

Novel Ni₂Mo₃N/zeolite catalysts used for aromatics hydrogenation as well as polycyclic hydrocarbon ring opening

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Abstract

A series novel of bifunctional catalysts consisting of bulk and zeolite-supported Ni₂Mo₃N were prepared., characterized and investigated in the hydrogenation of aromatics as well as ring opening of polycyclic hydrocarbons. All supported catalysts had shown high activity of aromatics saturation (almost 100%) at 523 K while different activity of ring opening at 603 K. The essential factor of ring opening activity was acidity of catalysts, while the pore structure of the supports also affected it. The results show that the suitable catalyst Hbeta-supported and USY-supported Ni₂Mo₃N provide high ring opening conversion (>90%) under mild moderate condition ($T = 603$ K, $P = 3.0$ MPa).

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1. Introduction

With the growing demand for diesel fuel, the proportion of the fluid catalytic cracking (FCC) in the diesel increases greatly. The aromatics were abundant (about 60% v/v) in the FCC diesel, and most of them are polycyclic aromatics (about 75% v/v). These aromatics in diesel fuel not only produce undesired emissions in the exhaust gases, but also debase the cetane number, which is one of the most important fuel specifications [1,2]. The ability of diesel fuel to burn with the proper characteristics is described by its cetane number, a measure of ignition delay. Excessively long ignition delays (low cetane number) cause rough engine operation, misfiring, incomplete combustion and poor stability. *n*-Hexadecane has a short delay period during ignition and is assigned a cetane number of 100; α -methyl naphthalene

has a very long delay period and is assigned a cetane number of 0 [3]. The cetane number order of hydrocarbons with the same number of carbon atoms is

alkane > monocyclic alkane > polycyclic alkane > monocyclic aromatic > polycyclic aromatic

The cetane number of diesel could be raised by about 1–4 units, when polycyclic aromatics in the fuels were merely converted to polycyclic alkane through conventional hydrotreating. While the cetane number of the fuels would increase greatly, if polycyclic aromatics in the fuels ring opened to monocyclic hydrocarbon and even to alkane. Therefore, ring opening of the polycyclic hydrocarbons must be carried out.

Nowadays, the catalysts used for ring opening of the polycyclic mainly based on supported noble metals at high pressure (6.0–10.0 MPa) and temperature (above 723 K) [4–9]. However, noble metals are known to be easily poisoned by small concentrations of sulfur and nitrogen organic compounds in the feed [10] and high

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cost. So finding out a new class of catalyst that is low-cost and highly active in ring opening reaction is necessary. Metallic nitrides such as Mo_2N have exhibited a superior activity in hydrodenitrogenation and hydrodesulfurization reactions [11–15]. Recently, it has been shown that the catalytic activity of molybdenum nitrides is enhanced by addition of another transition metal such as nickel. Weil et al. [16] have provided a vigorous crystal structure of $\text{Ni}_2\text{Mo}_3\text{N}$ by X-ray diffraction. High hydrogenation activity of the γ -alumina supported $\text{Ni}_2\text{Mo}_3\text{N}$ catalyst was found in our previous studies [17], while the use of the catalysts was limited because of its poor acidity. So using stronger acidity supports to prepare a series of novel bifunctional catalyst that have both hydrogenation and ring opening functions will be very significant. At present, few zeolite-supported bimetallic nitrides $\text{Ni}_2\text{Mo}_3\text{N}$ has been reported, in this study bulk and various zeolites (USY, Hbeta, HZSM-5, HMCM-41(Al)) supported $\text{Ni}_2\text{Mo}_3\text{N}$ were prepared successfully through the temperature-programmed reduction (TPR) method, and characterized by NH_3 temperature-programmed desorption (NH_3 -TPD), nitrogen adsorption analysis and ICP-AES techniques. A feedstock containing naphthalene, *p*-xylene and decalin was used as a model compound to evaluate the hydrogenation as well as ring opening activity of those catalysts under a continuous-flow condition. Once the catalytic pattern of those molecules has been determined, one can rationalize the influence of the catalysts on product distribution. The suitable catalyst for performing naphthenic ring opening that improves diesel fuel can then be selected.

