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Research Article

Study of Catalytic Properties of the $Ho_xMg_{1-x}Al_2O_4$ Modified HZSM-5 Zeolite in Conversion of Methanol to C_2-C_4 Alkenes and p-Xylene

Natavan I. Makhmudova[1], Eyyub S. Mammadov[2], Fuad Sh. Kerimli[1], Teymur M. Ilyasli[1], Nargiz F. Akhmedova[1], Sabit E. Mammadov[1]*

[1]Department of Physical and Colloid Chemistry, Chemistry Faculty, Baku State University, Baku AZ1148, Azerbaijan
[2]Chemistry Faculty, Branch of Moscow State University, Baku, Azerbaijan, Baku AZ1142, Azerbaijan.

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Abstract

Selective conversion of methanol to C_2-C_4 alkenes and p-xylene is one of the appealing chemical routes. Currently, there are no effective catalysts for the co-production of C_2-C_4 alkenes and *p*-xylene from methanol. To date, modified medium-pore ZSM-5 zeolites are considered one of the excellent candidates for the development of selective catalysts for the conversion of methanol to lower alkenes and aromatic hydrocarbons. In this paper, nanosized (30-33nm) powders of $Ho_xMg_{1-x}Al_2O_4$ spinel structure were obtained by the method of combustion of nitrate solutions of aluminium, magnesium, holmium, diethylmalonate and hydrazine monohydrate with the further calcination of nanopowders at 1000 °C. Obtained nanopowders used in the preparation of a solid-phase catalytic composition of $Ho_xMg_{1-x}Al_2O_4$-HZSM-5. Various physico-chemical properties of the catalytic composition were investigated using X-ray diffraction (XRD), pyridine adsorption (BİO-RAD FTS 3000 MX) and low-temperature nitrogen adsorption (BET) techniques. The textural properties and acidity of the catalysts were altered by adjusting the nanopowder concentration (1.0-5.0 wt.%) in the catalytic composition. The conversion of methanol in the presence of the catalytic compositions was carried out in flow-type fixed-bed catalytic reactor at 400 °C, in the presence of nitrogen carrier gas with 1.0 h^{-1} flow rate. A correlation between the selectivity to C_2-C_4 alkenes and *p*-xylene with a ratio of Lewis (L) and Brønsted (B) acid sites and the volume of the catalyst pore, the amount of the modifier in the catalytic system has been established. As the amount of $Ho_xMg_{1-x}Al_2O_4$ nanopowder increases, the ratio of B/L acid sites and the volume of the catalyst pore decrease, which play a significant role in the increase of the selectivity to C_2-C_4 alkenes and *p*-xylene. Maximum yield of C_2-C_4 alkenes (31.6%) and selectivity to *p*-xylene (80.5%) is achieved on a catalytic composition containing 5.0 wt.% $Ho_xMg_{1-x}Al_2O_4$.

Keywords: methanol, C_2-C_4 alkenes, p-xylene, HZSM-5, nanopowders $Ho_xMg_{1-x}Al_2O_4$

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1. Introduction

Light C_2-C_4 alkenes and aromatic hydrocarbons are crucial raw materials of the petrochemical industry, which are produced mainly in the processes of pyrolysis, catalytic cracking and reforming of hydrocarbon raw material [1-3]. The most promising way to obtain light alkenes and aromatic hydrocarbons from alternative raw materials is the conversion of methanol in the

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* Corresponding Author.
Email: sabitmamedov51@mail.ru (S.E. Mammadov)

presence of molecular sieves type SAPO-34 and zeolite catalysts [4-6]. The catalytic process developed by “Mobil Oil” to convert methanol on the HZSM-5 zeolite (MTG process) to a mixture of aliphatic and aromatic hydrocarbons, which can be used as a motor fuel, is currently of limited use [7-10]. The MTG processa series of reactions (oligomerisation, alkylation, isomerisation, hydrogen redistribution) which result in a wide range of products (olefins, paraffins, and aromatic hydrocarbons) [11-15].

