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Review Article

The Application of Transition Metal Nitride Catalyst in the HDO Reaction of Lignin and Its Model Compounds

Chang Sok Kim, Jong Nam Kim*, Hak myong Song, Hyon Il Do, Se Gwon O

Faculty of Chemical Engineering, Hamhung Branch of Science University, Hamhung 999092, Democratic People's Republic of Korea.

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Abstract

As the only abundant and renewable non-fossil resource that provides aromatic compounds in nature, lignin is an important raw material for the production of new energy and high-value chemicals. Transition metal nitride is widely used as a good hydrodeoxygenation (HDO) catalyst in the catalytic conversion reaction of lignin and its model compounds thanks to its crystal structure and properties, and good hydrodeoxygenation activity similar to noble metals. This paper reviewed the application of transition metal nitride catalysts in catalytic conversion of lignin and its model compounds. And the paper comprehensively analyzed the components of transition metal nitride catalyst, the nitriding method and the molar hourly space velocities (MHSV) in the preparation process, the carrier, the addition of other metals, the influence of reaction conditions on the catalytic activity and the reaction mechanism. In addition, the paper discussed the problems arising in applying the transition metal nitride catalysts in the reaction of lignin and its model compound HDO were proposed, and proposed the ways to develop nitride catalysts with higher catalytic performance and wider application prospect.

Keywords: Transition Metal Nitride; lignin; Hydrodeoxigenation; HDO; catalytic degradation; aromatic compound

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1. Introduction

Energy is absolutely indispensable for people's life and social development and with the development of society, the energy is more and more needed and consumed. Fossil fuels such as oil, coal and natural gas are the most important basic energy sources used by human beings. According to report, in 2015, fossil fuel consumption still accounts for 85% of the world's total energy consumption [1].

However, the rapid development of society and modern industry has led to the rapid depletion of fossil energy, as well as the serious environmental pollution caused by a large amount of greenhouse gases such as carbon dioxide, forcing humans to look for a new alternative energy source that is renewable and causes little or no environmental pollution. Among the numerous renewable energy sources, biomass can replace fossil fuels as it is renewable and helpful for environmental protection with its bio-dismantling property, and it has been widely researched [2-5]. Bio-oil is divided into four generations, the main raw materials of which are sugar, starch, vegetable oil, animal fat, lignocellulose, etc. Vegetable oil and animal fat are excluded as they are vital for people' life, thus lignocellulose is the main alternative energy source [6].

Lignin is the main component of lignocellulose, and the annual amount of lignin synthesized by plants in the world is as large as 1.5×10^{12} t [7]. It is also a major component in waste liquor of papermaking industry. Making 1 ton of paper produces 7 t of "black liquor", over 50% of

* Corresponding Author.
Email: kjn840124@163.com (J.N. Kim).

which is lignin or lignin decomposition products. The global pulp and paper industry produces over 5.0×10^7 ton of lignin every year, but only about 2% is effectively utilized and the rest is burned off or discharged into rivers. This is the waste of precious resources as well as the cause of serious envvironmental pollution [8-10].

Lignin stores 0.082% of the solar energy shielded by the earth's surface and about 95 billion tons of carbon in the earth's crust [7]. Lignin is the only renewable non-fossil resource with aromatic hydrocarbon structure in its structure, so it becomes the main chemical raw material, and it has a great energy value with its high content of carbon and hydrogen [1112]. Lignin is used to produce aromatic and aliphatic compounds which are needed for producing the chemical and pharmaceutical products, and it is used to produce bio-fuel which is vital for producing alternative fuel for aerial transportation.

However, the spatial structure and the bonding type of lignin are different and complicated with its sources and rich in its high oxygen content, so it has low calorific value and high viscosity, making it impossible to be used directly as fuel or chemical raw material [2]. In order to solve these problems, Hydrodeoxygenation (HDO) has been studied for the conversion of lignin and its decomposition products into useful chemicals and liquid fuels [13-18]. Typical structure of lignin is shown in Figure 1 [7].

As shown in the figure, the structural unit of lignin is not single, and its bonding types are different. Moreover, its spatial structures are different and complicated with its resources. Therefore, in order to study the hydrodeoxygenation reaction of lignin and its decomposition products, several model compounds with a structure similar to lignin have been proposed, and the development and application of catalysts for its HDO reaction have been studied. Catalyst is the most important research object in the HDO reaction of lignin and its model compounds.

At present, the catalysts, which is high in catalytic activity and widely researched, are mainly transition metal catalysts [19-25], sulfides [8,26-29], phosphatides [30-32], oxides [33-38], carbides [39-45], nitrides [67,77-85], etc. As the intercalation compound formed by nitrogen atoms inserted into transition metal crystals, transition metal nitride has the characteristics of atomic crystal, ionic crystal and transition metal, thus having specific physical and chemical properties.

These catalysts show good activity in the reduction of NO [46], the synthesis or decomposition of ammonia [47-49], hydrolysis (hydrodenitrification [50,51],

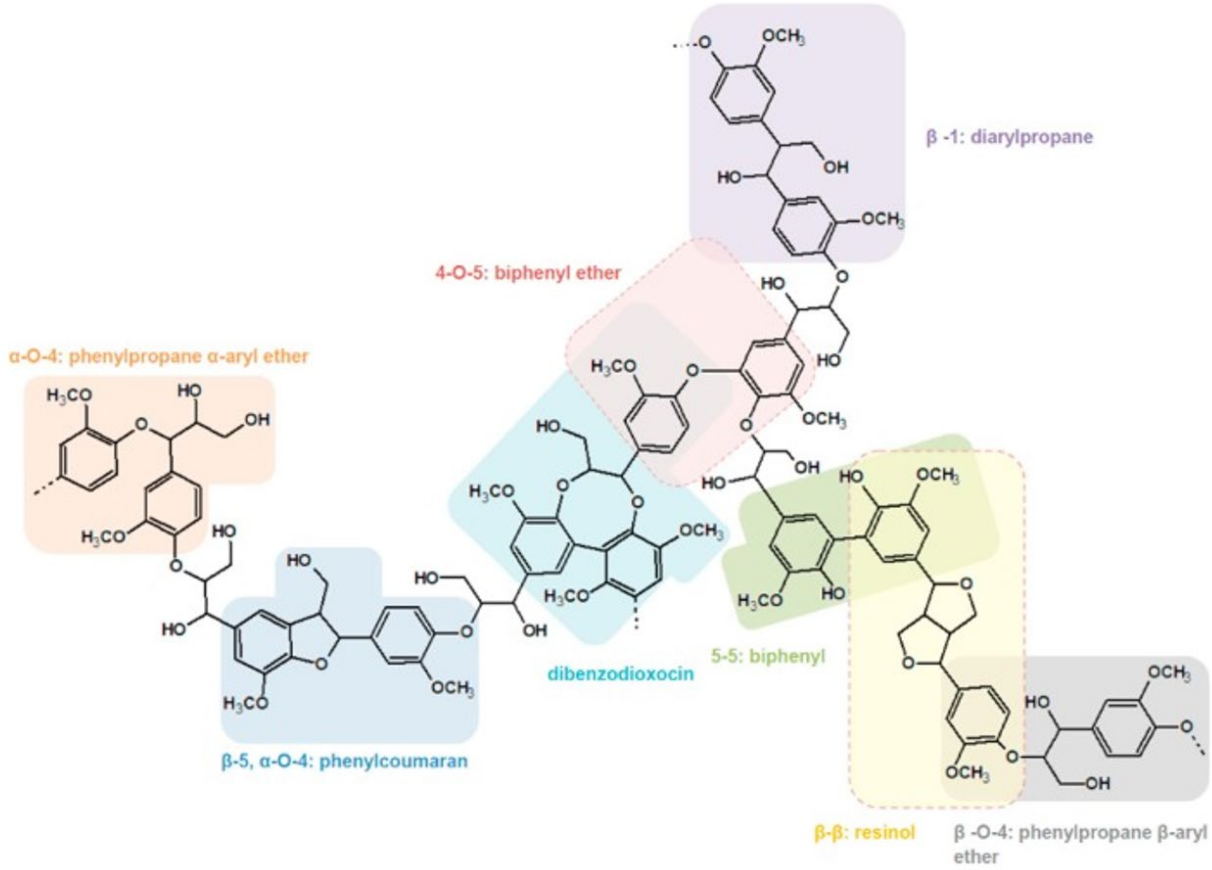


Figure 1. Typical structure and structural unit of lignin [7].

hydrodesulfurization [52,53], hydrodeoxygenation [54-57], etc.), isomerization of hydrocarbons [58] and other reactions. In particular, the catalytic activity of transition metal nitrides and carbides for hydrodeoxygenation reactions is similar or superior to that of noble metal catalysts, which is thanks to the fact that their crystal structures and electron densities are similar to that of noble metal [59,60]. So far, many literatures have reported the result of research on the catalytic activity, reaction characteristics and reaction mechanism of transition metal catalysts, sulfides and phosphatides in hydrodeoxygenation of lignin and its model compounds, but they have simply introduced transition metal nitride catalysts [8,10,13, 60-66]. Therefore, this paper is intended to provide a more detailed and comprehensive description of the hydrodeoxygenation characteristics of lignin or its model compounds over the transition metal nitride catalysts. We hope that this paper can contribute to improving the preparation process of nitride catalysts with high activity and selectivity from lignin for producing high value chemicals and bio-fuels.

2. Application of Transition Metal Nitride Catalysts in Hydrodeoxygenation of Lignin Model Compounds

The catalytic activity of transition metal nitride catalysts is similar to that of sulfide catalysts which are considered as typical hydrodeoxygenation catalysts, and its hydrodeoxygenation ability is very strong. Therefore, the transition metal nitride catalysts have a good application prospect [67]. At present, the research on the transition metal nitride catalysts mainly focuses on the molybdenum nitride catalysts, like on the transition metal sulfide catalysts. Therefore, the description of transition metal nitride catalysts is divided into the molybdenum nitride catalysts and the transition metal nitride catalysts.

