

A novel $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ catalyst for the hydrogenation of aromatics

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Bulk and MCM41-supported $\text{Ni}_2\text{Mo}_3\text{N}$ catalysts were prepared using a temperature-programmed reduction (TPR) method and characterized using XRD, TEM, ICP-AES, and N_2 adsorption analysis techniques. Their catalytic properties were measured for the simultaneous hydrogenation of *p*-xylene and naphthalene and compared with $\text{Ni}/\text{MCM41}$ and $\text{Mo}_2\text{N}/\text{MCM41}$ catalysts having similar metal loadings. The results indicate that the $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ catalyst exhibits excellent deep hydrogenation activity under mild condition ($T = 483 \text{ K}$, $P = 3.0 \text{ MPa}$), and that it is more active than either $\text{Ni}/\text{MCM41}$ or $\text{Mo}_2\text{N}/\text{MCM41}$ catalyst.

KEY WORDS: $\text{Ni}_2\text{Mo}_3\text{N}$; $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$; hydrogenation; aromatic; *p*-xylene; naphthalene.

1. Introduction

Due to the imposition of more stringent environmental regulations and the growing demand for high quality diesel fuels, dearomatization of petroleum fractions is becoming more important to society, and is playing a significant role in the modern refinery industry. Reducing the content of aromatics in diesel oil has a positive effect on the cetane number [1], and decreases the hazardous emissions from diesel engines [2]. Many have tried to develop new catalysts and processes for saturating aromatics to give them improved reactivity and stability at moderate temperatures.

Conventional hydrotreating catalysts containing sulfided mixed oxides (NiMo , NiW , CoMo) cannot accomplish a deep level of aromatic saturation in a single-step process because of thermodynamic limitations at their high reaction temperatures [3,4]. Recently, studies have focused on noble metal-based catalysts for hydrogenation in a two-step process [3–5]. It is well established that noble metal catalysts present excellent hydrogenation properties at low temperatures, where the thermodynamic limitations are not as severe as those of the metal sulfide-type. However, this type of catalyst has its own restrictions, since noble metals are known to be poisoned by small concentrations of sulfur and nitrogen organic compounds in the feed [6], and are generally not employed in commercial processes because of their high cost.

Transition metal nitrides have also been tested for hydrotreatments [7–12]. However, most studies in this area have concentrated on monometallic transition metal nitrides, and relatively few bimetallic nitrides have been studied. In recent years, alumina-supported $\text{Ni}_2\text{Mo}_3\text{N}$ has been used as an active catalyst for hydrosulfurization (HDS) [11] and hydrodenitrogenation

(HDN) [12]. In this work, we report on the use of $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ catalyst possessing good deep hydrogenation activity under mild conditions. Both bulk and MCM41-supported $\text{Ni}_2\text{Mo}_3\text{N}$ catalysts were prepared and characterized. The catalytic activities of the catalysts were measured for their hydrogenation properties using a model feed (40 wt% *p*-xylene, 10 wt% naphthalene, and 50 wt% decalin), and the results compared with the hydrogenation properties of $\text{Ni}/\text{MCM41}$ and $\text{Mo}_2\text{N}/\text{MCM41}$ catalysts. MCM41 zeolite was employed as a steady support in this work, due to its good thermal stability, high surface area, and large adsorption capacity for organic molecules. This material has been used as support in place of alumina by many research groups [4,13,14]. Our results demonstrate that MCM41-supported $\text{Ni}_2\text{Mo}_3\text{N}$ has the potential to be used as good sulfur and nitrogen-resistant catalyst for deep hydrogenation of aromatics in diesel oil.

2. Experimental

2.1. Catalyst preparation

The oxide precursor of $\text{Ni}_2\text{Mo}_3\text{N}$ 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 15% $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution, evaporating to dryness, and calcining at 773 K for 5 h in air. The precursor was converted to $\text{Ni}_2\text{Mo}_3\text{N}$ using a temperature-programmed reduction (TPR) process in flowing NH_3 gas. About 6 mL of the oxide precursor was placed in a stainless steel reactor located in a tube furnace. The flowing ammonia had a VHSV (volume hourly space velocity) of 6000 h^{-1} . The temperature was increased in two steps: rapidly from room temperature to 623 K (at 6 K/min), and then slowly from 623 to 923 K (at 1 K/min). The temperature was then held at 923 K for 2 h. The system was then

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cooled to room temperature in flowing NH_3 , and passivated overnight in flowing 1% O_2/N_2 (v/v) gas to avoid strong bulk oxidation.