Catalysts based on medium-porous ZSM-5 zeolite are more active and stable in the reaction of methanol conversion to light alkenes and liquid C_{5+} hydrocarbons [16-20]. In this regard, the formation of light alkenes and p-xylene on catalysts based on zeolite ZSM-5 is the most promising direction. Xylenes, especially p-xylene, are valuable intermediates for the production of terephthalic acid, polyethylene terephthalate, fibers, plasticizers and other valuable products [21-24]. The demand for light C_2-C_4 alkenes and para-substituted aromatic hydrocarbons grows steadily every year. Of great interest for the increase of resources of light alkenes and p-xylene is the selective production of these products from non-oil hydrocarbon feedstock - methanol in the presence of modified ZSM-5 type of zeolites. Notwithstanding the sufficient number of studies on the preparation of aromatic hydrocarbons in the presence of modified catalysts based on ZSM-5 zeolite, a limited publication on the production of p-xylene from methanol is available. The effect of the modification of HZSM-5 zeolite, the nature of the modifier concentration and the change of its acidic properties on its para-selectivity has not been sufficiently investigated [25-27].

In work of previous researcher [26], it is marked, that ZSM-5/silicalite-1 zeolite catalyst modified with zinc ions shows high efficiency in p-xylene production from methanol. The modification of HZSM-5 zeolite with multicharged cations and rare earth metals significantly affects the distribution of the xylenes. The catalyst 2.5%La-HZSM-5 achieves a p-xylene selectivity of up to 62.3% [27]. Preparation method and the nature of the modifier significantly affect the yield and distribution of aromatic hydrocarbons in the conversion of methanol. The impregnation of HZSM-5 zeolite with copper oxide changes the ratio of Brønsted and Lewis acid sites. The CuO/HZSM-5 catalyst prepared by the sonochemical method increases the yield of aromatic hydrocarbons to 84% [17]. Modified Zn/HZSM-5 and Cd/HZSM-5 catalyst obtained by impregnation also exhibit markedly higher selectivity to aromatic compounds [18,28,29]. Cd/HZSM-5 was more effective in encouraging the formation of aromatic compounds. However, these works do not report the effect of the modification on the p-xylene content in the xylene mixture.

ZSM-5 based catalysts modified with zinc and phosphorus were examined in the conversion of methanol to improve p-xylene selectivity. The total strength and concentration of the acid sites in the catalyst had a crucial influence on the yield of aromatic hydrocarbons. The weak acid sites on the outer surface of the zeolite played an essential role in increasing its para-selectivity. However, the different catalytic behaviour shown for the Cd/HZSM-5 and Zn/HZSM-5 catalysts is most probably due to the various ion radius of cadmium and zinc. It is worth underlining that there are no reports in the literature on the combined production of C_2-C_4 alkenes and p-xylene on ZSM-5 zeolites [28-31]. Enhancement of p-xylene selectivity can also be achieved by solid-phase modification of ZSM-5 zeolite with nanosized powders of spinel structure [32].

The aim of this paper is to establish the relationship between the textural, acidic and catalytic properties of the HZSM-5 zeolite composition with $Ho_xMg_{1-x}Al_2O_4$ nanopowders in the combined process of obtaining C_2-C_4 lower alkenes and p-xylene from methanol.