2.1. Molybdenum Nitride Catalysts

As shown in Table 1, the main products are aromatic compounds as the result of hydrodeoxygenation of typical lignin model compounds applying molybdenum nitride catalysts. The activity and selectivity of molybdenum nitride catalysts depend on the crystalline phase of the active component, the specific surface area of the catalyst, the type of support and the dispersion of the active component on the surface of the support.

2.1.1. Preparation method of nitride catalyst and its influence on catalyst activity

The crystallization phase and specific surface area of nitride catalysts totally depend on the type and process of nitride gas. So far, most of the transition metal nitride catalysts are prepared by using the TPR (Temperature programmed Reaction, TPR) method. This preparation method was first proposed by Boudart *et al.* of Stanford University in 1985 when they studied the preparation methods of nitrogen compounds and carbides with high specific surface area [68,69].

In this method, the carbonated gas (H_2+CH_4) or nitrogen gas (NH_3) is passed through the transition metal oxide while slowing down heating, and the reaction process and its end point is determined by analyzing the composition of the gas at the reaction outlet, so as to obtain the carbides and nitrides with high specific surface area. Due to the high value of its specific surface area, the product is prone to combustion in the air and cannot be stable, so it should be passivated by an inert gas containing trace oxygen (about 1%) before being exposed to the air.

Boudart *et al.* observed the reaction process of MoO_3 and NH_3 by using electronic microscope to investigate the formation of γ-Mo_2N [68]. MoO_3 is a lamellar structure, and MoO_6 octahedrons-its structural unit- share edges and angles, and layers are connected by Van der Waals force. With the increase of temperature, active hydrogen and active nitrogen are generated by NH_3 decomposition, and they are inserted between the two layers of MoO_6 to generate H_xMoO_3 and $Mo_2O_yN_{1-y}$ intermediate compounds. Mo_2N is generated and extended on the crystal plane parallel to MoO_3 (120), but the surface morphology of the obtained solid remains unchanged. Therefore, the morphology of the final product Mo_2N is similar to that of MoO_3. In the final product, the (100) surface of Mo_2N is parallel to the (010) direction of MoO_3.

Volpe and Boudart *et al.* conducted XDR analysis on the obtained products at different temperatures of the aborted reaction, and observed the phase change of Mo species during the heating process [68]. The results showed that, under 620 K, MoO_3 basically does not change, but, at about 630 K, MoO_3 changes to low state transition. At 660 K, the crystalline phase structure of MoO_3 disappears, and MoO_2 and another new phase containing Mo, O and N is formed.

Zhang *et al.* analyzed the change of products when nitriding MoO_3 at different temperatures by using XRD, BET, FTIR and XPS [70]. The results showed that $H_{0.3}MoO_3$ phase and MoO_2 phase appeared at 673 K, and MoO_3 phase completely

disappeared and MoO_2 became the main phase at 773 K. When the nitriding temperature reaches 973 K and maintains for 2 hours, the diffraction peaks of MoO_2 and γ-$Mo_2O_yN_{1-y}$ all disappear, and a very complete diffraction peak of γ-Mo_2N appears. At this time, the specific surface area of the obtained γ-Mo_2N reached 140 $m^2.g^{-1}$, and the stomatal diameter was 20~30 Å.

In 1994, Wise and Markel first proposed the TPR method for preparing nitrides using H_2/N_2 mixture [71]. By monitoring the composition of exhaust gas, they found that during the synthesis process from MoO_3 to γ-Mo_2N, 99.88% of NH_3 decomposed into N_2 and H_2 at high temperature. The results of NH_3 decomposition kinetics show that the decomposition reaction of NH_3 has a great influence on the bed temperature. The local heating rate is more than twice that of the furnace, even with just 0.1 g of reactant. As NH_3 decomposition hinders heat transfer, it is almost impossible to synthesize molybdenum nitride catalysts with high specific surface area in large quantities by NH_3. They successfully synthesized γ-Mo_2N with a specific surface area of 150 $m^2.g^{-1}$ by replacing NH_3 with H_2/N_2 mixture [72].

The specific surface area of the final product is related to the concentration of water vapor in the tail gas. When water vapor is added to the synthetic gas or the molar hourly space velocity of N_2/H_2 mixture is slow and the increase of heating rate, the specific surface area of the product will decrease. This is related to the reaction producing H_2O and increasing the concentration of water vapor. They believed that the increase of water vapor promotes the hydrothermal sintering or lattice fluidization of intermediate and final products, which resulted in the reduction of specific surface area. Therefore, high molar hourly space velocity of the gas and low heating rate should be adopted to slow down the reaction rate and remove the generated water as soon as possible.

Compared with NH_3, H_2/N_2 mixture has many advantages as nitride gas. For example, it

Table 1. The result of hydrodeoxygenation reaction of lignin model compound over molybdenum nitride catalysts.

Catalyst	Support	Model compound	Reaction conditions				Conversion	Yield	Ref.
			T, ℃	*P*, MPa	*t*, h	TPR Gas	%	%	
Mo_2N	-	Guaialcol	300	5	4	NH_3, 19 h^{-1}	~65	Phenol ~60	[77]
						NH_3, 29 h^{-1}	~90	Phenol ~85	
						N_2/H_2,19 h^{-1}	~30	Phenol ~30	
						N_2/H_2, 29 h^{-1}	~35	Phenol ~35	
CoMoN	-	Guaialcol	300	5	4	NH_3, 29 h^{-1}	~75	Phenol ~65	
Mo_2N	AC(Cudu)	Guaialcol	300	5	4	NH_3	~5	Chatechol~2.5 Phenol ~2	[79]
	AC(Norit)						~9.5	Chatechol ~2 Phenol ~7.5	
	AC(Pica)						~3	Chatechol<2 Phenol~1	
Mo_2N	Al_2O_3	Guaialcol	300	5	4	NH_3	66	Phenol ~20 Chatechol ~10	[78]
						N_2/H_2	62	Phenol ~15 Chatechol ~10	
Mo_2N	SBA-15					NH_3	44	Phenol ~25 Chatechol ~5	
						N_2/H_2	40	Phenol ~12 Chatechol ~3	
CoMoN	Al_2O_3					NH_3	58	Phenol ~25 Chatechol ~10	
	SBA-15						24	Phenol ~10 Chatechol ~2	
Mo_2N	AC(Darco)	Guaialcol	300	5	4	NH_3	~40	Phenol ~20	[80]
Mo_2N	AC(Darco)					N_2/H_2	~40	Phenol ~20	
Mo_2N	AC(CGran)					NH_3	~18	Phenol ~10	
						N_2/H_2	~60	Phenol ~40	
Mo_2N	AC(GAC)					NH_3	~45	Phenol ~20	
						N_2/H_2	~55	Phenol ~35	
Mo_2N	AC(GCA)					NH_3	~45	Phenol ~30	
						N_2/H_2	~50	Phenol ~35	
CoMoN	AC(Darco)					NH_3	~40	Phenol ~20	
	AC(CGran)					NH_3	~30	Phenol ~15	
	AC(GAC)					NH_3	~35	Phenol ~15	
	AC(GCA)					NH_3	~30	Phenol ~15	
6.8% Mo_2N	TiO_2	Phenol	400	2.5	2	NH_3	58	(Benzene~90 Cyclohexene ~7.5) [a]	[81]

can easily reach a high specific surface area at a lower temperature (the final nitride temperature is about 50 K lower than that of NH_3), and 100% synthetic gas can be recycled after drying. In particular, it is possible to overcome the large temperature gradient caused by the decomposition of NH_3 when NH_3 is used, so synthesizing large quantities of γ-Mo_2N is possible. Based on these results, nitride catalysts with higher catalytic activity were synthesized by adjusting the heating rate, heating step and molar hourly space velocity of nitride gas in TPR process [73,74].

Choi *et al.* studied the synthesis conditions and formation mechanism of γ-Mo_2N using the TPR method, and found that low heating rate and high NH_3 molar hourly space velocity are conducive to the formation of molybdenum nitride with high specific surface area [75]. They changed the rates of two heating stages (623~723 K, 723~973 K) and NH_3 air speed, combined with in-situ XRD analysis of the product and controllable atmosphere SEM analysis, and determined that the low heating rate in the first stage and the high heating rate in the second stage are conducive to the formation of molybdenum nitride with high specific surface area, and high NH_3 space velocity is always necessary.

Seetharamulu Podila *et al.* prepared Mo_2N and Co_3Mo_3N catalysts with high specific surface area by TPR method using ammonia treatment [76]. For this reason, the precursor was heated to 300 ℃ at the heating rate of 1 ℃/ min, then to 700 ℃ at the heating rate of 0.5 ℃/ min, and kept at 700 ℃ for 2 h. After the reaction, it cooled rapidly to room temperature in NH_3 atmosphere, and then passivated for 2 hours with 1% O_2/He mixture.

Ghampson *et al.* synthesized molybdenum nitride without support under different nitrogen/reducing gas and molar hourly space velocity conditions, and then evaluated its catalytic activity for the hydrodeoxidation reaction of guaiacol [77]. TPR reaction temperature program is divided into five steps; first, the air inside the reactor is eliminated by using nitrogen for 30 min at room temperature before starting the reaction, secondly, the precursor is heated upto 300 ℃ at the speed of 9.33 ℃/min, thirdly, upto 500 ℃ at the speed of 0.6 ℃/min, fourthly, upto 700 ℃ at the speed of 0.6 ℃/min in NH_3 or N_2/H_2 gas mixture, and finally maintained for 2 h at this temperature before it is nitrided. After the reaction is completed, the product is cooled down to room temperature in situ, followed by passivation with 1%O_2/N_2 mixture for 12 h. The main product is phenol in the hydrodeoxygenation reaction of guaiacol over the unsupported molybdenum nitride catalyst obtained by using TPR method in NH_3 or N_2/H_2 gas mixture. Also, small amount of deoxygenation products is generated in the long reaction process such as catechol, benzene, cyclohexane and cyclohexene.