2. Experimental

2.1. Materials

Organic reagents such as naphthalene, *p*-xylene, decalin and other compounds such as $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were of commercial AR grade. HMCM-41(Al)(Si/Al:24), USY(Si/Al:4.7), HZSM-5 (Si/Al:38) and Hbeta(Si/Al:25) were purchased from Nankai University Catalysts Plant.

2.2. Preparation of catalysts

An oxide precursor to $\text{Ni}_2\text{Mo}_3\text{N}$ was prepared by dissolving nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) in $\text{NH}_3 \cdot \text{H}_2\text{O}$, evaporated to dryness and calcined at 773 K for 5 h in air. The precursor was converted to $\text{Ni}_2\text{Mo}_3\text{N}$ using TPR method under a flow of NH_3 , at a mass rate of 6500 h^{-1} , the temperature was increased linearly at a rate of 6 K min^{-1} from room temperature to 623 K, and then at a rate of 1 K min^{-1} to 923 K, finally kept at that

temperature for 2 h. The product was cooled to 373 K and passivated for 12 h under O_2/N_2 (1.0 vol% O_2) flow to achieve bulk $\text{Ni}_2\text{Mo}_3\text{N}$.

The zeolite-supported oxide precursors to $\text{Ni}_2\text{Mo}_3\text{N}$ /zeolites were prepared by the following process: the supports were calcined and the powders were sieved, the fraction of samples below 80 mesh were impregnated simultaneously with an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ as required, dried in an oven at 393 K for 3 h and calcined in air at 773 K for 5 h. The solids were nitrated and passivated as described previously to achieve loads of 25 wt% zeolite-supported $\text{Ni}_2\text{Mo}_3\text{N}$ catalysts.

2.3. Characterization

Powder XRD patterns were obtained using a D/max-2500 powder X-ray diffractometer (Cu K radiation). Data acquisition, peak identification and data plotting were accomplished using a Data General Computer System. The pore size distribution data results by nitrogen adsorption were obtained using a Micromeritics ASAP 2010 instrument. The nickel and molybdenum analyses of the samples were carried out in an IRIS Advantage ICP-AES as well as nitrogen analyses of the samples were carried out in Elementar Vario El elemental analyzer.

The acid strength distributions of catalysts were measured by NH_3 temperature programmed desorption NH_3 TPD as following: before the adsorption of ammonia at 393 K, the samples were first reduced in H_2 at 20 ml min^{-1} (in accord with that of the reaction conditions) and then heated at 873 K in $10^{-0.1} \text{ Pa}$ vacuum for 30 min. The desorbed ammonia between 393 and 873 K (heating rate of 10 K min^{-1}) was analyzed by detector.

2.4. Model reaction

The feed was a ternary mixture of naphthalene (10 wt%), *p*-xylene (40 wt%) and decalin (50 wt%). The reactions were performed in a high-pressure fixed-bed continuous-flow stainless steel reactor with an electric furnace operated in the down-flow mode. The reaction temperature was measured with a thermocouple placed in direct contact with the middle of the catalyst bed. The organic feed was supplied by a pump. The mass of each catalyst (20–40 mesh) was 2.5 g (about 5.0 ml) in that study. Prior to the activity test, the catalysts were reduced at 0.3 MPa pressure with H_2 (flow rate 20 ml min^{-1}) at 673 K for 3 h. Catalytic activities were measured in the range of between 523 and 603 K, under 3.0 MPa pressure, and a liquid hourly space velocity (LHSV) of 1.0 h^{-1} , the H_2 /liquid volume ratio was 600:1. The reaction was kept at a steady state for 2 h, and then in the following hour, liquid samples were collected and kept in sealed vials to be analyzed by GC-MS

using a Hewlett–Packard GCD1800 system equipped with an HP5 column.