2. Materials and Method

2.1.Catalyst Preparation

The solution combustion method were used for $Ho_xMg_{1-x}Al_2O_4$ nanopowders synthesis. $Al(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Ho(CO_3)_3$, diethylmalonate $C_3H_{12}O_4$, hydrazine monohydrate $NH_2NH_2{\times}H_2O$, absolute alcohol - C_2H_5OH (density 0.7895 g/cm^3) and nitric acid (concentration 65% and density 1.41 g/cm^3) were used as initial reagents for catalyst synthesis. The synthesis of nanosized powders (25-30 nm) of spinel structure was performed by the combustion method described in [23,33]. The process proceeded according to the following chemical reaction:

$$\begin{aligned} &1(1-x)\ Mg(NO)_2.6H_2O + 4\ Al(NO_3)_3.9H_2O \\ &\quad +\ 5\ C_3H_8N_4O_2 + 2x\ Ho(NO_3)_3 \xrightarrow{300\ ^\circ C} \\ &\quad 2\ Ho_xMg_{1-x}Al_2O_4 + 15\ H_2O \\ &\quad + 15\ CO_2 + 21\ N_2 \end{aligned} \qquad (1)$$

We have synthesized nanopowders of the composition $Ho_xMg_{1-x}Al_2O_4$, (where x = 0.05; 0.10 and spinel $MgAl_2O_4$). Nanosized powders

(30-33 nm) were obtained by high-temperature treatment of $Ho_xMg_{(1-x)}Al_2O_4$ nanopowder at 1000 °C. High silica zeolite ZSM-5 with molar ratio of 61 ($SiO_2/Al_2O_3 = 61$) was used as zeolite, which was converted into NH_4-form by ion exchange. The H-form of zeolite was obtained by thermal decomposition of the NH_4-form at 500 °C for 4 hour [23]. The catalytic compositions were prepared by dry mixing H-form zeolites with nanopowders in an oscillating grinding machine followed by pressing and calcination in a muffle furnace at 550 °C for 4 h. The nanopowder content in the catalytic composition was 1.0-5.0 wt.%.

2.2. Catalysts Characterizations

X-ray phase studies were performed according to the method X-ray powder analysis using a RIGAKU MINIFLEX diffractometer with Cu-Kα radiation ($\alpha = 0.15042$ nm^{-1}, 40 kV and 30 mA). The catalysts were imaged in a 2θ scanning range from 10° to 80° in 0.0167° scanning increments [32].

IR spectra of adsorbed pyridine on modified zeolites were obtained on a BİO-RAD FTS 3000 MX device using the method described in [33]. The concentration of Lewis (L) and Brønsted (B) acid sites were determined by the intensities of the IR bands at 1450 cm^{-1} and 1550 cm^{-1} [32-34], respectively, at 200 °C and 350 °C.

The specific surface area and pore volume of the catalysts were determined by low-temperature nitrogen adsorption. The BET surface area and pore volume of the catalyst samples were determined by liquid nitrogen adsorption at 77 K using Micromeritics ASAP-2010 instrument. The sample (ca. 220 mg) was degassed at 250 °C and 1×10^{-3} Pa for 4h before the measurement of data.

2.3. Methanol Conversion

The catalytic experiments were carried out in a fixed bed, continuous flow type cylindrical quartz reactor (0.025 m ID and 0.30m in length) about 3.0 g of catalyst. The reactor was fitted with a preheater in the upstream and a condenser at its outlet. The reactor was heated electrically from outside and insulated to prevent heat loss. In a typical run, catalyst was leaded into the reactor and supported by inert leads on either side of the bed. The bed temperature was measured by a thermocouple placed in a thermowell extending from the top of the reactor to the middle of the bed. The catalyst was activated “in situ” for 4 h. in an atmosphere of nitrogen before contacting the catalyst. The reactant vapours along with carrier gas (nitrogen) entered the reactor from the top.

The product vapours along with unreacted reactants, were condensed in a condenser and the liquid samples collected were analysed in a gas chromatograph. Analysis of gaseous products was carried out on an Agilent GC 7820A gas chromatograph, supplied FID/TCD detector and steel columns (length 3 m, inner diameter 2 mm) filled with Porapac Q sorbents and molecular sieve grade 5A at 30-150 °C, and liquid products on a quartz glass capillary column (100 m × 0.25 mm × 0.25 µm) coated with a DB-Petro stationary phase.