The selectivity of the transformation of guaiacol is expressed as the value of phenol/catechol (Phe/Cat) ratio, which is calculated at 10% guaiacol conversion. Figure 2

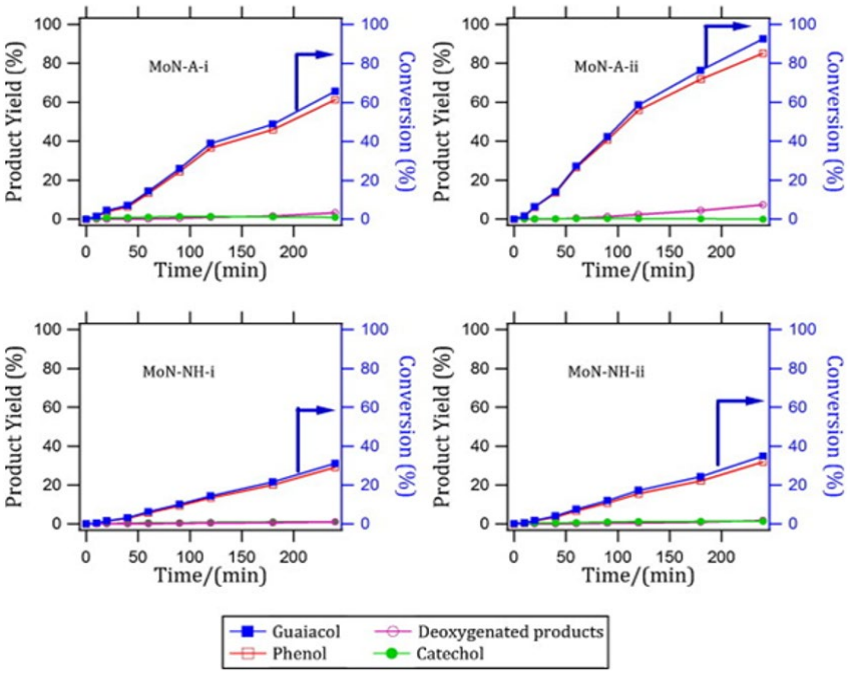


Figure 2. Change of conversion rate and product yield in the hydrodeoxygenation of guaiacol [73]. (The suffix "A" denotes nitride catalysts prepared from ammonia and the suffix "NH" denotes nitride catalysts prepared from N_2/H_2 mixtures. And the suffixes "i" and"ii" denote the nitride catalysts prepared at the molar hourly space velocities of 19 h^{-1} and 29 h^{-1}, respectively)

shows the change of conversion rate and product yield in the hydrodeoxygenation of guaiacol over the catalyst which is prepared under the molar hourly space velocities of NH_3 or N_2/H_2 is 19 h^{-1} and 29 h^{-1}, respectively. As shown in Figure 2, the catalyst with highest activity is MoN-A-ii prepared in 29 h^{-1} molar hourly space velocity by using flowing ammonia.

Figure 3 shows the XRD analysis result of the catalyst where MoN-A-ii is composed of single phase γ-Mo_2N, and its N/Mo atomic ratio is the highest. MoN-A-i is mainly dominated by γ-Mo_2N containing a little amount of molybdenum oxide, so its reaction is a little slow. MoN-NH-i contains β-$Mo_2N_{0.78}$, and MoN-NH-ii contains a large amount of molybdenum oxide and molybdenum metal impurities. In terms of the space velocity of nitride gas, the intrinsic activity and the reaction speed of MoN-A-ii and MoN-NH-ii prepared at the molar hourly space velocity of 29 h^{-1} were higher than that of MoN-A-i and MoN-NH-i prepared at the space velocity of 19 h^{-1}. The highest phenol/catechol ratio of MoN-A-ii reached 49, and the yield of phenol and catechol reached 9.7% and 0.2%, respectively. This is because only γ-Mo_2N exists in this catalyst and it has a strong ability of removing methoxy groups directly. These results indicate that the phase composition of catalysts depends on different nitriding/reducing gases and molar hourly space velocities, which affects the activity and selectivity of catalysts.

Ghampson *et al.* investigated the effects of nitride gas on the activity of molybdenum nitride catalysts supported by γ-Al_2O_3 and SBA-15 respectively [78]. The main active phase of the catalyst prepared by using TPR method with ammonia gas was γ-Mo_2N and its N/Mo ratio was

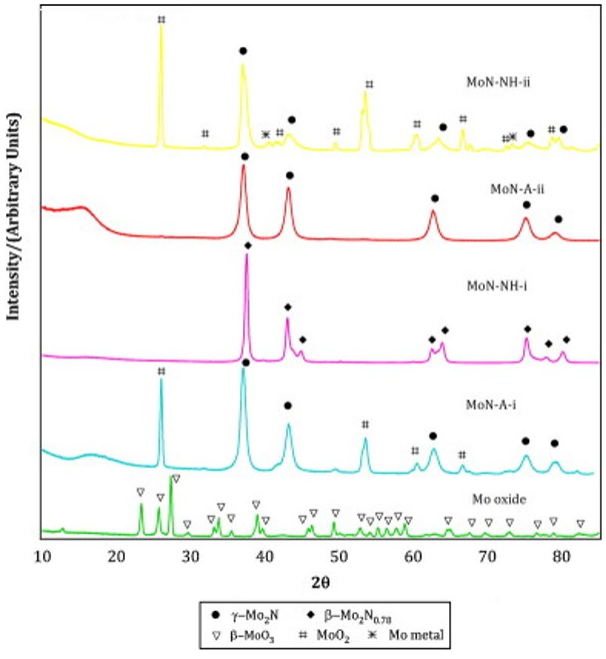


Figure 3. XRD of bulk oxides and nitrides [73].

relatively high. In these catalysts hydrodeoxygenation reaction speed of guaiacol is higher than those prepared in N_2/H_2 mixture with β-$Mo_2N_{0.78}$ as its main active phase. In particular, the phenol/catechins ratio was much higher in Mo_2N/SBA-15-A. These results indicate that the crystalline phase of the active component is the most important factor that determines the catalytic activity of nitride catalysts, that is, the conversion rate of guaiacol and the selectivity of the products, and it is greatly affected by the nitriding method and conditions.

2.1.2. Effects of support on catalyst activity

The catalytic effects of γ-Mo_2N catalysts supported on three different commercial activated carbons (e.g., Pica, Norit and Crdu) on the hydrodeoxygenation of guaiacol were investigated [79]. The reaction was conducted under the conditions of the initial hydrogen pressure of 5 MPa and 300 ℃, and the main product was also phenol. The average pore diameters of the three supports and the catalyst prepared by the reaction between the precursor prepared by impregnation and NH_3 were all within the mesopore field, and the mesopore volume of the catalyst was the largest when Norit was used as the support, which is shown in Table 2.

The Mo_2N/Norit catalyst had the smallest micropore volume and the largest mesopore diameter. The results indicate that the Mo_2N/Norit catalyst has the highest activity, which is due to the maximum mesopore volume of the catalyst that is conducive to the diffusion of the reactants on the inner surface of the main active point. The results also showed that improving the dispersion of active components on the catalyst was conducive to improving the HDO activity of the catalyst. In the case of Mo_2N/Norit catalyst, the phenol/catechol ratio in the product is the highest, which means that this catalyst has the highest selectivity for phenol. This shows that the ratio of the activity point of demethylation to the activity point of demethylation is also closely related to the dispersion of the active component of the catalyst.

I. T. Ghampson *et al.* prepared the activated carbon supported molybdenum nitride catalyst by using TPR method in NH_3 and N_2/H_2 mixture as nitride gas, and then investigated the influence of the support on the guaiacol HDO reaction [80]. They first took four kinds of activated carbons with different micropore/mesopore ratio, mesopore/macropore ratio and different surface chemical properties as the supports, prepared precursor by using deposition method, and then prepared molybdenum nitride catalyst by using TPR method with NH_3 and N_2/H_2 mixture as nitride gas. The hydrodeoxygenation reactions of

guaiacol were performed in initial hydrogen pressure of 5 MPa at 300 ℃ for 4 h, the results of which are shown in Table 3. As shown in Table 3, MoN/CGran-NH catalyst has the highest activity. The results show that the activity of catalyst is related to the existence of Mo_2N, but has nothing to do with the support. The activated carbon supported molybdenum nitride catalyst made of N_2/H_2 mixed gas is more active than the same series catalyst made of NH_3, which is related to better dispersion of molybdenum oxide. Oxygen functional groups on the surface of activated carbon do not participate in the conversion reaction of guaiacol, but interact with metal precursor compounds to promote its dispersion and increase catalytic activity. The higher the dispersion of molybdenum and the mesopore fraction of the support were, the higher the activity of the catalyst was, and the best combination was MoN/ CGran-NH.

The HDO catalytic activities of molybdenum nitrides on guaiacol also changed with γ-Al_2O_3 and SBA-15 mesoporous silica as supports [78]. In the molybdenum nitride catalyst supported by Al_2O_3 with higher acid point density, the reaction speed was more than twice as fast as that supported by sba-15, and the conversion rate of guaiacol was also higher (Table 1). However, the SBA-15 mesoporous silica supported molybdenum nitride catalyst had better selectivity for phenol, which is shown in Figure 4.

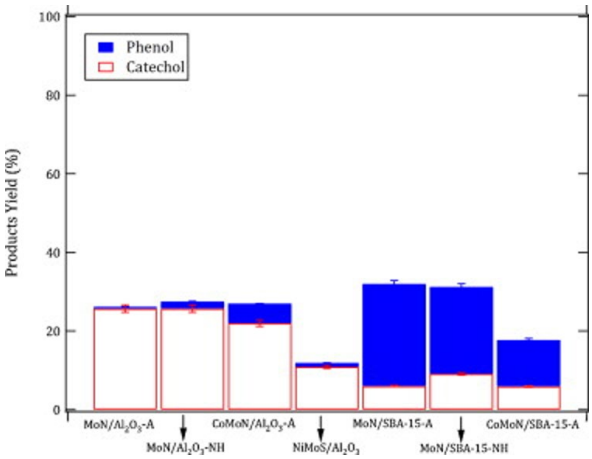


Figure 4. Phenol and catechol yields calculated at 10% guaiacol conversion [78].

