

A novel Ni₂Mo₃N/MCM41 catalyst for the hydrogenation of aromatics

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Bulk and MCM41-supported Ni₂Mo₃N catalysts were prepared using a temperature-programmed reduction (TPR) method and characterized using XRD, TEM, ICP-AES, and N₂ adsorption analysis techniques. Their catalytic properties were measured for the simultaneous hydrogenation of *p*-xylene and naphthalene and compared with Ni/MCM41 and Mo₂N/MCM41 catalysts having similar metal loadings. The results indicate that the Ni₂Mo₃N/MCM41 catalyst exhibits excellent deep hydrogenation activity under mild condition ($T = 483$ K, $P = 3.0$ MPa), and that it is more active than either Ni/MCM41 or Mo₂N/MCM41 catalyst.

KEY WORDS: Ni₂Mo₃N; Ni₂Mo₃N/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 Ni₂Mo₃N has been used as an active catalyst for hydrosulfurization (HDS) [11] and hydrodenitrogenation

(HDN) [12]. In this work, we report on the use of Ni₂Mo₃N/MCM41 catalyst possessing good deep hydrogenation activity under mild conditions. Both bulk and MCM41-supported Ni₂Mo₃N 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 Ni/MCM41 and Mo₂N/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 Ni₂Mo₃N 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 Ni₂Mo₃N was prepared by dissolving nickel nitrate (Ni(NO₃)₂·6H₂O) and ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) in 15% NH₃·H₂O solution, evaporating to dryness, and calcining at 773 K for 5 h in air. The precursor was converted to Ni₂Mo₃N using a temperature-programmed reduction (TPR) process in flowing NH₃ 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 NH₃, and passivated overnight in flowing 1% O₂/N₂ (v/v) gas to avoid strong bulk oxidation.

The MCM41-supported oxide precursor of the Ni₂Mo₃N/MCM41 catalyst with a theoretical content of 25 wt% Ni₂Mo₃N was prepared by impregnation of precalcined MCM41 (773 K, 5 h, in air) using aqueous solutions of (NH₄)₆Mo₇O₂₄·4H₂O and Ni(NO₃)₆·6H₂O, 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% Ni₂Mo₃N/MCM41 catalyst.

For comparison, Ni/MCM41 and γ-Mo₂N/MCM41 catalysts were also prepared with the same Ni and Mo loading (based on the support) as the Ni₂Mo₃N/MCM41 sample, respectively. The MoO₃/MCM41 and NiO/MCM41 precursors were prepared by impregnation of MCM41 using aqueous solutions of (NH₄)₆Mo₇O₂₄·4H₂O and Ni(NO₃)₆·6H₂O, respectively, followed by airing overnight, drying for 3 h at 393 K, and calcination for 5 h in air. The MoO₃/MCM41 precursor was then nitrated and passivated as described above to yield Mo₂N/MCM41 catalyst. The NiO/MCM41 precursor was pretreated in flowing H₂ at 673 K to get Ni/MCM41 catalyst prior to evaluation.

2.2. Characterization of the catalyst

XRD characterization was conducted using a Rigaku D/max-2500 powder diffractometer employing Cu-Kα 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 H₂ in the temperature range $T = 443$ – 573 K. Prior to evaluation, the catalyst was pretreated under flowing H₂ 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 H₂. The flow rate of H₂ 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 Ni₂Mo₃N samples is similar to that described by others for the preparation of alumina-supported Ni₂Mo₃N [15]. Figure 1 shows XRD patterns of bulk Ni₂Mo₃N, Ni₂Mo₃N/MCM41, the oxide precursor (NiMoO_x/MCM41), and the MCM41 support. The XRD pattern of NiMoO_x/MCM41 indicates that the supported phase consisted of β-NiMoO₄ and MoO₃. The XRD pattern of bulk Ni₂Mo₃N is consistent with that reported by others for phase-pure Ni₂Mo₃N [15, 16]. In addition to peaks associated with the MCM41 support, the XRD pattern of Ni₂Mo₃N/MCM41 shows additional peaks, which are all in good agreement with those of bulk Ni₂Mo₃N. An average crystallite size of 26 nm was calculated for the Ni₂Mo₃N/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 Ni₂Mo₃N.

