_4)_2CrO_4 + Cu(NO_3)_2 + NH_4OH \rightarrow Cu(OH).NH_4CrO_4\downarrow + 2NH_4NO_3 \quad (53)$$

$$2Cu(OH)NH_4CrO_4 \rightarrow CuO.CuCr_2O_4 + N_2 + 5H_2O \quad (54)$$

$$CuO.CuCr_2O_4 + 2CH_3COOH \rightarrow CuCr_2O_4 + (CH_3COO)_2Cu + H_2O \quad (55)$$

Adkins et al. [44] have hydrogenated a group of 21 organic compounds using above prepared catalyst and reported that 16 have been successfully hydrogenated with 100% yield and 100% selectivity.

Kawamoto et al. [315] prepared the catalyst following the co-precipitation method from aqueous solution of $K_2Cr_2O_7$ and $CuSO_4.5H_2O$ in the presence of ammonia at Cu/Cr molar ratios of 0.3 and 0.5. The fine precipitates of BCAC were filtered, washed with distilled water and dried at 110 ^{0}C to a constant weight. Then, they were powdered to a 250 mesh and heated at 500 ^{0}C for 2 hours. The formation of the catalyst can be represented by equations 56 and 57:

$$2CuSO_4 + K_2Cr_2O_7 + 4\,NH_3 + 3H_2O \rightarrow K_2SO_4 + 2Cu(OH)NH_4CrO_4 + (NH_4)_2SO_4 \quad (56)$$

$$2Cu(OH)NH_4CrO_4 \xrightarrow{110\text{-}500\ ^oC} CuO.CuCr_2O_4 + 5H_2O \quad (57)$$

They concluded that the samples synthesized by the co-precipitation method present a better granulometric distribution than solid state reaction and this has led to propellants with higher burning rate and higher pressure exponent.

3.1.2 Complexing-coprecipitation method

The most common method for mixed-oxide catalyst preparation is crystallization or precipitation or co-precipitation in solution of a precursor form (hydroxide, oxide, insoluble salt) of the catalyst [332]. Other specific steps, for example either addition of an extra component or its removal by partial extraction, may sometimes be necessary to adjust the final catalyst composition and ensure homogeneity [333]. Adkins et al. [44] described for the first time preparation of copper chromite catalyst for hydrogenation of organic compounds following this method. Subsequently, several workers used this method for the preparation of copper chromite catalysts using different compounds of copper and chromium with aqueous ammonia solution as precipitating agent.

3.2. Co-impregnation method

Co-impregnation method is the easiest method of preparation of copper chromite catalysts. In this method catalysts are obtained [291,334] by mixing of support (γ-Al_2O_3) with an aqueous solution of chromium anhydride and copper nitrate in required proportion. The amount of solution taken is sufficient for incipient wetness to be observed. The samples are dried and calcinated at appropriate temperatures to get the catalysts.

3.3 Solid state reaction (ceramic method)

The vast majority of the powder synthesis of high temperature superconducting oxides to date has been carried out using the traditional "solid-state reaction route" [335]. Copper chromite spinels are usually synthesized by the conventional high temperature method of solid state reaction (eqn. 58):

$$CuO(s) + Cr_2O_3(s) \xrightarrow[6h]{900\ ^oC} CuCr_2O_4\,(s) \qquad (58)$$

Kawamoto et al. [315] prepared copper chromite by ceramic method, mixing copper (II) and chromium (III) oxides at 3 different ratios Cu/Cr = 0.61; Cu/Cr = 1.0; Cu/Cr = 1.5. The mixtures of oxides were homogenized with acetone followed by subsequent calcination at 900 ^{0}C for 6 hours. This method results in spinel particles with low surface areas. In order to synthesize spinels with high surface area, they attempted different wet chemistry techniques.

3.4 Thermal decomposition of ammoniac copper oxalate chromate

Prasad [2] synthesized a novel precursor, ammoniac copper oxalate chromate (ACOC) and suggested the stoichiometric formula of the precursor closely approximating, $CuNH_3C_2O_4NH_4CrO_4$. ACOC was used for the production of active copper chromite catalysts. The precursor, ACOC was prepared by mixing ammoniacal solutions of copper oxalate and ammonium chromate in a Cu/Cr atomic ratio of 1:1 followed by evaporation on a steam bath and finally dried at 378 K in an oven for 5 h. No precipitation occurred during mixing. The dried greenish colored complex was stored in a desiccator over anhydrous calcium chloride. The homogeneous complex precursor is soluble in aqueous ammonia. The catalysts were prepared by calcination of the prepared complex precursor in air and in argon atmosphere around 623 K. The overall decomposition of ACOC in air was highly exothermic and can be exemplified by the following equation 59:

$$2CuNH_3C_2O_4NH_4CrO_4 + 2O_2 \rightarrow CuO.CuCr_2O_4 + 4CO_2 + 2N_2 + 7H_2O \text{ (highly exo.)} \qquad (59)$$

The overall decomposition of ACOC in argon was mild exothermic, can be represented as follows (eqn. 60):

$$2CuNH_3C_2O_4.NH_4CrO_4 \rightarrow Cu.CuCr_2O_4 + 2NH_3 + 4CO_2 + N_2 + 4H_2O \text{ (mild exo.)} \qquad (60)$$

The environments of calcinations of ACOC have strong influence on mechanism of decomposition and also on the chemical composition and physico-chemical properties of the resulting Adkins' catalysts. Violent exothermic oxidative-decomposition of ACOC in air leads to bi-dispersed bigger particles and consequently lowers specific surface area of resulting catalyst, $CuO.CuCr_2O_4$ in comparison to finely-divided mono-dispersed particles of active catalyst, $Cu.CuCr_2O_4$ obtained through mild exothermic decomposition in argon environment. Thus, decomposition of ACOC in argon produces novel active catalyst directly, minimizing a process step of catalyst reduction, leading to saving of not only reduction time but also reducing and diluent's gases.