The MCM41-supported oxide precursor of the $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ catalyst with a theoretical content of 25 wt% $\text{Ni}_2\text{Mo}_3\text{N}$ was prepared by impregnation of precalcined MCM41 (773 K, 5 h, in air) using aqueous solutions of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_6\cdot 6\text{H}_2\text{O}$, followed by airing overnight, drying for 3 h at 393 K, and calcination for 5 h at 773 K in air. The precursor was nitrated and passivated as described above to yield 25 wt% $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ catalyst.

For comparison, $\text{Ni}/\text{MCM41}$ and $\gamma\text{-Mo}_2\text{N}/\text{MCM41}$ catalysts were also prepared with the same Ni and Mo loading (based on the support) as the $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ sample, respectively. The $\text{MoO}_3/\text{MCM41}$ and $\text{NiO}/\text{MCM41}$ precursors were prepared by impregnation of MCM41 using aqueous solutions of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_6\cdot 6\text{H}_2\text{O}$, respectively, followed by airing overnight, drying for 3 h at 393 K, and calcination for 5 h in air. The $\text{MoO}_3/\text{MCM41}$ precursor was then nitrated and passivated as described above to yield $\text{Mo}_2\text{N}/\text{MCM41}$ catalyst. The $\text{NiO}/\text{MCM41}$ precursor was pretreated in flowing H_2 at 673 K to get $\text{Ni}/\text{MCM41}$ catalyst prior to evaluation.

2.2. Characterization of the catalyst

XRD characterization was conducted using a Rigaku D/max-2500 powder diffractometer employing $\text{Cu-K}\alpha$ radiation. Transmission electron microscope (TEM) images were acquired using a Philips EM400ST TEM operating at an excitation voltage of 100 kV. The nickel and molybdenum analyses of the samples were carried out using an IRIS Advantage inductively coupled plasma atomic absorption spectrometer (ICP-AES), and the nitrogen and carbon analyses of the samples were carried out using an Elementar Vario EL elemental analyzer. BET Surface area measurements employing nitrogen adsorption were obtained using a Micromeritics ASAP 2010 apparatus.

2.3. Activity

Hydrogenation of *p*-xylene and naphthalene was performed in a fixed bed reactor using 5 mL (about 2.5 g) of catalyst (20–40 mesh) under 3.0 MPa of H_2 in the temperature range $T = 443\text{--}573$ K. Prior to evaluation, the catalyst was pretreated under flowing H_2 at $T = 673$ K for $t = 3$ h. Then, the temperature was adjusted to the reaction temperature, and a stream of 40 wt% *p*-xylene, 10 wt% naphthalene, and 50 wt% decalin was introduced using a liquid feedstock pump in flowing H_2 . The flow rate of H_2 was maintained at 50 mL/min, and the liquid flow rate at 5.0 mL/h. The liquid samples were collected after a reaction time of 6 h, and the samples analyzed using a gas chromatograph with an attached capillary column.

3. Results and discussion

The synthesis procedure employed to prepare our MCM41-supported $\text{Ni}_2\text{Mo}_3\text{N}$ samples is similar to that described by others for the preparation of alumina-supported $\text{Ni}_2\text{Mo}_3\text{N}$ [15]. Figure 1 shows XRD patterns of bulk $\text{Ni}_2\text{Mo}_3\text{N}$, $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$, the oxide precursor ($\text{NiMoO}_x/\text{MCM41}$), and the MCM41 support. The XRD pattern of $\text{NiMoO}_x/\text{MCM41}$ indicates that the supported phase consisted of $\beta\text{-NiMoO}_4$ and MoO_3 . The XRD pattern of bulk $\text{Ni}_2\text{Mo}_3\text{N}$ is consistent with that reported by others for phase-pure $\text{Ni}_2\text{Mo}_3\text{N}$ [15, 16]. In addition to peaks associated with the MCM41 support, the XRD pattern of $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ shows additional peaks, which are all in good agreement with those of bulk $\text{Ni}_2\text{Mo}_3\text{N}$. An average crystallite size of 26 nm was calculated for the $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ catalyst using the Scherrer equation employing the FWHM value of the peak at $2\theta = 40.9^\circ$. This value is considerably smaller than the calculated average crystallite size of 52 nm for unsupported $\text{Ni}_2\text{Mo}_3\text{N}$.