For the estimation of external diffusion effects, two series of runs were taken with 1.5g and 3.0 g of catalyst. It has been determined that at a fixed molar ratio of nitrogen to methanol of 0.33, a temperature of 400 °C, a pressure of 1atm and a constant W/F ratio the alcohol conversion for both series is unaffected by the alcohol feed rate. The external mass transfer resistance is therefore, negligible.

3. Results and Discussion

Diffractograms of spinel phases thermally treated at 1000 °C for 2 hours are shown on Figure 1, where phases are Ho_2O_3, $MgAl_2O_4$, $Ho_{0,10}Mg_{0,90}Al_2O_4$ and $Ho_{0,05}Mg_{0,95}Al_2O_4$. It is observed that during synthesis, holmium almost completely penetrates the lattice of the magnesium-aluminum spinel, replacing the magnesium ions in the lattice nodes.

Table 1 shows the results of transformation of methanol into hydrocarbons on unmodified HZSM-5 (KT-1) and modified with nanopowders (1.0 wt.%): Ho_2O_3 (KT-2), $Ho_{0.05}Mg_{0.95}Al_2O_4$

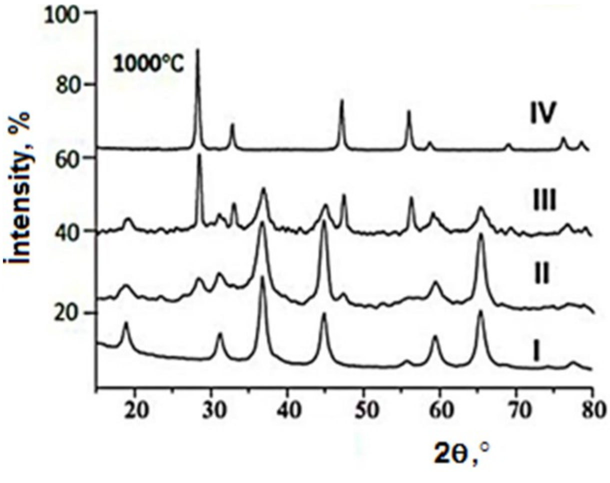

Figure 1. Diffractograms of powders obtained by the combustion method and corresponding phases $MgAl_2O_4$ (I), $Ho_{0.05}Mg_{0.95}Al_2O_4$ (II), $Ho_{0.10}Mg_{0.90}Al_2O_4$ (III) and Ho_2O_3 (IV)

(KT-3) and $Ho_{0,1}Mg_{0.9}Al_2O_4$ (KT-4). It can be seen that, as a result of the modification of HZSM-5, a significant change occurs in the distribution of methanol conversion products. The loading of 1.0 wt.% modifiers into the composition of HZSM-5 promotes an increase in the yield of C_2-C_4 alkenes, isoalkanes and cycloalkanes, as well as an increase in the content of xylenes. The greatest increase in the yield of C_2-C_4 alkenes (14.7 wt.%), isoalkanes and C_{5+} cycloalkanes (14.1 wt.%) is observed on HZSM-5 modified with 1.0 wt.% $Ho_{0.1}Mg_{0.9}Al_2O_4$ (KT-4). In the presence of KT-4 the yield of xylenes increases to 25.2 wt.%, and the content of aromatic hydrocarbons C_{9+} decreases to 5.7 wt.%. Table 2 presents the effect of the concentration of nano $Ho_{0.1}Mg_{0.9}Al_2O_4$ powder in the composition with HZSM-5 on the composition of methanol conversion yields.