3.5 Hydrothermal method

George and Sugunan [4] prepared the catalysts as follows: a mixture consisting of 10% solutions of copper nitrate, nickel nitrate and chromium nitrate for $Cu_{1-x}Ni_xCr_2O_4$ (x = 0, 0.25, 0.5, 0.75 and 1) series were taken in appropriate mole ratios and the mixture was heated to 343-353 K. To this hot mixture a 15% ammonia solution was added drop wise with constant and uniform stirring to maintain a constant pH of 6.5-8. The precipitate was maintained at this temperature for 2 h and aged for one day. The precipitate was filtered, washed and dried at 353 K for 24 h and calcined at 923 K for 8 h.

Arboleda et al. [336] synthesized a new single-phase copper chromate compound, (NH4) $1.5Cu_2Cr_2O_8(OH)_{1.5}H_2O$ by the hydrothermal method. The synthesized compound decomposed into $CuCr_2O_4$ and CuO after being calcined at 600 ^{0}C. The Cu-Zn-Cr catalysts derived from hydrotalcite (HT) structures were prepared by the hydrothermal method by Venugopal et al. [337]. Catalyst precursors were prepared by the co-precipitation method with mol% ratios of Cu:Zn:Cr = 44:44:12 and Cu:Zn:Cr = 47:38:15 with hydrothermal treatment. About 0.6 L aqueous solution of copper, zinc, chromium nitrates (solution A) and a solution B containing 2 M NaOH and 1 M Na_2CO_3 (1:1 = v/v) were added simultaneously to 2.0 L of distilled water under vigorous stirring. The rate of addition of solution A was approximately 0.5 L/h while maintaining a constant pH ~8.0 ± 0.1 by adjusting the flows of solutions A and B. The co-precipitation is carried out at room temperature. The precipitate was kept at 70 ^{0}C for 1 h subsequently washed several times until the pH of the gel reached the pH of the distilled water that has been used for the preparation. The precipitates were oven dried at 100 ^{0}C for 24 h and calcined in static air at 400 ^{0}C for 3 h. They found the presence of hydrotalcite structure and the finely dispersed copper species in the calcined form.

3.6 Nanocasting method (Template technique)

The common preparation methods of mixed oxides and mixtures of oxides usually require the unconfined precursors to be subjected to high temperature calcinations steps. This provokes the sintering of the resulting particles, with the concomitant reduction of active surface area, typically in the range of a few square meters (<10) per gram. Thermal treatments can be avoided by the use of "*chimie douce*"-based nanotechnological approaches, such as microemulsion techniques [338], but these are expensive procedures which, moreover, must integrate stages for the separation of the organic solvents and surfactants. These disadvantages, when using thermal methods for unconfined precursors or liquid phase preparations, have been recently overcome by means of nanocasting procedures, such as template methods with hard templates (porous solids such as silica gel and active carbon) [339-341]. Using this method the synthesis of the nanoparticles takes place in a confined space formed by the porosity of the template. The attraction of these methods is the confined calcination process that allows an effective control of the particle size of the resulting materials by adjusting the conditions of synthesis, thus favouring the formation of nanostructures [341].

Generally, the nanocasting methods involve two main steps: (a) preparation of a nanostructured template; and (b) filling the template nanopores with the desired precursor, followed by crystallization in the voids of the template and then removing the template framework. Liang et al. [106] firstly demonstrated that the carbon template route allows synthesizing high-surface area Cu-Cr catalysts, which show high activity and selectivity to 1,2-propanediol in glycerol hydrogenolysis. The method is as follows: about 3 g of the carbon materials were impregnated at room temperature with about 15 ml aqueous solution of copper nitrate and chromium nitrate mixture of different molar ratios for 30 min. Alternatively, impregnation was performed with a slight excess of solution. The slurry was then filtered and squeezed to remove the liquid on the carbon surface that could cause the formation of large oxide particles. After drying in air at 70 ^{0}C overnight, the resulting sample was transferred to a quartz reactor inside a tubular resistance furnace. The furnace was then ramped at 1 ^{0}C/min to final temperature and was held for 120 min. The atmosphere was of argon before 300 ^{0}C, and then shifted into a mixture gas of 20% O_2 in Ar at a flow rate of 120 ml/min. Finally, carbon template was removed at 550 ^{0}C in air for 8 h. The conversion is almost 100% from copper nitrate and chromium nitrate to final copper and chromium oxide catalyst, and the ratio of Cu to Cr was obtained from the initial molar ratio of copper nitrate to chromium nitrate.

Valdés-Solís, et al. [14] prepared high surface-area spinel-type complex oxides using a porous silica xerogel as template. To synthesize the metal oxides, a solution of the hydrated metal nitrates in the appropriate ratio was prepared in ethanol (0.4-0.6 M). The silica xerogel was stirred with this solution at moderate temperature (60 ^{0}C) until complete removal of the solvent. The impregnated sample was dried at 80 ^{0}C overnight and calcined in air at 5 ^{0}C/min up to the temperature required for the formation of the oxide and then left for 4 h. The mixed oxides were obtained after the dissolution of the silica framework in a NaOH solution (2 M) and final washing with distilled water to remove impurities. Copper-based catalysts ($CuMn_2O_4$ and $CuCr_2O_4$ spinels or CuO/CeO_2 and CuO/ZnO) exhibit a high activity and selectivity for the methanol-steam reforming process.

3.7 Hydrolysis of some soluble salts

Patron et al. [317] developed the hydrolysis method for obtaining chromium based oxides. It consists in the hydrolysis of the metal salts in presence/or absence of a complexant agent. The potential advantages of this synthesis route lies in the accessibility and moderate costs of the starting materials, in the low temperatures required by the procedure and the enhanced homogeneity and purity of the end products. They obtained a pure tetragonal $CuCr_2O_4$ with mean crystallite sizes varying in the range 133-210 Å between the temperatures limits 823 K-1073 K. The precursors were prepared by hydrolysis of $Cr(NO_3)_3.9H_2O$ and $Cu(NO_3)_2.3H_2O$ and $Cu(CH_3COO)_2.H_2O$. Working in different conditions two polynuclear coordination precursors $[Cr_2Cu(NH_3)_2(OH)_6](NO_3)_2$ and $[Cr_2Cu(OH)_8].4H_2O$ were obtained. The following reaction equations 61 and 62 may be written for precursors' synthesis:

$$Cu^{2+} \rightarrow [Cu(NH_3)_4]^{2+} \xrightarrow[\sim 10\text{-}11]{NH_4} [Cr_2Cu(NH_3)_2(OH)_6](NO_3)_2 \quad \text{(Precursor A)} \qquad (61)$$

$$Cr^{3+} \rightarrow Cr(OH)_3 \rightarrow [Cr_2Cu(OH)_8].4H_2O \quad \text{(Precursor B)} \qquad (62)$$

