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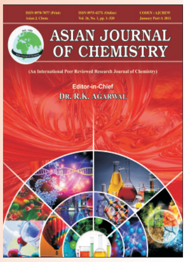

Hydroisomerization of *n*-Heptane over HPMo-Ni/Ce-MCM-48 Catalysts†

YANHUA SUO[1,2], GANG CHEN[1,*], YINGJUN WANG[2,*], WEI ZHANG[2], LILI LI[2] and XINYUE ZU[2]

[1]Department of Chemistry, Harbin Institute of Technology, Harbin 150001, P.R. China
[2]Chemistry and Chemical Engineering School of Northeast Petroleum University, Daqing 163318, P.R. China

*Corresponding authors: E-mail: gchen@hit.edu.cn; wangying-jun@163.com

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Ce-MCM-48 mesoporous material was prepared by hydrothermal method and used as a support to prepare HPMo-Ni/Ce-MCM-48 catalysts by impregnation process. The crystal structure of catalysts was determined by X-ray powder diffraction, Brunauer-Emmett-Teller methods and FI-IR and SEM. The influences of heteropoly acid loading on catalysts for *n*-heptane isomerization were studied. The optimum catalyst for *n*-heptane isomerization was HPMo-Ni/Ce-MCM-48 catalysts with 20 % loading of HPMo. The conversion of *n*-heptane and the isoheptane selectivity reached to 18.5 and 73.5 %, respectively (reduction temperature: 673 K (for 6 h); reaction conditions: 573 K (for 24 h), weight hourly space velocity = 3.52 h^{-1}, flow rate of H_2 = 50 mL/min).

Keywords: Phosphomolybdic acid, MCM-48, Isomerization, Heptane.

INTRODUCTION

n-Alkanes hydroisomerization is an important process of petroleum processing and many researchers have studied it in recent years[1-3]. Heteropolyacids with Keggin structure attracted much attention in the field of acid catalysis because of their strong Bronsted acids characteristic and unique quasi-liquid behaviour. However, heteropoly acids that acted as heterogeneous catalysts were limited in the practical application because of their small BET[4], bad thermal stability and solubility of polar solvent. Many researchers have been devoted to load heteropoly acids on the porous support to increase the specific surface area. Kresge *et al.*[5] found that the mesoporous silica MCM-48 with three-dimensional interwoven channel structure may have more superiorities on support. However, its relatively narrow synthesis of cubic phase zone range, harsh surfactant accumulation parameter and low thermal stability and weak acidity have greatly restricted its developments in the fields of catalyst and support. Researchers have attempt to incorporate the element such as cerium *etc*., to the silicate structure to enhance the acid properties and stability of the mesoporous materials[6]. Because the introduction of cerium into the silicate structure provided the acid sites of Lewis and Bronsted which affected the catalytic properties[7]. In addition, the introduction of cerium could improve the stability of molecular sieve to adapt the harsh hydrothermal conditions on the catalytic processes[8]. In this work, Ce-MCM-48 was as a carrier loading phosphomolybdic heteropoly acid and metals, *n*-heptane isomerization reaction is probes to study the influence of heteropoly acid content to the performance of catalyzed isomerization.

EXPERIMENTAL

Preparation of mesoporous materials: Ethyl orthosilicate (TEOS) and cetyl trimethyl ammonium bromide (CTAB) were used as a silicon source and template, respectively. The molar composition of the gel was 1.0TEOS:0.65CTAB:0.50NaOH:62.0H_2O. The preparation procedure was as follows: TEOS mixed with deionized water under continuous stirring for 40 min, followed by adding NaOH solution. Ce $(NO_3)_3 \cdot 6H_2O$ as cerium source was added after the NaOH solution and this mixture solution was stirred for 60 min at room temperature The molar ratio of Ce to Si was 0.02 in this paper. CTAB used as a structure-directing agent, was added to the mixture and stirred continuously 1 h. The resulting gel was transferred into a Teflon-lined stainless steel autoclave and heated statically for 72 h at 393 K. The resulting Ce-MCM-48 solid product was filtered off, washed extensively with deionized water and dried at 373 K for 10 h. The as-synthesized samples were calcined at 823 K for 4 h to obtain mesoporous Ce-MCM-48.