It is seen that with increasing the concentration of the modifier from 2.0 wt.% (KT-5) to 5.0 wt.% (KT-8) a further growth in the amount of C_2-C_4 alkenes (from 16.3 to 31.6 wt.%), isoalkanes and C_{5+} cycloalkanes (from 13.1 to 17.9 wt.%) is observed. Nevertheless, the amount of xylenes (from 23.5 wt.% (KT-5) to 18.8 wt.% (KT-8)) and C_{9+} aromatic hydrocarbons (from 5.7 to 4.5 wt.%) slightly declined. The growth of alkenes content and reduction of aromatic hydrocarbons amount can be explained by low activity of catalysts loaded 4.0-5.0 wt.% of a modifier. It should be noted that on nanopowders loaded HZSM-5 catalytic systems a higher amount of p-xylene in the xylene mixture is achieved. As the amount of the modifier in the composition increases, the p-xylene selectivity rises (Figure 2). The maximum selectivity for p-xylene (75.2-80.5 %) is achieved by catalytic system loaded 4.0-5.0 wt.% of the modifier. The enhancement of C_2-C_4 alkenes yield and growth of p-xylene selectivity seems to be related to changes in acid and textural properties of catalysts because of modification.

Table 1. Effect of modification of zeolite HZSM-5 with nanopowders on reaction yields of methanol conversion.

Products	Yield (%) for catalysts			
	KT-1	KT-2	KT-3	KT-4
Alkanes C_1-C_4	41.8	38.8	344	32.6
Alkenes C_2-C_4	5.4	8.2	12.1	14.7
ΣC_1-C_4	47.2	47.0	46.5	47.3
Alkanes C_{5+}	1.2	1.0	0.8	1.1
Alkenes C_{5+}	0.7	0.5	0.3	0.6
Iso-alkanes and cycloalkanes C_{5+}	9.7	11.4	13.3	14.1
Aromatic hydrocarbons (AH)	41.2	40.1	39.1	36.9
Benzene	2.1	1.8	1.5	0.9
Toluene	10.2	8.7	7.6	5.1
Xylenes	18.8	21.1	23.7	25.2
AH C_{9+}	10.1	8.5	6.3	5.7
ΣC_{5+}	52.8	53.0	53.5	52.7

Table 2. Effect of nano $Ho_{0.1}Mg_{0.9}Al_2O_4$ powders concentration in the catalysts composition on reaction yields of methanol conversion

Products	Yield (%) for catalysts			
	KT-5 (2%)	KT-6 (3%)	KT-7 (4%)	KT-8 (5%)
Alkanes C_1-C_4	30.9	26.3	24.3	20.3
Alkenes C_2-C_4	19.3	22.4	26.6	31.6
ΣC_1-C_4	48.2	47.7	51.0	51.5
Alkanes C_{5+}	1.1	1.1	0.9	1.2
Alkenes C_{5+}	1.0	1.2	1.1	1.3
Iso-alkanes and cycloalkanes C_{5+}	13.1	15.8	17.4	17.9
Aromatic hydrocarbons (AH)	34.6	31.8	29.6	27.7
Benzene	0.8	0.7	0.6	0.6
Toluene	4.9	4.4	4.0	3.8
Xylenes	23.5	21.7	20.3	18.8
AH C_{9+}	5.4	5.0	4.7	4.5
ΣC_{5+}	51.8	50.9	49.0	48.1

In a range of wave numbers from 3500 to 3900 cm^{-1} FTIR spectra of degassed at 200 ^{0}C unmodified and modified catalysts were registered. It can be seen from Figure 3 that these catalysts exhibit FTIR absorption bands at 3742, 3674, and 3610 cm^{-1}, which are attributed to vibrations of OH-groups in Si–OH (3742 cm^{-1}) and vibrations of bound OH- in Si(OH)Al (3674 and 3610 cm^{-1}) [19]. The OH-groups in Si(OH) and Si(OH)Al are known to provide Brønsted acid sites for the catalyst.