Table 2. Specific surface (S_{BET}), micropore volume (V_o), mesopore volume (V_m) and average pore diameter of the catalysts and supports, and zero-point charge (pH) of the activated carbon supports [79].

Sample	S_{BET} ($m^2.g^{-1}$)	V_o ($cm^3.g^{-1}$)	V_m ($cm^3.g^{-1}$)	Pore diameter (nm)	Zero-point charge (pH)
Norit	612	0.12	0.50	7.9	6.88
MoO_3/Norit	479	0.08	0.46	8.2	
Mo_2N/Norit	752	0.14	0.58	7.9	
Pica	1181	0.41	0.16	4.3	6.81
MoO_3/Pica	1072	0.31	0.2	4.4	
Mo_2N/Pica	1213	0.31	0.32	5.0	
Cudu	1057	0.33	0.18	5.0	7.81
MoO_3/Cudu	741	0.23	0.12	4.8	
Mo_2N/Cudu	811	0.23	0.19	4.9	
Unsupported			–		–
MoO_3	3.0	–		–	
Mo_2N	1.6	–	–	–	

Table 3. Catalytic activities of carbon-supported Mo nitride catalysts [80].

Catalyst	Activity ($\times 10^6$mol.$g^{-1}_{catalyst}$ s^{-1})	Intrinsic activity ($\times 10^4$ molec. Mo $at^{-1}.s^{-1}$)
MoN/Darco-A	6.4	60.5
MoN/Darco-NH	6.5	65.1
CoMoN/Darco-A	6.2	69.6
MoN/CGran-A	4.6	46.3
MoN/CGran-NH	9.0	83.6
CoMoN/CGran-A	5.3	49.9
MoN/GAC-A	5.9	74.1
MoN/GAC-NH	7.9	75.6
CoMoN/GAC-A	2.9	33.1
MoN/GCA-A	6.8	65.8
MoN/GCA-NH	7.5	81.8
CoMoN/GCA-A	5.4	61.2

These results indicate that γ-Al_2O_3 supported molybdenum nitride catalyst has stronger demethylation ability, while SBA-15 mesoporous silica supported molybdenum nitride catalyst has stronger demethoxylation ability. However, the result of experiment with γ-Al_2O_3 and SBA-15 mesoporous silica as catalysts indicates that γ-Al_2O_3 transforms guaiacol into catechol, while the SBA-15 mesoporous silica has no activity for HDO reaction. Therefore, the high selectivity of molybdenum nitride catalyst to phenol is believed to come from the DMO activity of molybdenum oxynitride and molybdenum oxynitride.

Sara Boullosa-Eiras *et al.* compared the HDO activities of TiO_2 supported molybdenum nitride, molybdenum phosphide and molybdenum oxide catalysts on phenol [81]. After the reaction for 2 h under the initial hydrogen pressure 2.5 MPa at 400 ℃, phenol conversion rate of 6.8% Mo_2N/TiO_2 catalyst reached 58%, which was lower than that of 6.8% Mo_2C/TiO_2 catalyst, but the selectivity of benzene was the highest level of more than 90% (Table 1).

In contrast, there was almost no selectivity of cycloalkanes, such as cyclohexane and methoxycyclopentane. It can be said that the support can improve the dispersion of the active components of catalysts, change their electronic structures and surface acidity, and improve their HDO activities. With high mesopore fraction and large surface acidity, the support can be good for nitride catalyst. The support can also have an indirect effect on the selectivity of the catalyst depending on its catalytic activity.

2.1.3. Effect of adding Co on the activity of molybdenum nitride catalyst

I. T. Ghampson and his colleagues considered that the addition of Co could improve the reactivity of bulk molybdenum nitride catalysts HDS [82] and HDN [83], so they added Co to the unsupported molybdenum nitride catalyst and investigated the activity of the catalyst for the HDO reaction of guaiacol [77]. The results showed that the addition of Co increased the production of deoxygenated products (benzene, cyclohexene and cyclohexane), but did not improve the catalytic activity of the catalyst for the HDO reaction of guaiacol. They believed that this was due to incomplete formation of the bimetallic nitride Co_3Mo_3N. In addition, they investigated the effect of adding Co to the activated carbon supported molybdenum nitride catalyst on the activity of guaiacol HDO [80]. The results showed that the addition of Co did not improve the activity of the catalyst (Tables 1 and 3). The researchers believed that this was also because the bimetallic nitride Co_3Mo_3N was not fully formed and the distribution of Co was not even.

The atomic ratio of Mo/Co on the surface determined by XPS analysis was higher than that of Mo/Co determined by metal content analysis, which indicated that the added Co was preferentially deposited in the support and buried by Mo, resulting in uneven distribution of Co. Therefore, the activity of the catalyst was not improved after the addition of Co. Co was added to γ-Al_2O_3 and SBA-15 supported molybdenum nitride catalysts, and the catalyst activity also was not significantly improved [78].

2.1.4. The HDO reaction pathway of lignin model compounds over the nitride catalysts

There are various formulations for the HDO reaction pathway of lignin model compounds under the action of nitride catalysts. Ghampson said that guaiacol was directly converted to phenol through DMO when talking about the HDO reaction of guaiacol involving the unsupported molybdenum nitride catalyst (Figure 5) [77]. The results showed that the conversion rate of guaiacol was determined by the presence of different phases in the unsupported catalyst, rather than by BET surface area and Mo content of the catalyst.

Ghampson discussed the catalytic activity of activated carbon supported molybdenum nitride catalyst for the HDO reaction of guaiacol, and also reported that under the action of molybdenum nitride catalyst, guaiacol was directly converted to

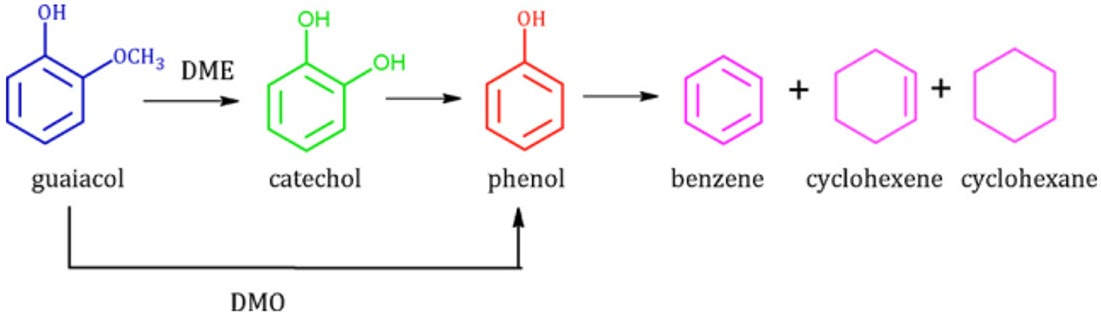


Figure 5. The HDO pathway of guaiacol [77].

phenol by DMO reaction [80]. They investigated the changes of the products on the molybdenum nitride catalysts supported on four activated carbons with different surface chemical properties, and pointed out that the HDO of guaiacol was carried out according to the reaction pathway proposed by Bui *et al.* [84] (Figure 6). And catechol is constantly generated in a long reaction time, which indicates that the conversion of catechol to phenols is not obvious in this catalyst although demethylation and demethoxylation occur directly. In the HDO reaction of guaiacol over Mo_2N/AC, activated carbon support has no activity, while DME and DMO can only be carried out at the active point of metal nitride [80]. Therefore, the possibility of two HDO pathways of guaiacol shown in Figure 6 proves that there are two active sites on the Mo_2N/AC catalyst.

It was assumed that the unsaturated Mo atoms are mainly responsible for the demethylation and hydroxylation, and the demethylation occurs at the deficient position of nitrogen [80]. However, it remains to be studied why the DMO pathway is preferred than DME pathway for nitride catalysts. The previous research results show that the activity and selectivity of the catalysts are significantly affected by the support properties during the HDO conversion of guaiacol under the action of cobalt-molybdenum sulfide catalysts [85,86].

Thanks to the high dispersion of the active phase of the catalyst on the Al_2O_3 support, the Al_2O_3 supported catalyst exhibits higher catalytic activity compared with other catalysts supported on SiO_2, activated carbon and others. This result was also observed in molybdenum nitride catalysts. Ghampson *et al.* obtainded similar results in the HDO reaction of guaiacol under the action of SBA-15 silica monomer and Al_2O_3 supported molybdenum nitride catalysts [78].

As shown in Figure 7, the time-based reaction product concentration changes are just opposite to each other under the action of Al_2O_3 supported molybdenum nitride catalyst and SBA-15 supported molybdenum nitride catalyst. Under the action of Al_2O_3 supported catalyst, the important early product is catechol, and the amount of phenol exceeds the amount of catechol after a long reaction time. Under the condition of using SBA-15 supported catalyst, the yield of phenol is higher than that of catechol whether the conversion rate of guaiacol was high or low. The result shows that guaiacol is transformed into phenol through DME and DMO under the supported catalyst Al_2O_3, while in the supported catalyst of mesoporous silica, it is directly transformed into phenol through DMO (Figure 6). The formation and subsequent methylation of catechol (Figure 8) are affected by the acidic nature of the support [85].

However, γ-Al_2O_3 has a higher acid point density than TiO_2 or ZrO_2, and the acid point density of MoN/Al_2O_3-A catalyst is 4 times higher than that of MoN/SBA-15 catalyst, so it is favorable for DME and methylation reactions. The acid point of Al_2O_3 is different from that of SBA-15, and the presence of Lewis acid point is the reason that Al_2O_3 promotes the formation of catechiol.