Through the synchronization dipping process, active metal and phosphomolybdic acid are loaded, the sample is denoted as 30 % HPMo-Ni/Ce-MCM-48 for example. 0.415 g of

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$Ni(NO_3)_2 \cdot 6H_2O$ and 0.6 g of $H_3PW_{12}O_{40}$ were dissolved in deionized water and the solution was dropped slowly to the Ce-MCM-48 zeolite whose weight was two gram, the mixture magnetic was stirred 3h at room temperature and then dried 12 h at 383 K and calcined at 623 K for 4 h. The catalyst is denoted as 30 % HPMo-Ni/Ce-MCM-48. The mass ratio of HPMo was 30 % and Ni was 4 % respectively in this paper. The final sample was sieved to 60-80 mesh as catalyst precursor.

Catalyst characterizations and testing: X-Ray powder diffraction of small-angle (XRD) patterns of all samples were recorded on Rigaku D/max-IIB diffractometer using CuK_α radiation in the range of $2\theta = 1.5\text{-}5.5°$ at a scanning speed of 4°/min, 40 kV and 20 mA. The specific surface area and total pore volume were assessed using Quantachrom NVOA/2000e Brunauer-Emmett-Teller at liquid N_2 temperature as N_2 adsorbate. Isomerization of *n*-heptane was carried out by using a continuous-flow, fixed-bed stainless-steel reactor (internal diameter, 6 mm) at atmospheric pressure. Products were analyzed by gas chromatography (SP-3420) with a flame ionization detector. Catalytic performance was expressed as conversion of *n*-heptane and selectivity of *iso*-heptane, which were defined by using the following equations:

$$\text{Conversion} = \frac{\text{consumed amount of } n\text{ - heptane}}{\text{added amount of } n\text{ - neptane}}$$

$$\text{Selectivity} = \frac{\text{generated amount of iso - heptane at the reaction}}{\text{consumed amount of } n\text{-heptane}}$$

RESULTS AND DISCUSSION

XRD analyses: Fig. 1 shows the powder small-angle XRD patterns of Ce-MCM-48 and HPMo-Ni/Ce-MCM-48 samples. The samples of Ce-MCM-48 mesoporous accord well with those reported for the cubic Ia3d pore network[5]. XRD patterns of all as-synthesized samples show four diffraction peaks corresponding to (211), (220), (420) and (332) reflexes. Ce-MCM-48 which is loaded on a small amount of the active ingredients remains the long-range order in the pore structure, which has a high level of the crystalline order. With increasing phosphomolybdic acid content, the diffraction peaks gradually broaden and the ordering level of its crystals is fairly low. In sample 5, diffraction peaks disappeared completely at 2θ = 4-5°. It is tested that the introduction of heteropoly acid damage the length range order of the cubic mesoporous structure and the zeolite pore structure partially collapsed. The silanol groups on the zeolite surface interact with the water molecule in the process of impregnation, which lead to the framework of silicon hydrolyze. Strong interaction of carrier and phosphomolybdic acid may lead to mesoporous structure partial collapsing.

BET analyses: The specific surface and pore volume are decreased after loading Ni and HPMo catalysts on the carrier of Ce-MCM-48 showed that the active component has been loaded on the carrier. With the increasing of HPMo loading, catalyst pore size becomes smaller, because the HPMo molecular diameter is smaller than the pore of the catalyst carrier, which can be interpreted as HPMo main load on the inner wall of mesoporous molecular sieve. When HPMo loading is less than 20 %, the catalyst surface area and pore volume changed very little, indicating that the active component is evenly distributed on the carrier and when the capacity of HPMo is above 30 %, the catalyst surface area and pore volume decreased significantly. This phenomenon may be due to the aggregation of the excess HPMo on the molecular sieve surface which blocked the zeolite pore. On the other hand, probably because the strong interaction caused by the increasing content of the heteropoly acid led to serious mesopore collapse and the results are consistent with the XRD analysis (Table-1).

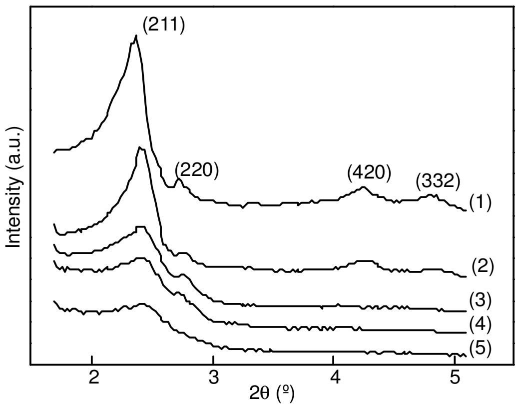

Fig. 1. XRD patterns of (1) Ce-MCM-48; (2-5) w % HPMo-Ni/Ce-MCM-48 w/%: (2)10; (3) 20; (4) 30; (5) 40

TABLE-1
BET ANALYSES WITH DIFFERENT CATALYSTS

Sample	S_{BET} ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)	D (nm)
Ce-MCM-48	1110	0.98	3.50
10 % HPMo-Ni/Ce-MCM-48	943	0.62	2.65
20 % HPMo-Ni/Ce-MCM-48	879	0.55	2.51
30 % HPMo-Ni/Ce-MCM-48	624	0.33	2.10
40 % HPMo-Ni/Ce-MCM-48	447	0.19	1.70

S = Specific surface area; V_p = Total pore volume; D = Average pore diameter.