Compared to HZSM-5, the IR bands belonging to the OH-groups in Si(OH) and Si(OH)Al for $Ho_{0,1}Mg_{0,9}Al_2O_4$/HZSM-5 are shifted toward the lower wave frequencies. As the content of $Ho_xMg_{1-x}Al_2O_4$ nanopowder in the zeolite increases, the intensity of these bands decreases. The obtained results indicate the interaction of the modifier with the surface hydroxyl groups of zeolite. Modification of HZSM-5 with $Ho_{0,1}Mg_{0,9}Al_2O_4$ nanopowder leads to a decrease in the density of acidic OH-groups. Thus, the modification of HZSM-5 zeolite with $Ho_xMg_{1-x}Al_2O_4$ nanopowder leads to a decrease in the strength and concentration of Brønsted acid sites. As the content of the modifier in the zeolite increases, the density of Brønsted acid sites decreases.

Table 3 summarizes the impact of the modifier content on the concentration and distribution of the Brønsted and Lewis acid sites in the catalysts. It is seen that with growing concentration of nano $Ho_{0.1}Mg_{0.9}Al_2O_4$ powder in HZSM there is a decline in concentration of strong Brønsted acid sites (desorption at 350 °C), increase in concentration of weak Lewis acid sites (desorption at 200 °C), reduction in concentration of stronger Lewis acid sites (desorption at 350 °C), which leads to a sharp reduction in the B/L ratio from 3.38 to 0.23.

The surface area and pore volume of the catalyst also reduce with growing amount of the modifier in HZSM-5 (Table 4). The considerable changes in the pore volume and surface area of the catalyst appear at the amount of nano $Ho_{0.1}Mg_{0.9}Al_2O_4$ powder that is equal to

Table 3. Effects of modification on the allocation of Brønsted (B) and Lewis (L) acid sites

Catalysts	Concentration B, µmol/g			Concentration L, µmol/g			B/L
	Weak and Medium, 200 °C	Strong, 350 °C	Total	Weak and Medium, 200 °C	Strong, 350 °C	Total	
КТ-1	528	352	880	150	110	260	3.38
КТ-4	100	220	330	220	80	300	1.10
КТ-5	90	180	270	260	75	335	0.81
КТ-6	75	165	240	470	70	540	0.44
КТ-7	70	150	220	725	65	790	0.28
КТ-8	65	140	205	840	60	900	0.23

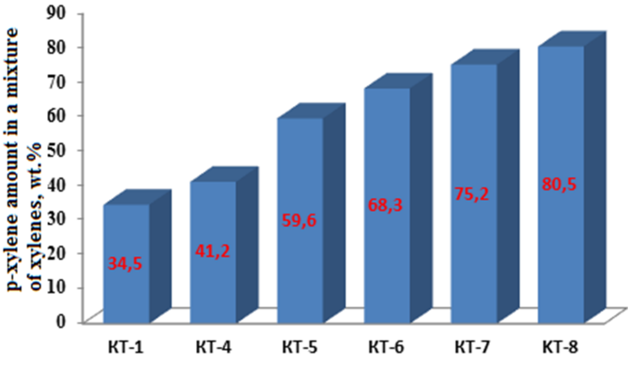

Figure 2. Diagram of the dependence of the p-xylene amount in the xylene mixture on modifier content in the catalyst

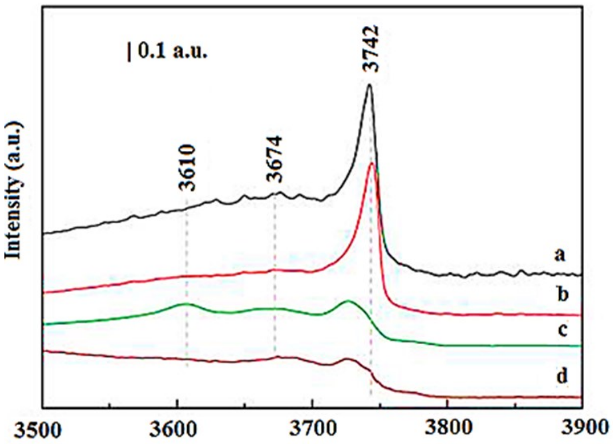

Figure 3. IR spectra of catalysts degassed at 200 °C: a - HZSM-5, b - 2 wt % $Ho_{0.1}Mg_{0.9}Al_2O_4$/HZSM-5, c - 3 wt % $Ho_{0.1}Mg_{0.9}Al_2O_4$/HZSM-5, d - 5 wt % $Ho_{0.1}Mg_{0.9}Al_2O_4$ /HZSM-5