Copper chromite was obtained through thermal decomposition of the precursors. Following decomposition mechanism (eqns. 63 and 64) has been predicted for the two compounds:

Precursor A :

$$[Cr_2Cu(NH_3)_2(OH)_6](NO_3)_2 \rightarrow [Cr_2Cu(OH)_6](NO_3)_2 \rightarrow Cr_2CuO(OH)_6 \rightarrow Cr_2O_2(OH)_2.CuO \rightarrow Cr_2O_{8/3}.CuO \rightarrow Cr_2O_3.CuO \rightarrow CuCr_2O_4 \qquad (63)$$

Precursor B:

$$[Cr_2Cu(OH)_8].4H_2O \rightarrow Cr_2Cu(OH)_8 \rightarrow Cr_2O_2(OH)_2\,CuO \rightarrow Cr_2O_3.CuO \rightarrow CuCr_2O_4 \qquad (64)$$

3.8 Microemulsion method

The use of an inorganic phase in water-in-oil microemulsions has received considerable attention for preparing metal particles. This is a new technique, which allows preparation of ultrafine metal particles within the size range 5-50 nm particle diameter [342].

Nanoparticles of copper chromium hexacyanide with varying particle-size are prepared by Kumar et al. [343] using the micro-emulsion method and Poly (vinylpyrrolidone) (PVP) as a protecting polymer. Two separate microemulsions of $Cu(NO_3)_2$ and $K_3Cr(CN)_6$ with PVP are prepared and subsequently mixed together to get the precipitate of copper-chromium hexacyanide nanoparticles. The nanoparticles are separated out by adding acetone in the resultant mixture and are washed many times with acetone and demineralized water. The different mixing ratios of PVP to Cu ion concentration (20 to 200) are used to control the size of the nanoparticles.

3.9 Combustion synthesis

Combustion synthesis (CS) [344] has emerged as important technique for the synthesis and processing of advanced ceramics (structural and functional), catalysts, composites, alloys, intermetallics and nanomaterials. In CS, the exothermicity of the redox (reduction-oxidation or electron transfer) chemical reaction is used to produce useful materials [345]. Depending upon the nature of reactants: elements or compounds (solid, liquid or gas); and the exothermicity (adiabatic temperature, T), CS is described as: self-propagating high temperature synthesis (SHS); low-temperature CS, solution combustion synthesis (SCS), gel-combustion, sol-gel combustion, emulsion combustion, volume combustion (thermal explosion), etc. Combustion synthesis processes are characterised by high-temperatures, fast heating rates and short reaction times. These features make CS an attractive method for the manufacture of technologically useful materials at lower costs compared to conventional ceramic processes. Some other advantages [346] of CS are:

(i) Use of relatively simple equipment
(ii) Formation of high-purity products
(iii) Stabilization of metastable phases and
(iv) Formation of virtually any size and shape products.

Combustion synthesis has been extensively used to prepare a variety of catalysts. Patil et al. [346] reviewed the recent developments in the field with special emphasis on the preparation of 'Catalysts' and 'Nanomaterials' by solid state combustion and solution combustion.

3.9.1 Self-propagating high-temperature synthesis (SHS)

The SHS method is being developed for the low-cost production of engineering and other functional materials, such as advanced ceramics, intermetallics, catalysts and magnetic materials. The method exploits self-sustaining solid-flame combustion reactions which develop very high internal material temperatures over very short periods. It therefore offers many advantages over traditional methods, such as much lower energy costs, lower environmental impact, ease of manufacture and capability for producing materials with unique properties and characteristics [347].

Xanthopoulou and Vekinis [348] prepared the SHS catalysts and carriers from initial batch mixtures consisting of nitrates and sulphates, metals and oxides, compacted under a pressure of 5 -10 MPa in the form of rods of diameter 1-5 cm and, in some cases, by extrusion as honeycomb carrier blocks with diameter 1-5 cm and channel size of about 5 mm. The samples were preheated in an electric furnace at temperatures of 700-900 ^{0}C for a few minutes prior to initiation of SHS. The specific area was increased by depositing a second oxide layer (wash-coat) on the surface of SHS carriers of about 0.9-4.9% aluminium oxynitrate (denoted as OX, 3.2% for the Cu-Cr-O catalyst). Pd was then deposited on the SHS carriers using standard aqueous impregnation followed by calcination and reduction. Standard 0.05% or 0.5% $Pd/Al(NO_3)_3/Al_2O_3$ catalyst systems produced by a conventional impregnation/ calcination/ reduction process were used for comparison [348] . The author reported that the Cu-Cr-O catalyst prepared by SHS is resistant to fuel impurity poisoning and used as carrier for 0.05% Pd, achieved 50% conversion (light-off) at temperatures about 50 ^{0}C lower than conventional 0.5% Pd/Al_2O_3 catalysts for CO oxidation [348].

3.9.2 Solution combustion synthesis

A highly exothermic and self-sustaining reaction, the so-called "solution combustion synthesis" method is described by Russo et al. [349]. Particularly, a concentrated aqueous solution of various precursors (metal nitrates and urea) was located in an oven at 600 ^{0}C for a few minutes in a crucible, so as to ignite the very fast reaction. Under these conditions nucleation of metal oxide crystals is induced, their growth is limited and nano-sized grains can be obtained. The innovative solution combustion synthesis technique was adopted successfully because it was possible to produce in an easy and low-cost "one shot" way catalysts [259] with a rather high surface area and pureness. The same technique could be used to deposit the catalyst on ceramic carriers with a very high surface area. They studied the catalytic decomposition of N_2O to N_2 and O_2 over $CuCr_2O_4$ and reported that the conversion of N_2O reached 50% in the absence and in the presence of oxygen at 630 ^{0}C and 745 ^{0}C respectively.