In figure 2, a TEM micrograph of the $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ catalyst shows that $\text{Ni}_2\text{Mo}_3\text{N}$ had an oval-shaped morphology with a particle size in the range 10–40 nm. This is in agreement with the calculated particle size from the XRD data. Table 1 lists the BET surface area and the elemental composition of the $\text{Ni}_2\text{Mo}_3\text{N}$ and $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ samples. The elemental composition of both the bulk and supported $\text{Ni}_2\text{Mo}_3\text{N}$

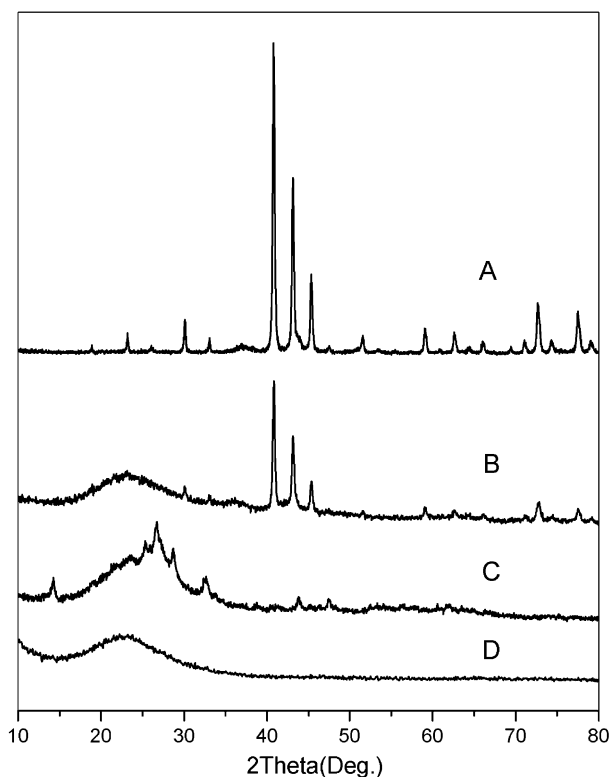


Figure 1. XRD patterns of the samples (A) $\text{Ni}_2\text{Mo}_3\text{N}$, (B) $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$, (C) $\text{Ni}_2\text{Mo}_3\text{O}_x/\text{MCM41}$ and (D) MCM41.

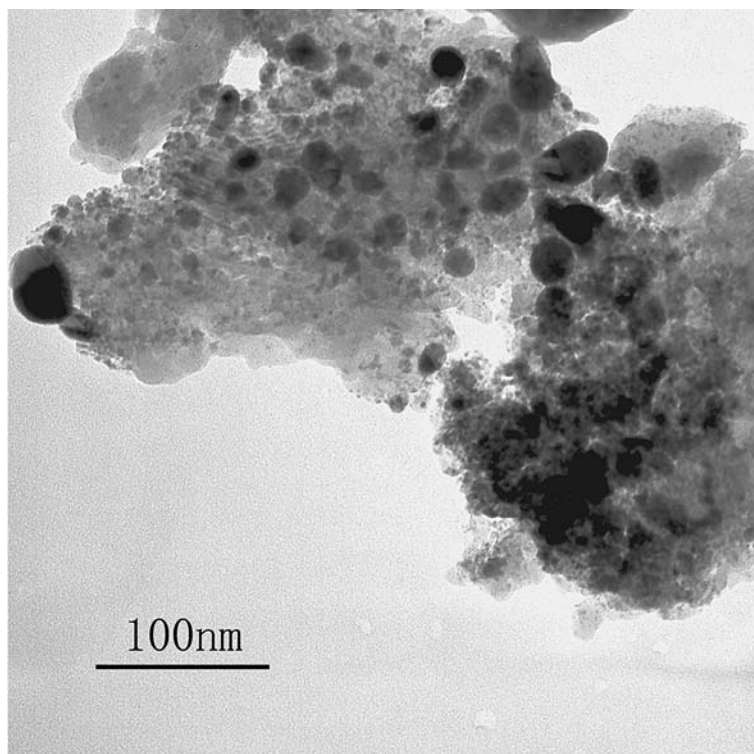


Figure 2. TEM micrograph of the $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ catalyst.

were approximately consistent with the theoretical values. The BET surface area of $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ was significantly higher than that of unsupported $\text{Ni}_2\text{Mo}_3\text{N}$.