Various zeolite-supported $\text{Ni}_2\text{Mo}_3\text{N}$ catalytic activities were compared. Conversion by hydrogenation and ring opening were calculated from the following equations:

(a) Aromatic hydrogenation conversion:

$$X_{\text{H}}(\%) = \frac{[(n\text{N})_{\text{o}} + (n\text{P})_{\text{o}}] - [(n\text{N})_{\text{f}} + (n\text{P})_{\text{f}}]}{[(n\text{N})_{\text{o}} + (n\text{P})_{\text{o}}]} \times 100,$$

(b) Polycyclic aromatic ring opening conversion:

$$X_{\text{R}}(\%) = \frac{[(n\text{N})_{\text{o}} + (n\text{D})_{\text{o}}] - [(n\text{N})_{\text{f}} + (n\text{D})_{\text{f}}]}{[(n\text{N})_{\text{o}} + (n\text{D})_{\text{o}}]} \times 100,$$

where the subscripts o and f denote initial and final weights, respectively, of the different compounds (in brackets). P = *p*-xylene, N = naphthalene and D = decalin.

3. Results and discussion

3.1. Catalyst characterization

The XRD pattern for the material prepared by nitridation, shown in Fig. 1, is identical to those reported by

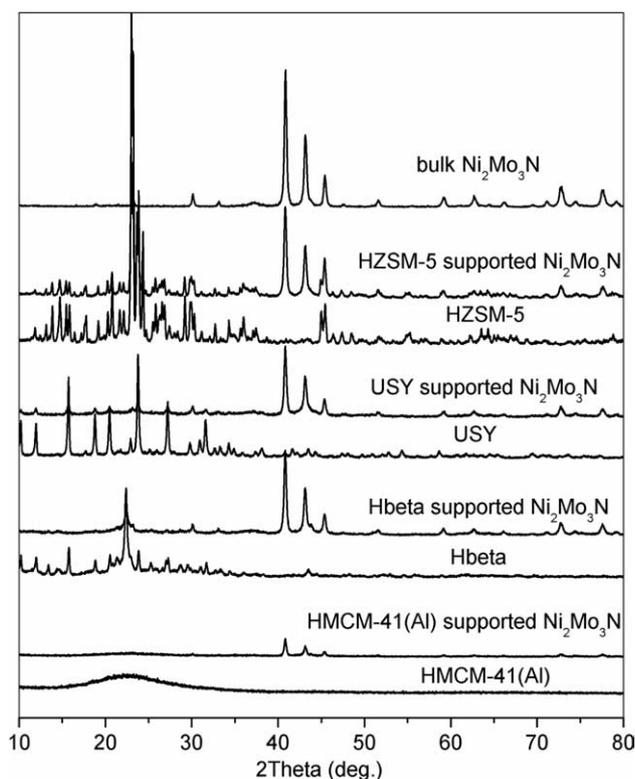


Fig. 1. Bulk zeolite and its supported $\text{Ni}_2\text{Mo}_3\text{N}$ catalyst XRD diffractograms.

others [16,18,19] for phase $\text{Ni}_2\text{Mo}_3\text{N}$ (card number 894564). The elemental composition of the unsupported $\text{Ni}_2\text{Mo}_3\text{N}$ is consistent with that expected of the theoretical value. The $\text{Ni}_2\text{Mo}_3\text{N}$ was supported on the zeolites, and all zeolites preserved their initial structure upon deposition of the $\text{Ni}_2\text{Mo}_3\text{N}$ (in order to prove that the carriers' zeolitic structure are still possessed after TPR procedure, the bulk support Hbeta is chosen as a typical sample and nitrated by TPR method in NH_3 flow, and the XRD patterns of original and nitrated Hbeta are exhibited in support informations. From it we can see that the zeolite is very stable and its zeolitic structure is not changed before and after nitridation procedure). The intensity of supported $\text{Ni}_2\text{Mo}_3\text{N}$ was weaker than that of the bulk $\text{Ni}_2\text{Mo}_3\text{N}$. The size of the $\text{Ni}_2\text{Mo}_3\text{N}$ supported on HMCM-41(Al) was smallest in the study while the size of other supported $\text{Ni}_2\text{Mo}_3\text{N}$ was almost same.