3.10 Flame spray pyrolysis method

Flame synthesis is an easy, single step method for the preparation of $CuCr_2O_4$ powder. The process is shorter than most wet chemical methods and is cost efficient [350]. The flame-synthesized sorbents have higher surface areas than particles synthesized by co-precipitation.

Akhuemonkhan et al. [351] produced high surface area $CuCr_2O_4$ sorbent for desulfurization in fuel cells using the flame spray pyrolysis method. They described the procedure as follows: The precursors used for making the sorbents are copper (II) nitrate trihydrate, chromium (III) acetate, copper (II) acetate monohydrate, chromium (III) nitrate nonahydrate. A series of 0.3 molar aqueous precursor solutions have been made with deionized water and mixed in the stoichiometric ratio. The solutions are then atomized with the help of compressed air in a medical nebulizer. The droplets from the nebulizer are then sent directly into a flame rector. The flame in the reactor is generated with methane, oxygen and nitrogen gases. The total flow rates for each gas including the contributions from the air used to atomize the precursor were methane 0.90 l/min, oxygen 2.61 l/min and nitrogen 5.95 l/min. The maximum temperature of the flame using these flow rates was in the range of 1400-1500 ^{0}C, which was measured by using S-type (Pt/10%Rh-Pt) thermocouple. In the reactor, the droplets undergo a series of physical and chemical steps including solvent evaporation and precipitation, intraparticle reaction and densification, to form the final product, a dense particle. The particles move from the reactor to a water-cooled surface placed directly over the reactor. The temperature gradient caused by placing the cooled surface above the flame reactor causes the particles to move from a hotter region to the cooler surface a thermophoresis process. The authors reported that the flame-synthesized sorbent has higher sulfur loading capacities than one synthesized by co-precipitation.

3.11 Electroless method

A critical comparison of those methods is needed to make the best choice for given boundary conditions of targeted eventual material properties, raw materials, investment, processing and waste disposal costs. Preparing catalysts using different methods also abet to compare the suitability of catalysts for specific applications for instance, Shiau and Tsai [352] showed that the electroless deposition method provides more uniform copper distribution than the impregnation method. The electroless method is an oxidation-reduction chemical deposition reaction, which can deposit certain metals on a substrate without an external electrical source [352].

Shiau and lee [104] prepared copper chromite catalyst via electroless plating process using Al_2O_3 as substrate. Before conducting electroless deposition, Al_2O_3 was pretreated with nitric acid to remove any impurities, and activated by palladium chloride solution to provide palladium nucleating centres on surface of Al_2O_3. The activated Al_2O_3 was finally contacted with copper solution for copper plating. In the copper solution, formaldehyde was added as reducing agent for the oxidation-reduction reaction. The plating bath was maintained at 70 ^{0}C and the pH was adjusted to 12.5. The plated Al_2O_3 was filtered and washed with distilled water, then dried at 110 ^{0}C for 24 h. The copper content was controlled at 15%. Chromium was then added on the catalyst by a traditional incipient wet impregnation method. Chromium contents varied from 1 to 5%. They reported that n-butanol dehydrogenation activity reaches a maximum at 2 wt. % of chromium addition, which corresponds to the saturated chromium loading that can penetrate into the bulk of copper layer. This penetrated chromium can reduce the particle size of copper crystallites and therefore can enhance the copper dispersion on γ-Al_2O_3.

3.12 Sonochemical method

Sonochemistry is a very useful process for preparing novel materials with unusual properties [353], and its utilization in the synthesis of catalysts has been reported [354,355]. The prominent advantages of catalysts prepared by sonochemistry are their high activity and nanosized particles. The driving force for sonochemistry is acoustic cavitation that is formed in liquid. During cavitation, bubble collapse produces intense localized hot spots (˜5000 K) and high pressure (˜1000 atm). The microjets of liquid and shockwave created by ultrasound can make great effect on solids in liquid.

Huang et al. [89] studied selective hydrogenation of furfural to furfuryl alcohol over $CuCr_2O_4$ catalysts prepared via sonochemical method. The method of preparation described is as follows: Preparation of catalyst S1: $K_2Cr_2O_7$ (6 g) and $CuAc_2.H_2O$ (6 g) is dissolved in $NH_3.H_2O$ (30 ml) solution. The solution is kept in a thermostatic bath (65 ^{0}C) under stirring. After NH_3 is removed completely, the formed precipitate is centrifuged and washed two times with water and once with acetone, and then dried at room temperature under vacuum. Preparation of catalyst S2: $K_2Cr_2O_7$ (6 g) and $CuAc_2.H_2O$ (6 g) are dissolved in water (20 ml), respectively. Then 1 ml of $NH_3.H_2O$ is added into the solution of $K_2Cr_2O_7$. Two solutions are mixed up and the mixture is sonicated for 3 h by employing a direct immersion titanium horn (Sonics and Materials model VCX-600, 20 kHz, 100W/cm^2). The reaction cell is cooled by water at ambient temperature during the sonication process. The mixture is centrifuged after sonication. The product is washed two times with water and once with acetone, and then dried at room temperature under vacuum. Samples S3, S4 and S5 are prepared in the same way of preparing S2 besides that 10, 15 and 20 ml of titanium (IV) isopropoxide $(Me_2CHO)_4Ti$ are injected into the mixture as soon as the sonication starts, respectively. They concluded that comparision with Adkins catalyst (S1) prepared by convenient method, the Adkins catalyst (S2) prepared via ultrasound has higher catalytic activity for hydrogenation of furfural.

3.13 Metal organic chemical vapour deposition (MOCVD)

Chemical vapor deposition (CVD) is a chemical process used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin films. In a typical CVD process, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber [356].