These results indicate that both the bulk and MCM41-supported $\text{Ni}_2\text{Mo}_3\text{N}$ samples were successfully prepared, and that the supported catalyst possessed a high surface area and good $\text{Ni}_2\text{Mo}_3\text{N}$ dispersion.

Table 2 shows the activities of the bulk and MCM41-supported $\text{Ni}_2\text{Mo}_3\text{N}$ catalysts in *p*-xylene and naphthalene hydrogenation performed under moderate operating conditions ($T = 483 \text{ K}$, $P = 3.0 \text{ MPa}$). The bulk $\text{Ni}_2\text{Mo}_3\text{N}$ sample, which had been diluted with MCM41, exhibited a low activity. However, the MCM41-supported $\text{Ni}_2\text{Mo}_3\text{N}$ catalyst, on which the *p*-xylene and naphthalene were completely saturated, was more active than the unsupported $\text{Ni}_2\text{Mo}_3\text{N}$ sample due to the dispersion of $\text{Ni}_2\text{Mo}_3\text{N}$ on the support, as well as the high surface area of the catalyst.

For comparison, a MCM41-supported nickel catalyst and a MCM41-supported $\gamma\text{-Mo}_2\text{N}$ catalyst were prepared and tested to assess the hydrogenation of *p*-xylene

and naphthalene employing the same reaction conditions. As listed in table 1, for both *p*-xylene and naphthalene, the conversion ranking was: $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41} > \text{Ni}/\text{MCM41} > \text{Mo}_2\text{N}/\text{MCM41}$. Comparing the activities of the three catalysts clearly demonstrates that the incorporation of Ni into the molybdenum nitride in the form of MCM41-supported $\text{Ni}_2\text{Mo}_3\text{N}$ catalyst resulted in a considerable increase in hydrogenation activity. This result is very similar to that reported by others, in which $\text{Ni}_2\text{Mo}_3\text{N}$ catalyst was more active than Mo_2N catalyst for HDS and HDN reactions [11,12], and indicates that such bimetallic molybdenum nitrides are more suitable for use as hydrotreating catalysts than monometallic molybdenum nitride. It is confirmed that the $\text{Ni}_2\text{Mo}_3\text{N}$ is the unique existing species on the support and the better hydrogenation activity of $\text{Ni}_2\text{Mo}_3\text{N}$ catalyst than Ni catalyst probably owes to the special structure of $\text{Ni}_2\text{Mo}_3\text{N}$, which contains net of nickel atoms, the holes in which are filled by Mo_6N octahedral [17].

The results of catalytic measurements performed at different temperatures for the $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ catalyst are listed in table 1 and are compared in figure 3. The results show that increasing the reaction temperature to 483 K leads to an increase in the conversion of *p*-xylene and naphthalene, accompanied by a corresponding decreasing in tetralin yield. The higher reactivity of naphthalene versus *p*-xylene is in accord with the literature, and could be related to a decrease in the resonance energy per aromatics ring, as well as to

Table 1
BET surface areas and elemental composition of the bulk and MCM41-supported $\text{Ni}_2\text{Mo}_3\text{N}$ catalysts.

Catalyst	S_{BET} (m^2/g)	Elemental composition
$\text{Ni}_2\text{Mo}_3\text{N}$	10.61	$\text{Ni}_2\text{Mo}_{3.09}\text{N}_{0.94}$
$\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$	179.12	$\text{Ni}_2\text{Mo}_{2.88}\text{N}_{1.06}\text{C}_{0.08}$

Table 2
Hydrogenation of the *p*-xylene and naphthalene: a comparison of catalysts and reaction temperatures^a.

	Metal loading (wt%) ^b	Reaction temperature (K)	<i>p</i> -xylene conversion (%)	Naphthalene conversion (%)	Tetralin yield (%)
Ni/MCM41	Ni 9.3	483	72.7	87.9	2.8
$\text{Mo}_2\text{N}/\text{MCM41}$	Mo 22.9	483	0	8.2	0
$\text{Ni}_2\text{Mo}_3\text{N} + \text{MCM41}^c$	Ni 9.3 Mo 22.9	483	21.0	37.1	7.5
$\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$	Ni 9.3 Mo 22.9	483	100	100	0
$\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$	Ni 9.3 Mo 22.9	463	79.2	98.4	0
$\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$	Ni 9.3 Mo 22.9	443	53.2	84.2	9.7

^aReaction conditions: pressure = 3.0 MPa, LHSV = 1.0 h⁻¹, H₂/feed = 600 v/v, reaction time = 6 h.