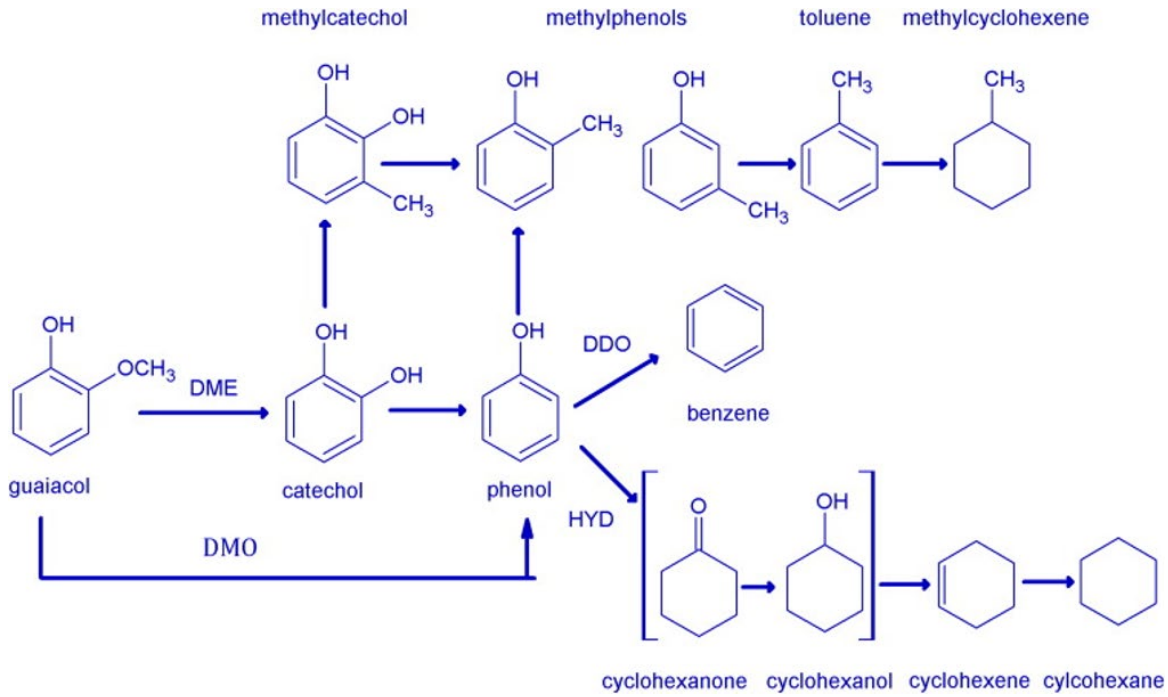


Figure 6. Hydrodeoxygenation pathway of guaiacol. Adapted from Bui *et al.* [80,84].

2.2. Other Nitride Catalysts

2.2.1. Cobalt nitride catalyst

Xiao Hao Liu *et al.* prepared magnetic nitrogen-doped carbon supported cobalt nitride catalysts (CoN_x@NC) by co-pyrolysis of cellulose and cobalt nitrate under NH_3 atmosphere, and studied HDO activity of catalyst in eugenol conversion [87]. α-cellulose/acetone solution and $Co(NO_3)_2 \cdot 6H_2O$ acetone solution were mixed together and concentrated through rotary evaporation, and then dried for 10 h at 105 ℃ to obtain precursor. The precursor was heated in NH_3 flow through the heating temperature program, reacted for 2 h at 500 ℃ ~ 900 ℃ to obtain magnetic CoN_x@NC.

HDO activity of eugenol was measured under the condition of 200 ℃,2 MPa of H_2, which showed that the CoN_x@NC-650 pyrolyzed at 650 ℃ exhibited the best HDO activity. After 1.5 h, the eugenol conversion rate reached 100%, and the yield of the main product propyl cyclohexanol reached 86.6%. When the reaction period was prolonged to 2 h, the yield of propyl cyclohexanol reached 99.9%. When solid acid HZSM-5 was added to the catalyst system, the main product was propylcyclohexane (96%) and contained a small amount of propylcyclohexene (3.2%).

Under the condition of the initial hydrogen pressure 2 MPa, 200 ℃, 2 h of reaction, CoN_x@NC-650 also showed high HDO activity for other

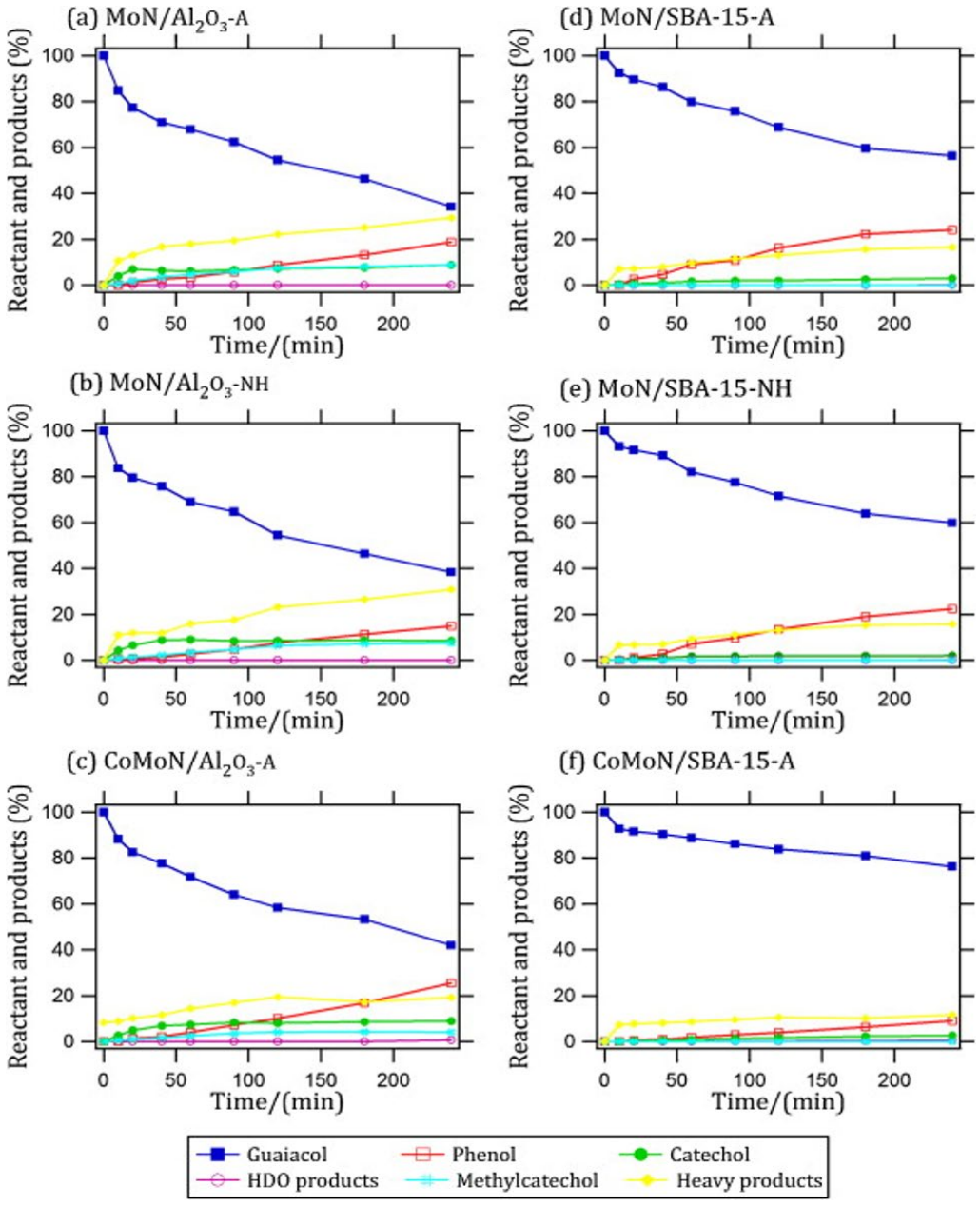


Figure 7. Changes of the transformation of guaiacol and the yield of products with time for (a) MoN/Al_2O_3-A, (b) MoN/Al_2O_3-NH, (c) $CoMoN/Al_2O_3$-A, (d) MoN/SBA-15-A, (e) MoN/SBA-15-NH, and (f) CoMoN/SBA-15-A catalysts [78].

lignin-derived phenolic compounds (Table 5). The stability of CoNx@NC-650 catalyst was estimated in the conversion of eugenol to propylcyclohexanol, which showed that the yield of propylcyclohexanol was decreased to a certain degree after four runs (Figure 8).

2.2.2. Titanum niride catalyst

Valerio Molinari *et al*. synthesized the TiN-Ni nanocomposite, which is a heterogeneous catalyst, and applied it to the hydrolysis of aryl ethers (*β*-O-4, *α*-O-4, 4-O-5, etc.), known as representative dimers to study their activities [88] (Tables 6,7). They synthesized TiN

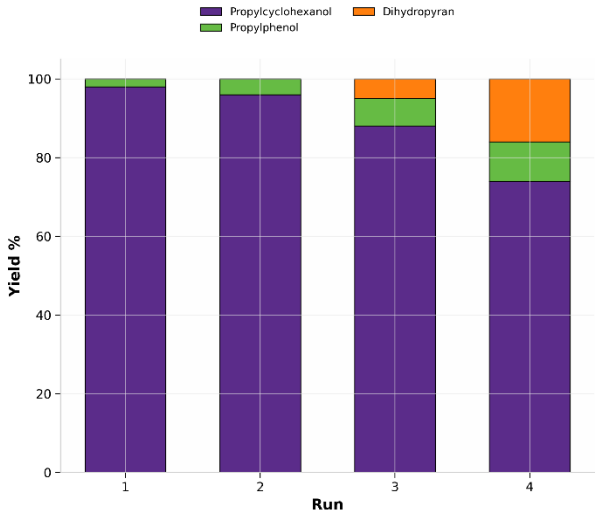
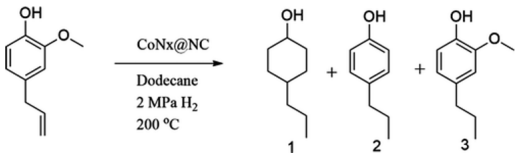


Figure 8. Recycle of the catalyst. Reaction conditions: 164 mg (1 mmol) of eugenol, 10 mL of n-dodecane, 76 mg of CoNx@NC-650, 2 MPa H_2, 200 ℃, 2 h [87].