SEM analyses: Fig. 2 shows field emission scanning electron micrographs (SEM) for Ce-MCM-48 and 20 % HPMo-Ni/Ce-MCM-48 samples obtained flowing the above procedure. Examining numerous SEM images of the sample, we found that almost all the products are Ce-MCM-48 dodecahedron single crystal with 150-200 nm in diameter[9]. Some of Ce-MCM-48 was destroyed in 20 % HPMo-Ni/Ce-MCM-48, then Ni and phosphomolybdic acid particles are adsorbed onto the surface.

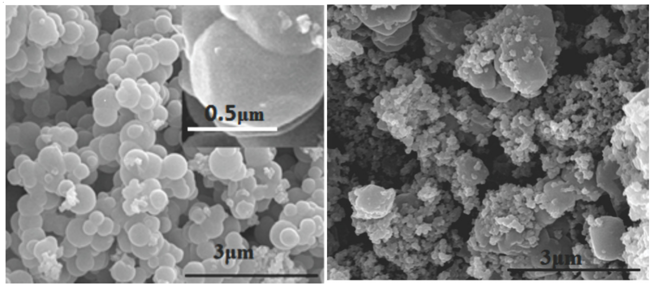

Fig. 2. SEM images of (1) Ce-MCM-48 and (2) 20 % HPMo-Ni/Ce-MCM-48

FT-IR analyses: Fig. 3 shows the FT-IR of Ce-MCM-480$H_3PM_{O12}O_{40}$ and 20 % HPMo-Ni/Ce- MCM-48. In IR spectra SAPO-11 shows the peak at 460, 810 and 1080 cm^{-1} (1200 cm^{-1})are assigned to the δ(Si-O-Si), ν_s(Si-O-Si), ν_{as}(Si-O-Si), respectively. $H_3PM_{O12}O_{40}$ have four characteristic peaks of Keggin structure. From FT-IR figure, we could see the peak at 1060, 960, 880 and 780 cm^{-1} are assigned to the ν_{as}(P-O), ν_{as}(Mo=O), ν_{as}(Mo-O_b-Mo) and ν_{as}(Mo-O_c-Mo), respectively. b and c shows the angle-shared and edge-shared. 20 % HPMo-Ni/Ce-MCM-48 have characteristic peaks of Keggin structure. The peak shows phosphomolybdic acid still keep the common structure of heteropoly acid on the surface of Ce-MCM-48. The loaded heteropoly acid shows the infrared spectrum peak width and move to higher wave number compare with pure $H_3PM_{O12}O_{40}$. It is because of interaction between heteropoly acid and the carrier and made the structure deformation.

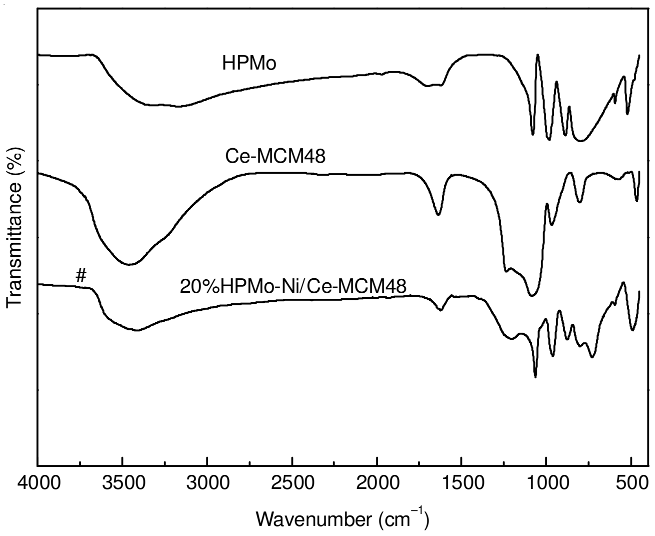

Fig. 3. FT-IR spectra of Ce-MCM-48, HPMo and 20 % HPMo-Ni/Ce-MCM-48; #: Subtraction of the FT-IR spectrum of 20 % HPMo-Ni/Ce-MCM-48 catalyst from that of the Ce-MCM-48 support