3.0-5.0 wt.%. By raising the content of the modifier up to 5.0 wt.%, the surface area and pore volume of the catalytic system drops, respectively, from 288 m^2/g to 230 m^2/g and 0.22 cm^3/g to 0.16 cm^3/g.

Figure 4 explains the dependence of p-xylene selectivity on the ratio of B/L acid sites and catalyst pore volume. It is seen that as the ratio B/L of acid sites and the catalyst pore volume decrease, the selectivity for p-xylene (Figure 4) and C_2-C_4 alkenes grows (Table 2). The narrowing of zeolite channels, a decline in the concentration of Brønsted acid sites, and the formation of new Lewis acid sites that occur because of modification explain the above correlations.

4. Conclusion

Solid phase modification of HZSM-5 zeolite with $Ho_xMg_{1-x}Al_2O_4$ spinel nanopowders leads to a remarkable alteration of the acidic, textural and catalytic properties of the catalysts. Modification and calcination of catalytic nanopowder-zeolite composition leads to localization of nanoparticles of the modifier in pores and their distribution on the zeolite surface, where they interact with the crystal lattice to form additional Lewis acid sites, and upon interaction with the surface OH-groups to reduce the concentration of strong Brønsted and the number of new Lewis acid sites increases. Hence, modification of HZSM-5 zeolite with $Ho_{0.1}Mg_{0.9}Al_2O_4$ nanopowders results in reduction of pore volume and B/L ratio of acid sites, playing an important role in selective conversion of methanol to C_2-C_4 alkenes and p-xylene. Because of an optimal combination of B/L ratio (0.23) and pore volume (0.16 cm^3/g), the catalytic composition containing 5.0 wt. % of $Ho_{0.1}Mg_{0.9}Al_2O_4$ nanopowder exhibits a higher activity and para-selectivity in the combined process of producing C_2-C_4 alkenes and p-xylene from methanol. The maximum alkene yield and p-xylene selectivity are 31.6 and 80.5 %, respectively.

Table 4. Effect of modifier amount on textural properties of catalysts.

Catalysts	Amount of modifier $Ho_{0.1}Mg_{0.9}Al_2O_4$, wt.%	S, m^2/g	V_{pore}, Sm^3/g
KT-1	0	288	0.22
KT-4	1	282	0.21
KT-5	2	269	0.20
KT-6	3	258	0.18
KT-7	4	241	0.17
KT-8	5	230	0.16

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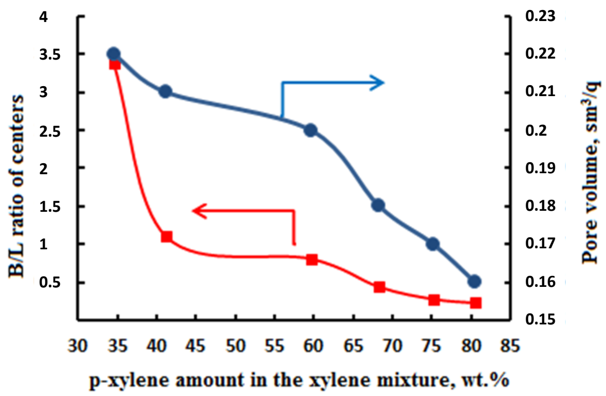

Figure 4. The effect of the pore volume and B/L ratio in the catalyst on the *p*-xylene content in the xylene mixture

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