^bMetal loading based on the MCM41 support.

^cA mixture of bulk $\text{Ni}_2\text{Mo}_3\text{N}$ and MCM41 support, in which the $\text{Ni}_2\text{Mo}_3\text{N}$ content is similar to that of the 25 wt% $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ catalyst.

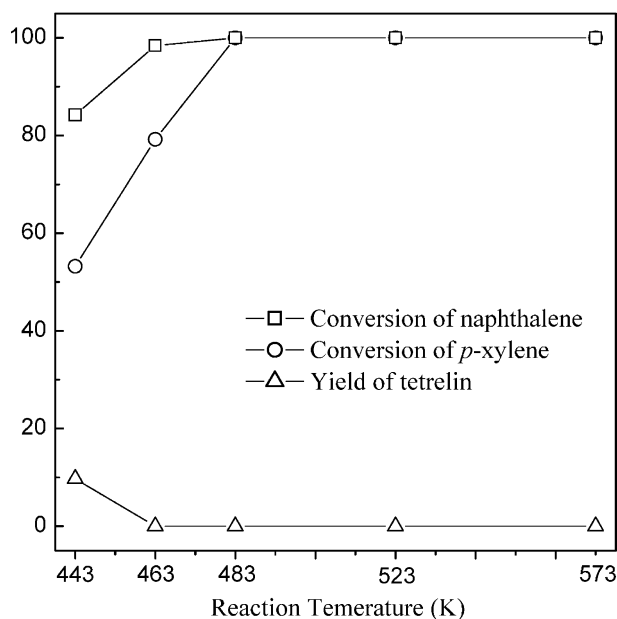


Figure 3. Conversion of *p*-xylene (○) and naphthalene (□) and yield of tetralin (△) at different temperatures.

differences in the π -electron density of the aromatic ring from the inductive effect of the methyl group [18]. The presence of tetralin at 443 K is attributable to the low conversion rate of the naphthalene. Corma [4] has reported that the hydrogenation of the second ring only occurs to a significant extent at very high conversion rates. Furthermore, the tetralin results also show that a sequential path of the hydrogenation of naphthalene is: naphthalene $\rightarrow$ tetralin $\rightarrow$ decalin (*cis* and *trans* form), which is similar to the general reaction scheme proposed for the hydrogenation of naphthalene. The conversion of *p*-xylene and naphthalene reach 100% above 483 K, and this shows that the $\text{Ni}_2\text{Mo}_3\text{N}/\text{MCM41}$ catalyst possesses good deep hydrogenation activity, because it is able to function at low temperatures, thus avoiding any thermodynamic constraints. This is similar to the noble-metal based catalysts. Even at 573 K, the high activity is still maintained, and there was no high molecular weight (HMW) product. This is

in agreement with the absence of strong Brønsted acid sites, which have been claimed to play a key role in ring-opening reactions leading to HMW products [19].

4. Conclusions

Both bulk and MCM41-supported $\text{Ni}_2\text{Mo}_3\text{N}$ catalysts have been prepared and characterized. Their catalytic properties were investigated for the hydrogenation of *p*-xylene and naphthalene, and the results were compared with those obtained using Ni/MCM41 and $\text{Mo}_2\text{N}/\text{MCM41}$ samples having similar metal loadings. The results demonstrate that the incorporation of Ni into the molybdenum nitride in the form of MCM41-supported $\text{Ni}_2\text{Mo}_3\text{N}$ catalyst resulted in a considerable increase in hydrogenation activity. The MCM41-supported $\text{Ni}_2\text{Mo}_3\text{N}$ samples exhibit excellent deep hydrogenation activity under mild conditions ($T = 483$ K, $P = 3.0$ MPa), which is similar to noble-metal based catalysts. Furthermore, these nitride catalysts possess good HDS and HDN activities, which are beyond the capacity of noble-metal based catalysts. Our results demonstrate that MCM41-supported $\text{Ni}_2\text{Mo}_3\text{N}$ catalysts have the potential to be used as good sulfur and nitrogen-resistant catalysts for the deep hydrogenation of aromatics in diesel oil.

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