Effect of the content of HPMo: Fig. 4 shows the isomerization selectivity of *n*-heptane first increased and then the isomerization selectivity of *n*-heptane decreased with the increase of HPMo. Besides isomerization reaction and catalytic cracking reaction at the acid center of molecular sieve, the polycondensation could get the precursors of the carbon deposition of the catalyst, because the conversion of *n*-heptane decreased with the decrease of the acid sites. When HPMo is over 20 %, such heteropoly acid may prevent the intermediate material from diffusing on the pore channel and may induce the decrease of the hydrogenolysis conversion. Meanwhile, the isomerization selectivity would increase. The Bronsted acid center has the effect on isomerization and Lewis acid center has an effect on the catalytic cracking. So the amount of HPMo is higher 20 %, isomerization selectivity process declined.

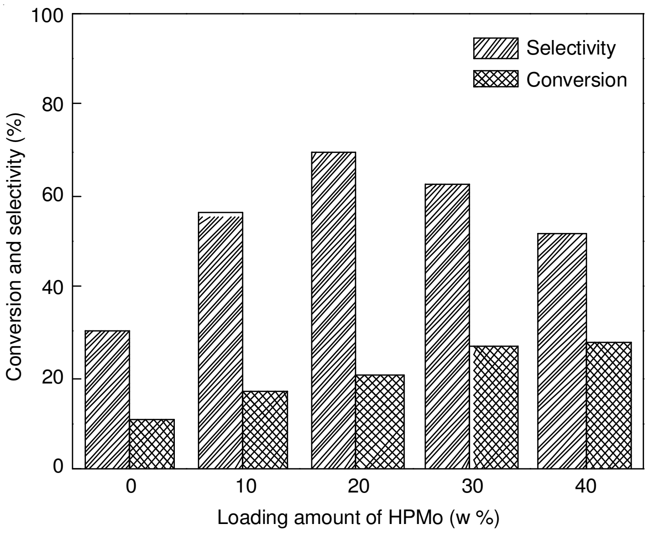

Fig. 4. Variation of conversion and isomerization selectivity on HPMo-Ni/Ce-MCM-48 with different content of HPMo. Reduction temperature: 673 K (for 6 h); reaction temperature: 573 K (for 6 h), weight hourly space velocity = 3.52 h^{-1}, flow rate of H_2 = 50 mL/min

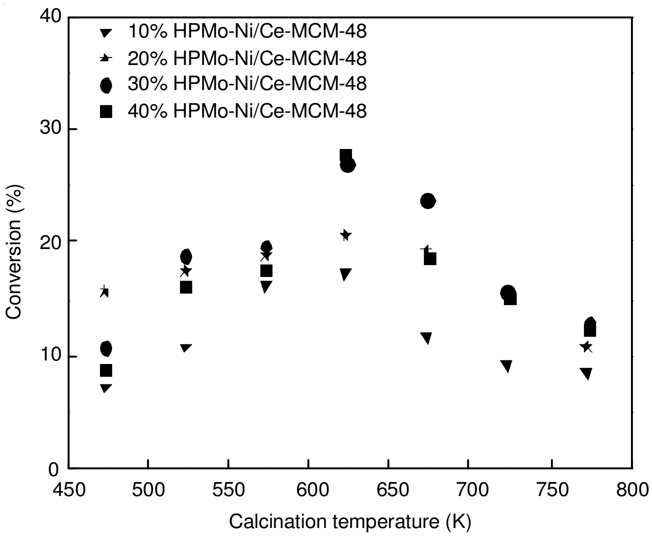

Fig. 5. Influence of calcination temperature on the activity of HPMo-Ni/Ce-MCM-48 catalyst. Reduction temperature: 673 K (for 6 h); reaction temperature: 573 K (for 6 h), weight hourly space velocity = 3.52 h^{-1}, flow rate of H_2 = 50 mL/min

Influence of calcination temperature: Fig. 5 shows that the conversion of catalyst's increases first and then decreases with the calcination temperature increasing. One possible reason is that the metal dispersion increases which is helpful to the increase of the utilization rate of the metal. So the conversion of the catalyst's increases when the calcination temperature is less than 400 ºC. Another possible cause is that heteropoly acids are unique acid catalysts and the crystal water is important component for the heteropoly acids and the acid center of the heteropoly acids changes with the change of the number of the crystal water. The results show that the acid center of heteropolyacids increases first and then decreases with the crystal water decreasing, which indicates that the number of the crystal water of HPMo is influenced by the change of the calcination temperature when the catalysts were calcined under different calcination temperatures. The conversion of catalyst's increases first and then decreases with the change of the acid center of heteropoly acids. The effect of the temperature on the conversion is increasingly apparent with the increase of the content of the heteropoly acids, which confirms that the acid is influenced by the calcination temperature. The conversion is influenced by the temperature as well as the acid. The conversion