Table 5. HDO of other phenolic compounds* [87]. Reaction conditions: 1 mmol of substance, 50 mg of HZSM-5, 10 mL of n-dodecane, 76 mg of CoNx@NC-650, 2 MPa H_2, 200 ℃ for 2 h. [a]Reaction time = 12 h. [b]Reaction time = 8 h. [c]The dosage of the substance was 0.5 mmol, and the yield was calculated by 1 mol of substance generating 2 mol of cyclohexane. [d]The dosage of HZSM-5 was 100 mg.

No	Substrates	Conv. (%)	Products	Yield (%)
1	Phenol	100	Cyclohexanol	91
2	2-Methoxyphenol (Guaiacol)	100	Cyclohexanol	99.6
3	3-Methoxyphenol	100	Cyclohexanol	95
4	2,6-Dimethoxyphenol	43.4	Cyclohexanol + 2-Methoxycyclohexanol	9.1 / 9.7
5[a]	2,6-Dimethoxyphenol (modified)	100	Cyclohexanol	99.9
6	4-Isopropylphenol	100	4-Isopropylcyclohexanol	98.2
7	3-Isopropylphenol	100	3-Isopropylcyclohexanol	99.9
8	1,2-Benzenediol (Catechol)	100	Cyclohexanol + Cyclohexane-1,2-diol	5.2 / 62.4
9[b]	1,2-Benzenediol (modified)	100	Cyclohexanol	99.9
10	1,3-Benzenediol (Resorcinol)	100	Cyclohexanol + Cyclohexane-1,3-diol	45 / 43.2
11[ab]	1,3-Benzenediol (modified)	100	Cyclohexanol	98.6
12[c]	Diphenyl ether	100	Cyclohexanol	92
13[c]	4,4'-Dihydroxydiphenyl ether	100	Cyclohexanol	65
14[bc]	4,4'-Dihydroxydiphenyl ether (modified)	100	Cyclohexanol	99.9

Table 4. HDO of eugenol over CoNx@NC catalysts[a] [87].



Entry	Catalyst	Time (h)	Conversion (%)	Yield (%)		
				1	2	3
1	CoNx@NC-500	1.5	5.2	0.5	0	4.6
2	CoNx@NC-600	1.5	100	45.5	15.6	38.8
3	CoNx@NC-650[b]	1.5	100	86.6	8.6	4.7
4	CoNx@NC-700	1.5	100	38.9	48.7	9.3
5	CoNx@NC-800	1.5	100	3.7	4.7	90.2
6	CoNx@NC-650[b]	2	100	99.9	0	0
7	NC-650	2	2.9	0	0	2.9
8	Co@C-650	2	24.7	0	0	21.7
9	Co/NC	2	100	0.6	0.2	99.1

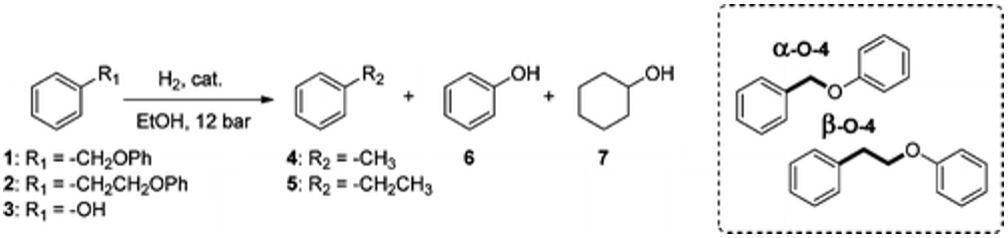
[a] 164 mg (1 mmol) of eugenol, 10 mL of n-dodecane, the dosage of catalysts contained 5 mg of cobalt.
[b] For CoNx@NC-650, the content of cobalt was 6.53 wt% and the dosage of the catalyst was 76 mg.

precipitated them in an ethanol solution of nickel acetate tetrahydrate (NiAc), and calcined it to make a catalyst. As shown in Table 6, when TiN - Ni composites were applied to hydrolysis of *α*-O-4 model compound, the conversion rate already reached 100% at 125 ℃, and the main products were toluene and phenol, the selectivities of which were 54% and 46%, respectively.

In case of *β*-O-4 as reactant, the conversion rate reached 100% at 150 ℃, and the main products were ethyl bebzene and cyclohexanol, the selectivities of which were 54% and 46% respectively. TiN-Ni catalysts were applied to hydrolysis of phenol at 150 ℃, cyclohexanol was obtained at the conversion rate of 55%, which showed the high hydrogenation ability of TiN-Ni. TiN-Ni catalysts were applied to hydrolysis of 4-O-5 compounds known as one of the solid lignin model compounds, and the result showed its excellent hydrolysis activity (Table 7).

The conversion rate reached 99% under the condition of 150 ℃, 0.3 mL/min H_2, concentration of 25 mM, and the main products were benzene and cyclohexanol, the selectivities of which were

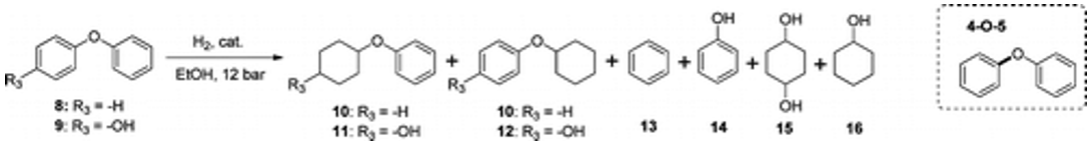
Table 6. Effect of Ni, TiN, and TiN-Ni catalysts on hydrogenolysis of different lignin model molecules [88].



Entry	Cat.	Substrate	*T* (°C)	Conversion (%)[c]	Selectivity (%)[c]				Productivity ($mmol.h^{-1}.g_{cat}^{-1}$)
					4	5	6	7	
1[a]	TiN	1	150	0	–	–	–	–	–
2[a]	Ni	1	100	0	–	–	–	–	–
3[a]	Ni	1	125	18	51	–	49	–	0.225
4[a]	Ni	1	150	90	57	–	43	–	1.282
5[a]	TiN-Ni	1	100	67	53	–	47	–	0.666
6[a]	TiN-Ni	1	125	>99	54	–	46	–	1.013
7[a]	TiN	2	150	0	–	–	–	–	–
8[b]	Ni	2	150	0	–	–	–	–	–
9[a]	TiN-Ni	2	150	65	–	57	–	43	0.695
10[b]	TiN-Ni	2	150	>99	–	54	–	46	0.608
11[b]	TiN-Ni	3	150	55	–	–	–	100	0.620

[a] Conditions: 0.05 M solution of starting material in EtOH, 12 bar, 0.5 $mL.min^{-1}$.
[b] 0.3 $mL.min^{-1}$.
[c] Determined by GC-MS analysis. Accordingly, control experiments on phenol 3 at 150 °C and 0.3 $mL.min^{-1}$ resulted in a conversion of 55% into 7.

Table 7. Effect of Ni, TiN, and TiN-Ni catalysts on hydrogenolysis of different diaryl ethers [88].



Entry	Cat.	Substrate	*T* (°C)	Conversion[c] (%)	Selectivity (%)[c]							Productivity ($mmol.h^{-1}.g_{cat}^{-1}$)
					10	11	12	13	14	15	16	
1[a]	TiN	8	150	0	–	–	–	–	–	–	–	–
2[a]	Ni	8	150	<5	–	–	–	–	–	–	–	–
3[a]	TiN-Ni	8	125	68	42	–	–	35	–	–	23	0.223
4[b]	TiN-Ni	8	150	99	5	–	–	46	–	–	49	0.259
5[b,d]	TiN-Ni	9	150	65	–	22	–	49	–	25	4	0.179

[a] a Conditions: 0.025 M of starting material in EtOH, 12 bar, 0.5 $mL.min^{-1}$.
[b] 0.3 $mL.min^{-1}$.
[c] Determined by GC-MS analysis.
[d] Uncorrected GC data.

46% and 49% respectively. Based on the confirmation of high HDO activity of the TiN-Ni composites, Valerio Molinari *et al.* compared the activities of TiN-Ni catalyst and TiO_2-Ni catalyst for the *α*-O-4 compound [90]. In the relatively low temperature range of 100 ℃ - 130 ℃, TiN - Ni already reached a higher conversion rate, and the selectivities of benzene and phenol were 54% and 45% respectively, while the conversion rate of TiO_2 - Ni reached about 60%. In particular, the review of stability of the catalyst showed that HDO activity for *α*-O-4 compounds were not significantly reduced even after TiN-Ni contact with lignin for 60 h or 500 h, and the conversion rate was very close to that of fresh catalyst when heated to 150 ℃.

3. Application of Nitride Catalyst in HDO Reaction of Lignin and Biomass Pyrolysis Vapors

The research was conducted to apply the nitride catalyst directly to degradation of kraft lignin, a by-product of papermaking industry. Xiao Lei Ma *et al.* investigated the ethanolysis of Kraft lignin based on molybdenum catalyst in supercritical ethanol medium [91]. The ethanolysis of Kraft lignin was conducted for 6 hours over four catalysts including molybdenum, molybdenum oxide, molybdenum nitride and molybdenum carbide at 10.6 MPa and 553 K. Molybdenum nitride is obtained by reacting the oxide precursors with N_2/H_2 mixture for 1 h at the final temperature of 973 K. As a result, the main products were aliphatic alcohol, ester, phenol, benzyl alcohol and aromatic compounds, and the total yield was 1185 mg/g lignin in case of molybdenum nitride. The result showed that the activity of molybdenum nitride is lower than that of carbide and metal molybdenum, and much higher than that of oxide when compared with the other three kinds of catalyst.