Chang et al. [22] prepared for the first time copper chromite films by metal organic chemical vapour deposition (MOCVD) with temperature below 500 ^{0}C. The processing window was: deposition temperature above 420 ^{0}C, partial pressures of oxygen, above 190 torr, copper acetylacetonate(Cu(acac)$_2$), 0.21 torr, and chromium acetylacetonate (Cr(acac)$_3$), 0.4 torr, respectively. Keeping the more volatile reactants as Cr(acac)$_3$ in excess amount is essential for depositing stoichiometric films. Higher deposition temperature is essential for depositing oxide films with complex crystalline structure. SEM results showed $CuCr_2O_4$ films exhibited different morphologies such as equiaxed fine grain, truncated polyhedron, and hillocks, depending on the process condition. Both substrate temperature and precursor partial pressures have significant impact on film morphology and reflect the basic natures of film growth mechanism. XRD patterns indicate that CVD films are polycrystalline, which exhibit highly textured, normal spinel structure.

3.14 Chemical reduction method

The chemical reduction is a convenient method with simple procedures for preparing amorphous nano-size metal particles for catalysis [357]. The ultrafine copper chromite catalyst is obtained using this method [45]. Liaw and Chen [45] prepared the catalyst by reducing copper nitrate (0.1 M) in an aqueous solution with sodium borohydride (1 M). The aqueous sodium borohydride solution was added into the copper nitrate solution by a micropump under a flow of nitrogen. Cr introduced to copper by reducing/co-precipitating with sodium borohydride in an aqueous solution of copper nitrate and an appropriate amount of Cr salt. The resulting black precipitate was thoroughly washed with distilled water three times to remove the residual ions and then washed with ethanol to remove water. The precipitate are then dried and calcined. They studied catalytic properties of catalyst prepared by this method for hydrogenation on monofunctional (olefinic and carbonyl) and bifunctional (conjugated and nonconjugated) compounds and compared with those of a commercial catalyst of copper chromite. The ultrafine catalysts of Cr-CuB containing a much lower content of chromium (Cr<5mol%) were more active than the commercial copper chromite (Cr > 50mol%). The authors proposed that these Cr -CuB catalysts are highly promising for replacing copper chromite for liquid-phase hydrogenation reactions.

3.15 Sol-gel method

The sol-gel methods show promising potential for the synthesis of mixed oxides catalysts. The versatility of the sol-gel techniques allows control of the texture, composition, homogeneity, low calcination temperatures (minimizing the undesired aggregation of the particles), and structural properties of solids, and makes possible production of tailored materials such as dispersed metals, oxidic catalysts and chemically modified supports [358].

Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (sol) which acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers [359]. Typical precursors are metal alkoxides and metal nitrates, which undergo hydrolysis and polycondensation reactions to form either a network 'elastic solid' or a colloidal suspension (or dispersion) - a system composed of discrete (often amorphous) submicrometer particles dispersed to various degrees in a host fluid.

The hydrolysis of precursor molecules and the condensation between the resulting reactive species, are the essential reactions of the sol-gel process [360]. The resulting processes involved and the properties of the precursor molecules have a decisive influence on the resulting material properties [360]. On addition of water, the metal alkoxides [M(OR)n] readily hydrolyze as represented by Eqn. 65.

$$M(OR)n + H_2O \rightarrow M(OR)_{n-1}OH + ROH \qquad (65)$$

Hydrolysis is followed by condensation to form -M-O-M- bonds via either dehydration or dealcoholation as described in Eqs. (66) and (67), respectively:

$$(RO)_mM\text{-}OH + HO\text{-}M(OR)_m \rightarrow (RO)_mM\text{-}O\text{-}M(OR)_m + H_2O \qquad (66)$$

$$\text{-}M\text{-}OH + RO\text{-}M\text{-} \rightarrow \text{-}M\text{-}O\text{-}M\text{-} + ROH \qquad (67)$$

In this manner, inorganic polymeric oxide networks are built up progressively. The hydrolysis, condensation and polymerization reactions are governed by several factors, including the molar ratio of water to alkoxides, choice of solvents, temperature and pH (or concentration of acid or base catalysts). There are essentially three different kinds of sol-gel or gel technology for preparation of catalysts.

3.15.1 Citric acid complexing method

Citric acid (CA)-assisted sol-gel method (namely Pechini approach) is a facile synthesis for producing homogeneous nanocomposites [10], in which the use of citric acid as chelating agent ensures the formation of homogeneous transparent metal-citrate gels, and the intimate mixing of components ensures homogeneity of the final product. Li et al.[10] have prepared Cu-Cr-O nanocomposites by citric acid (CA) complexing approach in which 0.01 mol $Cu(NO_3)_2$ and 0.02 mol $Cr(NO_3)_3$ are dissolved in 100 mL deionized water to obtain a mixed metal nitrate solution. Then citric acid is added to this solution and the molar ratio of citric acid to the total metal ions is fixed to be 2:1. After stirring for 30 min, the solution is heated at 95 ^{0}C for several hours to evaporate the water solvent to produce dark brown transparent viscous gels. The gels are then dried at 160 ^{0}C for 2 h to obtain the foamy dark powders, which are denoted as precursors of Cu-Cr-O nanocomposites (CA-Cu-Cr). After grinding, the precursors are successively heated at 600 ^{0}C for 3 h to obtain the final black Cu-Cr-O nanocomposites.

Li and cheng [229] have prepared Bi_2O_3/$CuCr_2O_4$ core/shell nanomaterials following the facile synthesis and show that the nanomaterials demonstrate high catalytic activities towards the oxidation of CO. Yan et al. [12] also synthesized $CuCr_2O_4/TiO_2$ heterojunction via a facile CA-assisted sol-gel method for photocatalytic H_2 evolution. The optimized composition of the nanocomposites has been found to be $CuCr_2O_4.0.7TiO_2$. And the optimized calcination temperature and photocatalyst mass concentration are 500 ^{0}C and 0.8 g/l, respectively.