TABLE-2
SELECTIVITY OF THE VARIOUS LUMP PRODUCTS
OVER THE 20 % HPMo-Ni/Ce-MCM-48 CATALYST

Temperature (K)	Conversion (%)	Selectivity (%)	Isomer distribution (%)		
			Mono-iC$_7$ *	Multi-iC$_7^{\#}$	R
533	10.9	81.9	60.9	39.1	0.74
553	15.5	72.5	61.8	38.2	0.62
573	20.6	69.4	63.5	36.5	0.57
593	24.3	53.8	59.5	40.5	0.68
613	28.4	45.4	62.7	37.3	0.59

Reduction temperature = 673 K (for 6 h); weight hourly space velocity = 3.52 h^{-1}; flow rate of H_2 = 50 mL/min. *Mono-branched products include 2-MH(42), 3-MH(52); #Multi-branched products include 2,2-DMP(98), 2,3-DMP(91), 2,4-DMP(83),3,3-DMP(81), 2,2,3-TMB(112):The number in parenthesis is the research octane number.

decreases under high temperature because the heteropoly acids are decomposed under high temperature and then the channels of the catalysts are blocked by the oxides after the decomposition, which goes against the diffusion of the gas molecule. The metal dispersion decreases under high temperature that attributes to the phenomenon of aggregation.

Influence of reaction temperature: Table-2 shows the product distribution of 20 % HPMo-Ni/Ce-MCM-48 catalyst at different temperature. It can be seen from Table-2 that the conversion rate increased with the increase of the reaction temperature, while the selectivity decreased with the increase of the reaction temperature. It is known that *n*-heptane isomerization reaction is exothermic, while the cracking reaction is endothermic. Thus, a lower temperature is favorable for the isomerization reaction, while a higher temperature is favorable for the cracking reaction. When the reaction temperature was lower than 573 K, *n*-heptane isomerization conversion rate would increase with the increase of temperature. When the reaction temperature was higher than 573 K, the cracking reaction rate increased quickly and the increased cracking reaction rate would be more quickly than the increased isomerization conversion rate. Therefore, the conversion rate increased and the selectivity decreased with the increase of the reaction temperature. Thus, the reaction temperature of 573 K was relatively suitable for the isomerization conversion.

As seen from Table-2, the catalyzates have many isomers of C_7 at different temperature. Monobranched isomers are dominated by 2-methylhexane and multibranched isomers are dominated by 2,3-dimethylpentane. The proportion of multibranched isomers of C_7 of catalysts doesn't increase with the increase of the conversion, which indicate that there is a parallel reaction with a intermediate between branched products and multibranched products of isomerization reaction. R (multibranched isomers/monobranched isomers) keeps 0.6-0.8, which is obviously better than traditional zeolite (R = 0.2-0.5), which shows that gasoline components with high octane number are obtained by *n*-heptane hydroisomerization of 20 % HPMo-Ni/Ce-MCM-48 catalyst.

Evaluation of catalytic stability: The stability of the catalyst is an important considering factor in the design of industrial catalysis. Thus, the reaction stability of 20 % HPMo-Ni/Ce-MCM-48 catalyst is studied. In stability test of the 20 % HPMo-Ni/Ce-MCM-48, with reaction time increasing, the conversion of *n*-heptane decreased and iso-heptane selectivity increased, but the changes were not obvious. The reason was that the coke formed at the active center led the conversion of *n*-heptane decrease slightly, whereas carbon deposition on the cleavage preferentially occurs at the strong acid sites of catalytic reactions. Hence, isomerization selectivity showed a slightly increasing trend. The overall trend showed that the stability of the catalyst was very good.

Conclusion

Compared with the ordered crystalline Ce-MCM-48, the specific surface area of HPMo-Ni/Ce-MCM-48 decreased, indicating that the main active components were dispersed on the catalyst surface. The isomerization reaction of n-heptane showed that after adding the active component to the catalyst, both the conversion and selectivity were increased. The catalytic activity of the HPMo-Ni/Ce-MCM-48 with an HPMo loading of 20 % exhibited the best catalytic performance for *n*-heptane isomerization. The conversion of *n*-heptane and isomerization selectivity to *i*-heptane reached 18.5 and 73.5 %, respectively.

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