In addition, Meng Meng Chen *et al.* studied the ethanolysis of Kraft lignin in the supercritical ethanol reaction system by using alumina supported molybdenum nitride catalyst [92]. They investigated the effects of reaction conditions and molybdenum content on the catalytic activity, and said that 30 wt % Mo_2N/Al_2O_3 nitrided at 700 ℃ has the best catalytic performance. The main products of this reaction are alcohols, esters, aromatic compounds and other sulfur free products, in addition to a little thioether. They investigated the effect of nitriding temperature on the ethanolysis of Kraft lignin over alumina supported molybdenum nitride catalyst. The catalysts were prepared by nitriding supported Mo oxide precursors with nitrogen–hydrogen mixtures via temperature-programmed reaction. The reaction was carried out through a four-stage temperature program; the temperature was increased from room temperature to 350 ℃ at the heating speed of 10 ℃/min, then to 500 ℃ at the heating speed of 1 ℃/min, and finally to a preset temperature at the heating speed of 2 ℃/min and kept for 2 hours to obtain nitrides. The total yield of sulfur-free production increased with the rise of nitriding temperature, and at 700 ℃, it reaches the maximum of 1189 mg/g lignin and aliphatic compounds and aromatic compounds accounted for 907 mg/g lignin and 282 mg/g lignin, respectively.

The formation of thioethers and the presence of hydrogen sulfide in the gas phase products show that the molybdenum nitride catalyst synthesized at this temperature has good sulfur resistance and hydrodesulfurization performance. The yield of aromatic products in the product increased with the increase of molybdenum content of the main active component of the catalyst, and reached the maximum value of 282 mg/g lignin in case of the molybdenum content of 30%. In contrast, the yield of aliphatic compounds such as alcohols and esters decreased monotonously with the increase of molybdenum content.

With the extension of the reaction period, the total yield of the products increased sharply, especially the yield of aromatic compounds. When the reaction period was extended from 2 h to 6 h, the lignin increased from 48 mg/g to 282 mg/g, reaching about 6 times. Reaction temperature has a great influence on the yield and selectivity of aromatic products. Appropriate increase of reaction temperature is conducive to the cleavage of C-O-C bond and C-C bond, thus improving the yield of aromatic hydrocarbons and phenols.

Chen L. *et al.* studied the depolymerization of lignin over transition metal (Ti, Mo, Nb, W) nitrides in supercritical ethanol, indicating that these catalysts have good catalytic activity [93]. They synthesized TiN nanoparticles using urea glass method [89] and then passivated them in diluted oxygen to produce the catalyst. And they depolymerized soda lignin (GreenValue P1000, obtained by NaOH pulping of wheat straw) in supercritical ethanol at 300 ℃ to obtain aromatic monomers in 12% yield. Based on the previous studies [94] that the *β*-O-4 ether bonds occupying the majority of the lignin structure break at 200 ℃-400 ℃, the yield of aromatic monomers reached 19% when the reaction temperature was raised to 340 ℃.

Compared with NbN, Mo_2N and W_2N catalysts prepared in the same method, these catalysts have better function. In case of NbN, the yield of aromatic monomers and tar formation were similar, while, in case of Mo_2N and W_2N, the yield of aromatic monomers was very low and tar

formation was high. However, compared with TiO_2, all nitride catalysts had better activity. They also indicated that alkylation of aromatic compounds in the process of reaction was the key to improve the yield of aromatic compounds, based on detailed studies of main products and investigation of reaction pathways.

TiN-Ni composites with high HDO activity on aryl ether also showed high catalyst activity in hydrogenation of sulfate lignin in paper making engineering [90]. Phenol derivatives and various aromatics with small molecular weight (60 wt%) were obtained by hydrogenolysis under the condition of 150 ℃, 2.5 MPa. The research was conducted to prepare monocyclic aromatic hydrocarbons by catalytic cracking of biomass fast pyrolysis vapors over nitride catalyst.

Yan Zheng *et al.* studied the online catalytic cracking of lignin fast pyrolysis vapors using $Mo_2N/\gamma\text{-}Al_2O_3$ catalyst [74]. The results showed that the highest yield of aromatic products as main pyrolysis products of lignin was 17.5% in the presence of $Mo_2N/\gamma\text{-}Al_2O_3$ catalyst, pyrolysis temperature T = 700 ℃, and the weight ratio of catalyst to lignin C/L = 4 (1.4% without catalysis). Figure 9 shows the reaction pathway of catalytic cracking of lignin fast pyrolysis vapors over $Mo_2N/\gamma\text{-}Al_2O_3$ catalyst [74].

Aromatic products are mainly benzene and methanol, and in addition, a small amount of xylene, ethylbenzene, trimethylbenzene, naphthalene, etc. With the increase of pyrolysis temperature, the yield of aromatic hydrocarbons increases reaching the highest value at 700 ℃, and the yield of aromatic hydrocarbons decreases sharply at above 800 ℃. At 500 ℃, the selectivities of benzene and toluene changed from 38.9% and 34.8% to 70.1% and 14.1% at 850 ℃ respectively. The results showed that the selectivity of benzene in aromatic hydrocarbons increased with the promotion of demethylation reaction (DME) with the increase of temperature, while the selectivity of toluene decreased. At 850 ℃ (C/L=4), monocyclic aromatic hydrocarbons (MAH) account for more than 95% of the total yield of aromatic hydrocarbons. They also pointed out that the catalyst quantity has a great influence on the yield and selectivity of lignin pyrolysis products. With the increase of the catalyst quantity, the yield of aromatic hydrocarbons and the selectivity of benzene, the major product, considerably increase, while the selectivity of toluene decreases.

When C/L was increased from 1 to 4, the yield of aromatic hydrocarbons (AH) increased from 6.7% to 17.5%, which was more than 10 times of that in the non-catalytic process. Biomass rapid pyrolysis is an effective technology to obtain liquid biological oil from solid lignocellulosic biomass [96]. Many studies have been carried out on the preparation of aromatic hydrocarbons from biomass by using this method with microporous zeolites catalysts such as HZSM-5 [95-99]. At this time, not only monocyclic aromatic hydrocarbons (MAH) but also many polycyclic aromatic hydrocarbons (PAH) are produced [100,101].

Therefore, studies have been carried out to increase the selectivity of monocyclic aromatic

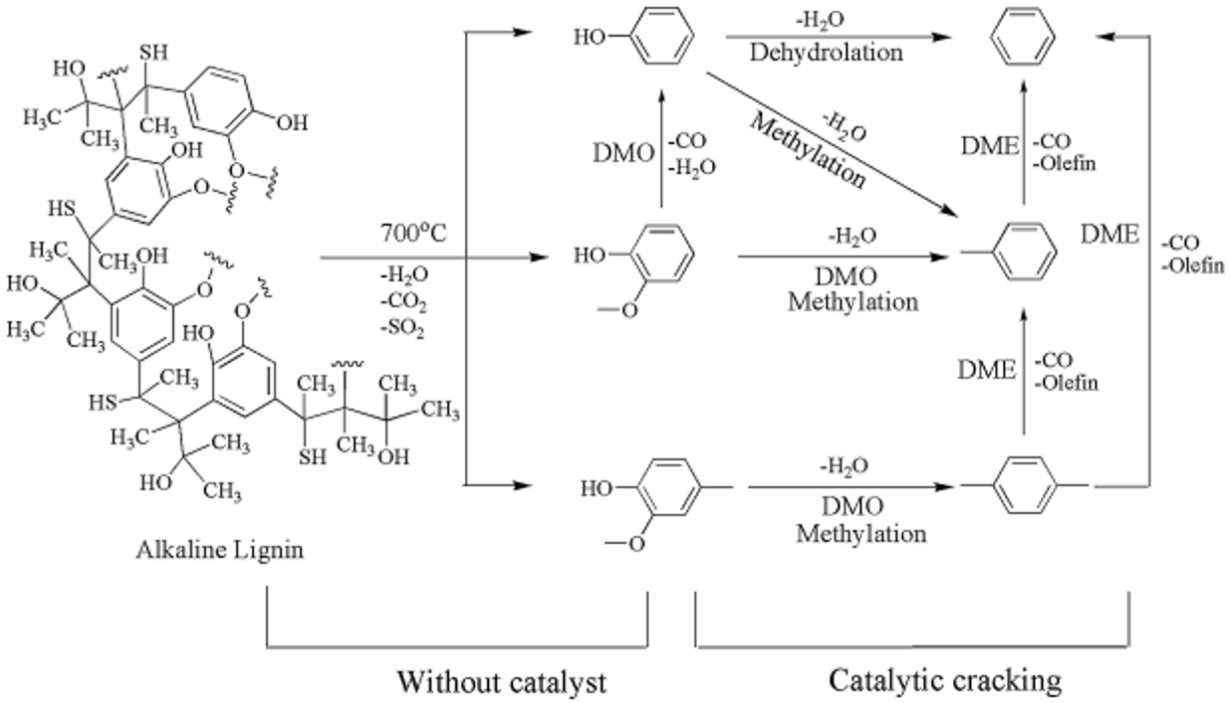


Figure 9. Proposed reaction pathway of lignin pyrolysis vapor catalytic cracking using $Mo_2N/\gamma\text{-}Al_2O_3$ [74].

hydrocarbons (MAH) and the inhibition of polycyclic aromatic hydrocarbons (PAH) formation by loading active components such as transition metals and their nitrides, carbides and phosphides on zeolites [102-104]. Qiang Lu *et al.* used HZSM-5 zeolites supported Mo_2N to increase the selectivity of monocyclic aromatic hydrocarbons in catalytic degradation products of fast pyrolysis vapors of pine trees and inhibit the generation of polycyclic aromatic hydrocarbons [102]. With Hbeta, HY, HZSM-5 zeolites as supports and Mo_2N, W_2N, MoP, WP as catalytic active components, the pine catalytic pyrolysis was carried out, and the distributions of aromatic hydrocarbons in the products were compared. Vapor was fast pyrolysed for 20 s at the heating speed of 20 ℃/ms using He (99.999%) as carrier gas under the optimum conditions of 750 ℃ and the ratio of catalyst to pine tree 5, and then the vapor was passed through Mo_2N/HZSM-5 catalyst layer, which showed the best selectivity of monocyclic aromatic hydrocarbons (MAH) in the product. Among the three zeolites, the yield of aromatic hydrocarbons was 73.7 wt% when HZSM-5 with the best catalytic activity was used, and the ratio of MAH to PAH was 1.8:1 (MAH 46.9 wt%, PAH 26.8%). Among the 12 catalysts, Mo_2N/HZSM-5 was the best one, and aromatic hydrocarbons accounted for 60.6% of the total volatile compounds. Among them, MAH:PAH was 4.7:1 (MAH was 50.0%, PAH was 10.6%). Compared with the carrier HZSM-5, the yield of aromatic hydrocarbons decreased, and the selectivity of MAH increased significantly, while the selectivity of PAH decreased significantly. In HZSM-5 and Mo_2N/ HZSM-5 catalysts, the actual yield of MAH was 8.08 wt%, 8.19 wt%, and the actual yield of PAH was 2.37 wt%, 0.83 wt%. During the three consecutive recycling experiments of HZSM-5 and Mo_2N/HZSM-5 catalysts, the yield changes of MAH and PAH were investigated. The results showed that if Mo_2N was loaded on HZSM-5, the life of the catalysts would be prolonged.