3.15.2 Alkoxide sol-gel method (Pechini Method)

The Pechini method [361,362] based on polymeric precursors, is used to prepare spinels and it does not require high temperature calcinations and permits good stoichiometric control as well as reproducibility. This method consists of the formation of a polymeric resin between a metallic acid chelate and polyhydroxide alcohol by polyesterification. The metal nitrate solution is mixed with a stoichiometric amount of citric acid. The resulting solution is stirred for about 1 hour on a hot plate and the temperature is stabilized at 70 ^{0}C. The mixture is heated to 900 ^{0}C, at which point ethylene glycol is added at a mass ratio of 40:60 with respect to citric acid. The temperature is maintained constant up to resin formation, which polymerizes at 300 ^{0}C. The precursor powders are then calcined for 4 hours at various temperatures, ranging from 500 to 900 ^{0}C, or at 900 ^{0}C for 8 hours [363]. The crystallization of the spinel structure starts upon calcining at 700 ^{0}C. $Cu_{0.8}Ni_{0.2}Cr_2O_4$ is the only phase present upon calcination at 900 ^{0}C. The process of the Pechini method is almost the same as that of the citrate gel method, except that metal nitrates are dissolved in alcohols, instead of water [364].

The major disadvantages of using the metal alkoxide based sol-gel process are its moisture sensitivity and the unavailability of suitable commercial precursors especially for mixed-metal oxides. The sol-gel synthesis of mixed oxides from alkoxide mixture usually suffers from the different hydrolysis susceptibilities of the individual components and the benefits of improved homogeneity can be lost during the hydrolysis of the alkoxides, which may ultimately lead to component segregation and mixed phases in the final materials. To achieve homogeneous mixed oxides with predetermined compositions, the difference in reactivity has been minimized by controlled prehydrolysis of the less reactive precursor [365], by chemical modification of the precursors [366], by using single-source heterobimetallic alkoxide precursors [367], or by non-hydrolytic sol-gel processes [368].

3.15.3 Non-alkoxide sol-gel method

Non-alkoxide sol-gel process, involving hydrolysis and condensation of metal salts, avoids the disadvantage of alkoxide sol-gel process (high sensitivity to moist environment), however, has still the disadvantage of different hydrolysis susceptibilities of the individual components [25]. One of the advantages of this method is the important reduction of the required calcination temperatures, minimizing the undesired aggregation of the particles. This method was found to be an effective route to synthesize mixed oxide nanoparticles with narrow size distribution [25]. Ma et al. [369] presented a non-alkoxide sol-gel route to synthesised highly active and selective Cu-Cr catalysts for glycerol conversion. The synthesis involves dissolving 3.3 g of Cr $(NO_3.3.9H_2O$ and 1.0 g of $Cu(NO_3)_2.3H_2O$ in 16 mL of ethanol at 60 ^{0}C to give a clear dark blue solution. After adding 5.0 mL of propylene oxide, a dark green transparent gel is formed within a few minutes under stirring. After drying overnight in air at 70 ^{0}C, the resulting xerogel is transferred to a quartz reactor inside a tubular resistance furnace. The furnace is then ramped at 1 ^{0}C/min to a final temperature and is held for 120 min under 20% O_2 in Ar at a flow rate of 120 ml/min. The yield of copper and chromium in the oxide catalyst is about to 100%, and the ratio of Cu to Cr could be varied by the initial molar ratio of copper nitrate and chromium nitrate.

The results show that the surface area of the Cu -Cr catalyst is adjusted by the hydrolysis conditions, Cu/Cr molar ratio, and treatment conditions (such as gas atmosphere and final temperature). For the sample with Cu/Cr = 0.5, the surface area of Cu-Cr xerogel can reach 94 m^2/g and decreased to only 31 m^2/g after calcination at 500 ^{0}C. The catalysts show significant catalytic activity and selectivity in glycerol conversion, i.e. above 52% conversion of glycerol and above 88% selectivity to 1,2-propanediol at 210 ^{0}C and 4.15 MPa H^2 pressure. $CuCr_2O_4$ supported Cu catalysts are much more active than Cr_2O_3 supported Cu catalysts. This indicates a strong interaction between Cu and $CuCr_2O_4$ that is significantly improving the effectiveness of the catalyst for glycerol conversion.

4. Conclusions

Depending on the ratio of oxides of Cu-Cr and preparation technique the final products are usually called copper chromite ($CuCr_2O_4$) and Adkins' catalyst ($CuO.CuCr_2O_4$). This review summarized the potential applications of unsupported and supported Cu-Cr catalysts and advances in their preparation methods. The Cu-Cr catalysts exhibit versatile applications as catalysts being used in the unit processes of organic synthesis, pollution abatement, ballistic modifier for composite solid propellants, production of H2 and clean energy carrier, drugs and agro chemicals, electrodes and sensors, etc. In addition to these applications recently, Cu-Cr catalysts finds use in hydrogenolysis of bio-glycerol to produce value added product such as propylene glycol.

A properly designed Cu-Cr catalyst should have the essential attributes of activity, stability, selectivity, and regenerability. These can be related to the physical and chemical properties of the catalyst, which in turn can be related to the variable parameters inherent in the method used for the preparation of the catalyst. The various methods used for preparation of Cu-Cr catalysts have their own importance and limitations. The sol-gel methods show promising potential for the synthesis of mixed oxides of homogeneous nanocomposite catalysts. The versatility of the sol-gel techniques allows control of the texture, composition, homogeneity, low calcination temperatures, and structural properties of solids, and makes possible production of tailored materials such as dispersed metals, oxidic catalysts and chemically modified supports. There is a significant increase in the thermal stability of the material by the addition of chromia with other refractory materials like alumina, silica gel, etc.; because of the formation of copper chromite and higher dispersion, inhibiting the sintering at high temperature.