The elemental compositions of the bulk $\text{Ni}_2\text{Mo}_3\text{N}$ and the metal loadings of the supported $\text{Ni}_2\text{Mo}_3\text{N}$ are approximately consistent with the theoretical values. Those results indicate that both bulk and zeolite-supported $\text{Ni}_2\text{Mo}_3\text{N}$ are successfully prepared by the TPR method.

Based on the acidity results provided by the spectrophotometric method used, the zeolite-supported $\text{Ni}_2\text{Mo}_3\text{N}$ possessed a different acidity from these materials. Fig. 2 shows the curves for all the zeolite-supported $\text{Ni}_2\text{Mo}_3\text{N}$ s studied. It can be seen that HZSM-5, USY and Hbeta are similar, having a large number of acid sites, and the Hbeta-supported $\text{Ni}_2\text{Mo}_3\text{N}$ has the strongest acid sites, while HMCM-41(Al) possesses the smallest and fewest strong acid sites.

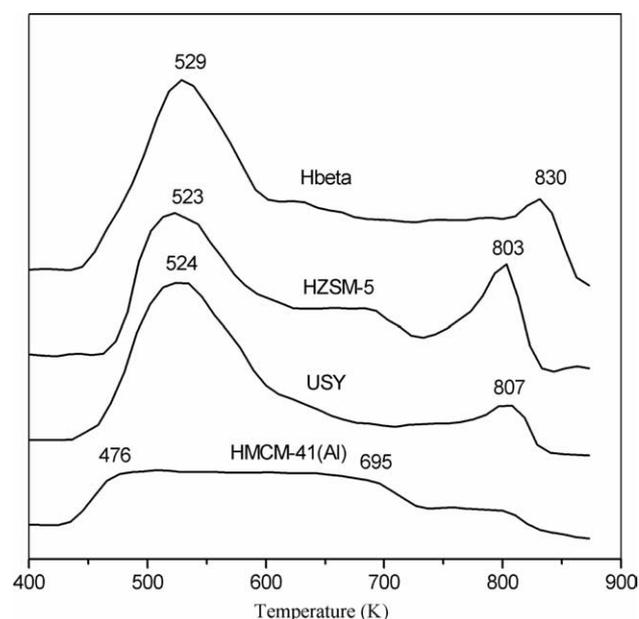


Fig. 2. In situ NH_3 -TPD profiles for zeolite supported $\text{Ni}_2\text{Mo}_3\text{N}$.

Table 1
Metal loadings and the catalytic activity of zeolite-supported Ni₂Mo₃N catalysts

Catalysts	Metal loadings (wt%)	Catalytic activity		
		Temperature (K)	Hydrogenation conversion (%)	Ring opening conversion (%)
Ni ₂ Mo ₃ N/Hbeta	Ni 7.8 Mo 19.1	523	100	–
		603	81.3	92.7
Ni ₂ Mo ₃ N/USY	Ni 7.8 Mo 19.1	523	100	–
		603	80	92.5
Ni ₂ Mo ₃ N/HZSM-5	Ni 7.7 Mo 18.9	523	100	–
		603	83.4	7.5
Ni ₂ Mo ₃ N/HMCM-41	Ni 7.9 Mo 19.3	523	100	–
		603	79.8	0

3.2. Catalytic activity

A comparison of the different zeolites at identical condition shows that the Hbeta-supported Ni₂Mo₃N and USY-supported Ni₂Mo₃N are more active in ring opening than other supported Ni₂Mo₃N, while pure Ni₂Mo₃N has low activity of hydrogenation and no ring opening ability, and bulk supports used in the study have no ability of hydrogenation and ring opening. All the supported catalysts' hydrogenation conversions are similar in 603 K (seen from Table 1), so the Ni₂Mo₃N disperses uniformly on the supports, the origin of the differential ring opening activity of the catalysts should be the acidity and pore size of the catalysts.