In addition, Qian Lu *et al.* impregnated $Ti(SO_4)_2$ in Mo_2N/HZSM-5 and dried it for 12 hours at 105 ℃ to prepare the catalyst, which significantly increased the selectivity of monocyclic aromatic hydrocarbons in fast pyrolysis vapors catalytic degradation products of pine trees [103]. The maximum MAH yields of HZSM-5, Mo_2N/HZSM-5, $Ti(SO_4)_2$/HZSM-5, $Ti(SO_4)_2$-Mo_2N/HZSM-5 catalysts were 7.57 wt%, 8.11 wt%, 8.71 wt%, and 12.53 wt%, respectively, and the maximum PAH yields were 2.55 wt%, 0.97 wt%, 1.47% and 1.10 wt% respectively under the optimum conditions of 650 ℃ and the ratio of catalyst to pine tree 7. It can be seen that in $Ti(SO_4)_2$-Mo_2N/HZSM-5 catalyst, the formation of MAH is significantly increased, while the formation of PAH is significantly inhibited. The actual yields of MAH and PAH for $Ti(SO_4)_2$-Mo_2N/HZSM-5 catalyst were 9.71 wt% and 1.45 wt%, respectively, under the condition of 650 ℃ and ratio of catalyst to pine 4/3. The main components of MAH are benzene, alcohol and xylene (BTX). With the increase of pyrolysis temperature, the total yield of MAH and the yield of BTX, especially the yield of benzene, also increase significantly. When pyrolysis temperature is higher than 650 ℃, the product decomposes and the yield decreases. The results of the study on the deactivation resistance of the catalysts show that in the HZSM-5 supported $Ti(SO_4)_2$ and Mo_2N catalysts, the deactivation of the catalysts is reduced compared with that of HZSM-5, although the activity of the catalysts shows a significant loss in the three-cycle experiments. The selectivity of MAH increases and PAH formation is inhibited in $Ti(SO_4)_2$ -Mo_2N /HZSM-5 catalyst due to the synergistic catalysis of Mo_2N and $Ti(SO_4)_2$.

Studies have shown that Mo_2N has excellent dehydrogenation and hydrogenolysis capacity, providing enough hydrogen to improve the formation of MAH, and the reaction between MAH and oxidation products inhibits the formation of PAH[105]. In addition, when $Ti(SO_4)_2$ was used to improve HZSM-5, the yield of aromatic hydrocarbons was improved by increasing the B acid point and B/L ratio, which are the key factors for the generation of aromatic hydrocarbons during the catalytic degradation process of biomass pyrolysis vapors.

A study was also published on the production of monocyclic aromatic hydrocarbons from pyrolysis vapors of pine trees using Ce-Mo_2N/HZSM-5 catalyst [104]. When pine pyrolysis vapors obtained by rapid pyrolysis at 700 ℃ passes through the catalyst layer, the production of oxygen-containing products decreases significantly, while the yield of aromatic hydrocarbons increases sharply in HZSM-5-based catalysts. In HZSM-5 supported 10% Mo_2N catalyst compared with HZSM-5 catalyst, the yield and selectivity of monocyclic aromatic hydrocarbons (MAH) increased by 17.4% and 8.5% respectively, while the yield and selectivity of polycyclic aromatic hydrocarbons (PAH) decreased by 47.7% and 12.5% respectively. The effect of adding transition metals (Fe, Cu, Cr, Ce and La) was investigated, and the best results were obtained when Ce was added. Compared with 10% Mo_2N/HZSM-5 catalyst, the yield and selectivity of MAH were increased by 9.9% and 8.4% respectively, and the yield and selectivity of PAH were reduced by 39.8% and 5.2% respectively. The results showed that MAH and PAH over Ce-10% Mo_2N/HZSM-5 catalyst (catalyst to biomass ratio 5) were obtained from

the fast pyrolysis vapors of pine trees obtained at 700 ℃ in 99.8 mg, 7.5 mg and 7.5 mg/g yields respectively. At this time, the selectivity of aromatic hydrocarbons was 71.4% (MAH 62.5%).

The research was conducted on catalytic conversion of fast pyrolysis vapors of lignocellulose to benzene, toluene and dimethylbenzene (BTX) over Co_4N catalyst prepared by NH_3 decomposition TPR method at 700 ℃ in the absence of oxygen inert gas [106]. In order to obtain aromatic hydrocarbons using biomass fast pyrolysis vapors, Ramirez C M M et al. developed a new catalyst composed of zeolites, transition metal, metal nitride, metal carbide and/or metal sulfide, basic materials and binders [107].

Lu Q *et al.* proposed nitride catalysts and biomass treatment projects for the preparation of benzene, methanol, xylene (BTX) from biomass fast pyrolysis vapors [108,109]. As the source of lignocellulose, wood, crops, bamboo and herbs were selected and fast pyrolysed into vapors for less than 50 s at 400-800 ℃. Then the vapors were converted to BTX-containing high-grade liquid fuels over metal nitrides (tungsten nitride, molybdenum nitride, vanadium nitride and iron nitride) catalysts supported on molecular sieves [108] and titanium nitride and zirconium nitride catalysts [109]. As mentioned so far, transition metal nitride catalysts have good catalytic activity and selectivity for the direct catalytic degradation of lignin and biomass pyrolysis vapors. The main products of direct degradation of biomass are monocyclic aromatic hydrocarbons such as benzene, methanol and xylene with this catalyst, which open up a broad prospect for the production and utilization of bio-oil.

However, the project of using nitride catalyst to produce bio-oil still has some shortcomings where it has harsh reaction conditions and low yield of products, and further studies need to be conducted to solve these problems.

4. Future Outlook and Authors' Perspectives

Based on our comprehensive review of the literature, we offer the following perspectives on future research directions in this field. While bimetallic nitrides such as CoMoN have been investigated, the full potential of ternary and quaternary nitride systems remains largely unexplored. We believe that systematic investigation of transition metal combinations (e.g., Ni-Mo-N, Fe-W-N, Ni-Co-Mo-N) could yield catalysts with synergistic effects that surpass current monometallic and bimetallic systems.

A significant gap in the current literature is the limited understanding of the active site structure and reaction mechanisms at the molecular level. Future work should prioritize in-situ and operando characterization techniques including XPS, EXAFS, and DRIFTS under realistic reaction conditions. Current HDO reactions over nitride catalysts typically require harsh conditions (300-400 °C, 2-5 MPa H_2). From an industrial perspective, the development of nitride catalysts capable of operating under milder conditions (e.g., <250 °C, atmospheric pressure) would substantially improve economic viability. Catalyst deactivation remains a critical challenge for practical applications. Future research should focus on understanding deactivation mechanisms (coking, sintering, leaching) and developing regeneration protocols. We propose that support engineering and the addition of stabilizers could enhance catalyst lifetime.

5. Concluding Remarks

HDO conversion catalyst plays a very important role in the effective utilization of biomass containing lignin. Transition metal nitride catalysts have been widely used in petroleum processing industry and chemical industry thanks to their lower cost than noble metals and similar catalytic activity. They also show excellent catalytic performance in the production of bio-oil and high-value chemicals through the HDO reaction of lignin and its model compounds.

Recent results provide valuable experience in improving the performance of catalysts by improving the nitriding method, carriers and the reaction conditions of HDO. The selection of nitridation gas, the adjustment of molar hourly space velocities (MHSV) and heating speed and the reasonable adjustment of temperature stage in TPR engineering are the key factors for the synthesis of suitable catalytic active phase, thus determining the activity and selectivity of the catalyst. The dispersion of the catalytic active phase is determined by the well-developed pore structure and the surface characteristics of the carrier, and the electronic structure and catalytic properties of carrier itself affect the catalytic reaction pathways and the selectivity of catalyst. The conversion products of lignin and its model compounds produced by transition metals, especially molybdenum nitride catalysts, are aromatic hydrocarbons, such as benzene, phenols and other monocyclic aromatic hydrocarbon, which have high selectivity and good application prospects.

However, many problems still need to be solved in the process of transition metal nitride catalyst used in HDO reaction of lignin and its model compound. In fact, it is well known that nitride catalysts have good catalytic activities of HDO, HDS and HDN in a series of chemical reactions such as petroleum processing. However, the application of transition metal nitride catalyst in HDO reaction of lignin and its model compound is less than that of sulfide catalyst. The HDO activity and selectivity of some nitride catalysts are not as high as that of sulfides with the same metal composition, and its reaction conditions are harsh as well. In addition, the HDO reaction pathway and the final product vary according to the nature of the active phase and the carrier in the catalyst. Therefore, in order to obtain the necessary active phase, there needs to be further research on controlling the nitriding process and the corresponding reaction pathway.

In addition, we believe that there needs to be further research to improve the performance of nitride catalysts and make the reaction easier by adding the second and third metal components or selecting reasonable carriers. In order to improve the effect of nitride catalyst in practical application, it is important to solve the problem of stability of catalyst.

CRedit Authors Statement

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