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Table 2: Recent literature review at a glance on Cu-Cr catalysts development for various reactions

Ref. No	Catalyst prepn. method	Expmnt. Operating conditions	Remarks
1. Hydrogenation			
a) Hydrogenation of edible oils			
69	CuCr$_2$O$_4$	Soybean oil hydrogenation, 200 ^{0}C and 6 atm	Pre-reduced catalyst deactivates due to disappearance of Cu(II) and Cu(I) species and to the decrement of Cu/Cr ratio on the catalyst surface
b) Hydrogenation of polyunsaturated organic compounds			
20	Cu-Cr O, co-ppt. of hydroxide, caln 370 ^{0}C	Citral hydrogenation, 300 mg of catal, 0.5 mL of substrate in 5 mL of decalin at 140 ^{0}C, atm & subatm pressure, batch reactor	At high pressure, unsaturated alcohol competes with initial reagent on hydro-genation site; at low pressure, this comp-etition decreases, but the allylic alcohol is isomerized on another active site.
c) Hydrogenation of allylic alcohol			
20	Cu-Cr/Al, co-ppt. of Cu and Al hydroxides	Crotyl alcohol, ß-methallyl alcohol, flow apparatus, reagent-constant pp-20 Torr, atm. pressure	Allylic alcohols react with H$_2$ and lead to several primary products, Cu^{+1} promote hydrogenation, Cr^{+3}/Al^{+3}- isomerisation and hydrodeoxygenation
d) Hydrogenation of fatty acids			
71	CuCr$_2$O$_4$	Fatty methyl ester hydrog. to fatty alcohol, semibatch reactor, low H$_2$ press elevated temp.	Both activity and selectivity correlate well with the crystallinity of the copper chromite surface; they increase with decreasing crystallinity.
e) Hydrogenation of Furfural			
1	CuCr$_2$O$_4$ pre-reduced cat at 473, 573, or 673 K for 4 h	Furfural/ crotonaldehyde , fixed bed, 15 g cat, temp. 423 & 473 K, press 730 Torr H$_2$ & 10 Torr furfural	Both activity & TOF for furfural and crotonaldehyde hydrogenation reached their highest values after reduction at 573 K, compared to 473 and 673 K,
f) Selective hydrogenation of furfural			
3 9 89	CuCr$_2$O$_4$	Selective hydrogenation of furfural to furfuryl alcohol	Cu^0 is the active phase, reduction with H$_2$ at 573 K for 4 h produced the highest specific activity of catalyst due to the existence of maximum accessible Cu^0 species
g) Selective hydrogenation of nitrobenzene to aniline			
82	Cu(Fe$_x$Cr$_{2-x}$)O$_4$	250^{0}C, fixed bed flow reactor	Optimum composition, x=0.4, Cu^{+1} at octahedral sites is more active than Cu^0
h) Perfumery and synthesis of fragrances			
84	CuCr$_2$O$_4$	Partial hydrogenation of vegetable oils & fatty acids	Selective formation of allylic alcohols for perfumery & synthesis of fragrances
i) Hydrogenation of ketones			
91	CuCr$_2$O$_4$	Treatment of CuCr$_2$O$_4$ in H$_2$ at 180-370 ^{0}C	Exhibit activity in hydrogenation reactions including ketone & olefin
2. Cyclization			
124	Cu-Cr-Fe/γ Al$_2$O$_3$, sol-gel	Cyclization of alkanol- amines, fixed-bed reactor	Excellent activity, selectivity & long life Modified sol-gel method > common impregn. or co-ppt. method
6	Cu-Cr-Ba-Al$_2$O$_3$	Cyclization of N-ß-hydroxy-ethyl-1,3-propanediamine to homopiperazine, fixed-bed	Ba improved the dispersion of Cu and prevented it from sintering, conversion-93.2%-100%, selectivity-90%
3. Dehydrocyclisation			
329	CuCr$_2$O$_4$, CuCr$_2$O$_4$/SiO$_2$	Low temperature, 2-ETAN/ EG molar ratios ≥10.0	Dehydrogenation of EG to 2-hydroxy acetaldehyde, followed by N-alkylation of 2-ETAN to form a Schiff's base, that cyclises to 7-ETI

Table 2: (cont'd)

4. Dehydrogenation			
a) Dehydrogenation of Methanol			
92	$CuCr_2O_4$, CuO-75%, $CuCr_2O_4$-25%	CH_3OH dehydrog. to HCOH, slurry reactor, temp. 598-673 K	$CuCr_2O_4$ deactivate slowly than Cu-catalyst at 673 K
40	$CuCr_2O_4$	Dehydrog. of CH_3OH to $HCOOCH_3$, micro-reactor operated at atm. press.	Order half with respect to the partial pressure of CH_3OH, follow L-H model
b) Dehydrogenation of Ethanol			
93	$CuCr_2O_4$, thermal decomp. of co-ppt. Cu-Cr hydroxyl carbonate	Methanol dehydrogenation to formaldehyde or methyl formate	Highly selective to methyl formate (> 95%)
c) Dehydrogenation of Iso-propanol			
27	$CuCr_2O_4$, wet impregnation	Isopropanol dehydro-genation to acetone	High selectivity and satisfactory activity
d) Dehydrogenation of butanol			
104	$CuCr_2O_4$/electroless plating method	Dehydrogenation of n-butanol	5 wt.% addition of chromium to Cu have higher activity than the 2 wt.% Cr, especially at higher chromium loading.
e) Dehydrogenation of isoamylic alcohol			
105	CrCuMg layered double hydroxides with hydro -talcite structure, co-ppt.	Dehydrogenation of isoamyl alcohol to isovaleraldehyde	Show a high conversion and selectivity, catalytic activity attributed to copper content,
5. Dehydration			
a) Dehydration of Glycerol			
32	$CuCr_2O_4$	Dehydration of glycerol, semibatch reactive distillation	> 90 % acetol selectivity, hydrogenation of acetol to propylene glycol
106	Cu-Cr catalyst, carbon materials as templates & nitrates precursors	High surface area Cu-Cr catalysts	Reduced Cu-Cr, selectivity- 51% in glycerol conversion, 96% to 1,2- propanediol
6. Hydrogenolysis			
a) Hydrogenolysis of glycerol to propylene glycol			
110	$CuCr_2O_4$,	Temperature 200 ^{0}C, Pressure 200 psi, specially designed stainless steel multi clave reactor capable of performing eight reactions simultaneously	Yield >73% achieved at moderate reaction conditions. Cu^{+1} as active sites for hydrogenation
111	$CuCr_2O_4$	Convert glycerol to PG, Low-pressure vapour-phase processing, Semibatch reactive distillation	At lower temp. & pressures, 50-100% conversion, little selectivity towards ethylene glycol and other by-products, Acetol as transient intermediate with selectivity levels >90%
28	$CuCr_2O_4$, Co-ppt., impregn. method	Hydrogenolysis of glycerol to propylene glycol, Pre-reduced cat at 320^{0}C, flow reactor	Precipitated catalyst >impregnated catalyst
3	Cu-Cr, non-alkoxide sol-gel route, Cal 500^{0}C	Temp. 210^{0}C, H_2 Press 4.15 MPa,	Glycerol conversion > 52%, 88% selectivity to 1,2-propanediol, $CuCr_2O_4$ supported Cu catalysts are much more active than Cr_2O_3 supported Cu catalysts, highly active and selective for glycerol conversion
7. Alkylation			
a) Alkylation of amines			
119	BaO promoted $CuCr_2O_4$ & unpromoted $CuCr_2O_4$	The red. alkyl. of $C_6H_5NH_2$ with $(CH_3)_2CO$ to $C_9H_{13}N$, CuO44%, CrO45%, BaO9%, catalyst-10 g, pre-reduced	The active sites of $CuCr_2O_4$ used for red. alkyl. of amines are Cu(I) species, catalyst reduced at 573 K showed the highest activity