Actually, the ring opening activity of zeolite-supported Ni₂Mo₃N is mainly dependent on its acidity, (viz. its number of acid sites and their strength), which is highly influenced by the temperature and space velocity required to obtain a given conversion level. The NH₃-TPD curves of Fig. 2 shown, the strong acid strength of the catalysts decreases in the following order

Hbeta > USY > HZSM-5 ≫ HMCM-41(Al).

The order of the catalysts' number of strong acid sites is

HZSM-5 > Hbeta ≈ USY > HMCM-41(Al).

However, the conversion obtained with the different zeolite-supported catalysts decreased in the following sequence (from Table 1):

Hbeta > USY > HZSM-5 > HMCM-41(Al).

These orders are based on the ring opening conversion of Hbeta-, USY- and HMCM-41-supported Ni₂Mo₃N. Following from this order, the HZSM-5-supported catalyst should have the highest ring opening conversion (from Fig. 2), however, the observation is that HZSM-5 has low ring opening activity because the HZSM-5 is the 10 member-ring (MR) zeolite and the pore size is

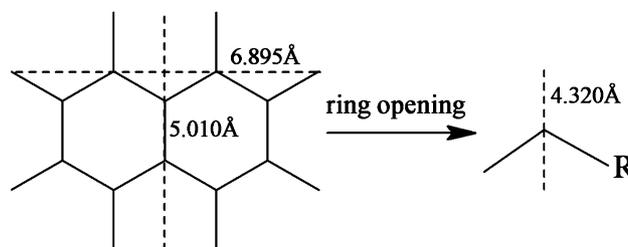


Fig. 3. Model of decalin molecule and ring opening product.

Table 2
Properties of the zeolites used in the present study [20]

Zeolites	Number of rings of apertures	Pore size (Å) ^a	Pore size (Å) ^b
USY	12	7.4	6.8
Hbeta	12	7.2 × 6.2	5.7
HZSM-5	10	5.1 × 5.5	5.0
HMCM-41(Al)		10–20	13.8

^a Theoretic minimum of unsupported zeolites' pore size.

^b Pore size distribution by Horvath–Kawazoe (HK) method.

about 5.1 × 5.5 Å wide, so that naphthalene and decalin cannot easily diffuse in that catalyst, the model of decalin molecule and ring opening can be seen from Fig. 3. On the other hand, Hbeta and USY are 12 MR zeolites. After being loaded the pore size decreased, respectively. All the Properties of the zeolites used in the work are listed in Table 2. Those results suggest that a good light cyclic oil (LCO) cracking catalyst for the production of naphthene should involve a large pore zeolite and suitable acidity.

4. Conclusion

A new set of bifunctional catalysts consisting of 25 wt% Ni₂Mo₃N supported on various types of zeolites (viz. Hbeta, USY, HMCM-41 and HZSM-5) were prepared, and the hydrogenation and ring opening of a mixture of naphthalene, *p*-xylene and decalin on these catalysts were studied. All the catalysts possess good

hydrogenation activities, showing that the catalysts have the catalysts have similar $\text{Ni}_2\text{Mo}_3\text{N}$ dispersion. The Hbeta and USY zeolites were the supports exhibiting the higher ring opening conversion because of their suitable acidity and pore size. Those results show that the importance of the nature of the support in determining catalytic performance. The strong sites of acidity in the catalysts were the key factor in ring opening activity, and the pore size of the supports influenced the ring opening too. This work will be of great benefit to improving the quality of diesel fuel.

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