Table 2: (cont'd)

8. Hydrogen Production			
a) Sulphur based thermo-chemical water splitting cycles			
16	AB_2O_4 structures	H_2 production, through S-base thermo-chemical water split-ing cycles, temp.725-900 ^{0}C	Highest activity at temp. >850 ^{0}C, Activity order: $CuCr_2O_4 > CuFe_2O_4 > NiCr_2O_4 \approx NiFe_2O_4 > MnTiO_3 \approx FeTiO_3$.
16	Nanocomposit CuCrO, Pechini method,	5 wt% catalyst, burning rate catalysts for AP solid propellants	Cu/Cr molar ratio of 0.7 exhibits the most stable combustion at all pressures
b) Photocatalytic H_2 evolution			
12	$CuCr_2O_4$ /TiO_2, facile CA-sol–gel method	$CuCr_2O_4$/TiO_2- 0.7, calc.-500 ^{0}C catalyst mass conc.0.8 g/l	H_2 evolution from oxalic acid solution under simulated sunlight irradiation, consistent with the Langmuir model
13	$CuCr_2O_4$, co-ppt.	H_2 evolution, solutions containing NaOH-0.5 M, $Na_2S_2O_3$-0.025 M with an average rate of 0.013 cm^{3}h^{-1} (mg catalyst)$^{-1}$ and a quantum efficiency of 0.2%	Thiosulfate gives best performance, excellent chemical stability, corrosion potential of -0.775 V_{SCE} and an exchange current density of 16 µA cm^{-2}, exhibits p-type extrinsic conductivity.
129	$CuCr_2O_4$, solid state reaction, delafossite $CuCr_2O_4$,	H_2 evolution based on a dis-persion of $CuCrO_2$ powder in aq. electrolytes containing various reducing agents (S^{-2}, SO_3^{-2} & $S_2O_3^{-2}$)	Low cost H_2 photocathode, inertness to corrosion, prolonged irradiation (>80 min) leads to a pronounced decrease of the photoactivity
c) Water Gas Shift Reaction and Methanol Steam Reforming			
145	skeletal copper catalysts+ Cr_2O_3	Role of additives in MSR and WGSR	Enhance the activity for the WGSR, MSR and methanol synthesis reactions
d) Water Gas Shift Reaction			
15	Different cats. co-ppt. method	Production of H_2 via WGSR, 150 & 250 ^{0}C	Cu-Zn-Al>Cu-Al>Cu-Mn, Cu-Cr>Cu-Fe>>Zn-Al>Cu-Co
e) Reforming of alcohols			
Methanol Steam Reforming			
14	$CuCr_2O_4$ nano-particulate ternary oxides	Using template technique - silica xerogel , 250 ^{0}C, WHSV = 52-57 h^{-1}	High activity and selectivity
Partial oxidation of methanol			
150	Cu/M/Cr (M = Zn, Ce, Fe, etc), co-ppt. method	Production of hydrogen by Partial oxidation of methanol	Exhibits high CH_3OH conversion and H_2 selectivity
Oxidative steam reforming of methanol			
151	Cr/Cu-spinel	Compact micro-structured string reactor	High activity, and selectivity to carbon dioxide (98%) and hydrogen, methanol conversion 91.5%
Steam reforming of ethanol			
159	$CuCr_2O_4$	Ethanol steam reforming at low temps using 12 wt.% C_2H_5OH in water mixtures	H_2 productivity 9-25 g H_2 (kg cat.)$^{-1}$(h)$^{-1}$ at 250-300 ^{0}C.
9. Pollution Abatement			
a) Abatement of CO/Soot			
280	$CuCr_2O_4$/ Al_2O_3 Impregn. method	CO-n-C_6H_{14} air-oxid: CO 1.6% ,n-C_6H_{14} 1.1%; reduction : 0.8% NO and 0.9 % CO in a flow reactor; S.V. 20000 h^{-1}	$CuCr_2O_4$ most active catalyst coating of soot filters in CO and n-hexane oxidation and in combustion of soot.
229	Bi_2O_3/$CuCr_2O_4$-CuO, comple-xing-coppt. method	Oxidation of CO, pre-coating of NH_4^+ on the surfaces of Bi_2O_3 nano-particles	High catalytic activities
b) Hydrocarbon abatement			
213	$CuCr_2O_4$/Al_2O_3, Co-impregn, metal 20%; Cu/Cr=1 calc. 500^{0}C	CO-propene oxidation, Temp. 300-900^{0}C; prereduced cat.	Mech.: adsorbed propene transforms to a unidentate CO_3^{2-} and liberates H_2O vapour
170	$CuCr_2O_4$, impre-method, calc. 600^0 C	CH_4 oxidation, Temp. range 300-700^{0}C at constant, CH_4 : air ratio of 1 : 30, constant CH_4 1.2%.	Activation energy- 110 kJ/mol, reaction rates between 10^{-3} and 10^{-4} (mol$_{CH4}$)/(g h)
254	$CuCr_2O_4$/ Al_2O_3	CH_4 oxidn.	Mechn.: adsorb. O_2 on active sites, oxid.→red. form R-E or L-H model