In figure 2, a TEM micrograph of the Ni₂Mo₃N/MCM41 catalyst shows that Ni₂Mo₃N 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 Ni₂Mo₃N and Ni₂Mo₃N/MCM41 samples. The elemental composition of both the bulk and supported Ni₂Mo₃N

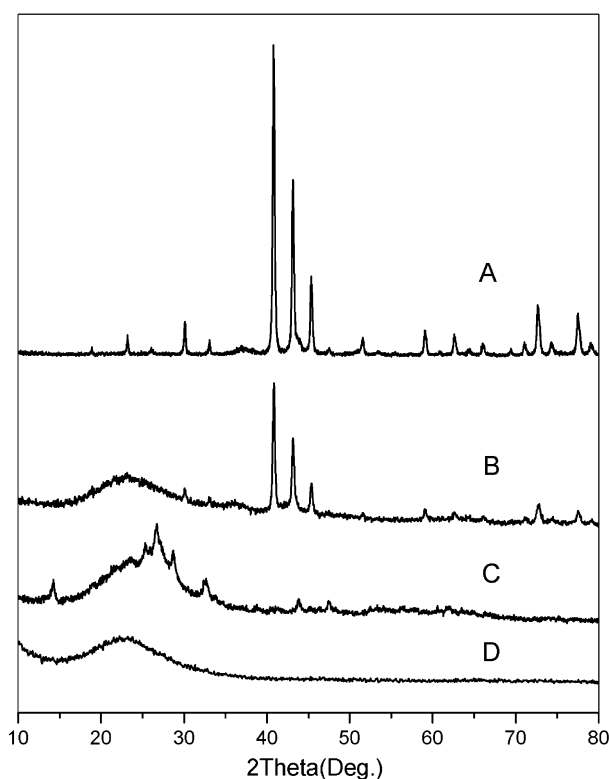


Figure 1. XRD patterns of the samples (A) Ni₂Mo₃N, (B) Ni₂Mo₃N/MCM41, (C) Ni₂Mo₃O_x/MCM41 and (D) MCM41.

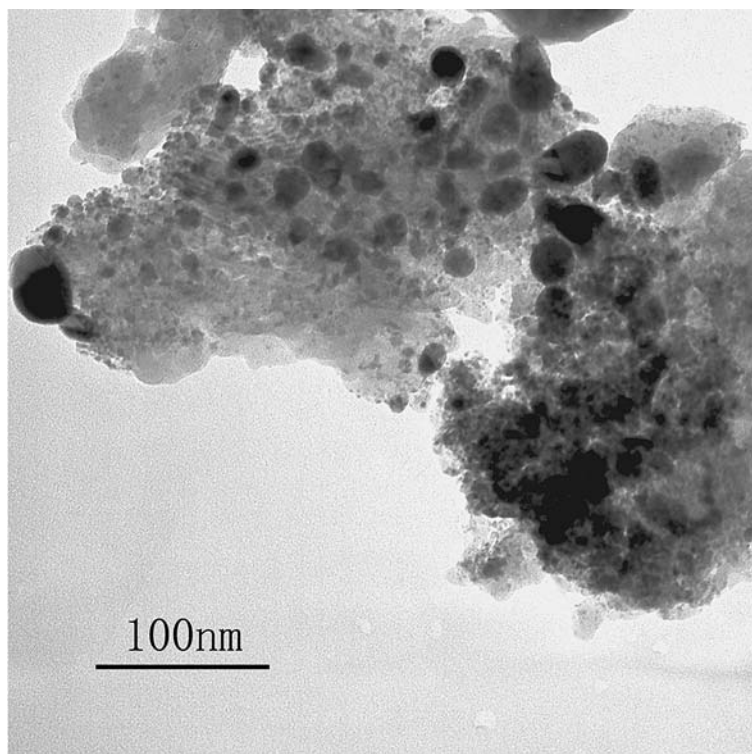


Figure 2. TEM micrograph of the Ni₂Mo₃N/MCM41 catalyst.

were approximately consistent with the theoretical values. The BET surface area of Ni₂Mo₃N/MCM41 was significantly higher than that of unsupported Ni₂Mo₃N.

These results indicate that both the bulk and MCM41-supported Ni₂Mo₃N samples were successfully prepared, and that the supported catalyst possessed a high surface area and good Ni₂Mo₃N dispersion.

Table 2 shows the activities of the bulk and MCM41-supported Ni₂Mo₃N catalysts in *p*-xylene and naphthalene hydrogenation performed under moderate operating conditions ($T = 483$ K, $P = 3.0$ MPa). The bulk Ni₂Mo₃N sample, which had been diluted with MCM41, exhibited a low activity. However, the MCM41-supported Ni₂Mo₃N catalyst, on which the *p*-xylene and naphthalene were completely saturated, was more active than the unsupported Ni₂Mo₃N sample due to the dispersion of Ni₂Mo₃N on the support, as well as the high surface area of the catalyst.

For comparison, a MCM41-supported nickel catalyst and a MCM41-supported γ -Mo₂N 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: Ni₂Mo₃N/MCM41 > Ni/MCM41 > Mo₂N/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 Ni₂Mo₃N catalyst resulted in a considerable increase in hydrogenation activity. This result is very similar to that reported by others, in which Ni₂Mo₃N catalyst was more active than Mo₂N 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 Ni₂Mo₃N is the unique existing species on the support and the better hydrogenation activity of Ni₂Mo₃N catalyst than Ni catalyst probably owes to the special structure of Ni₂Mo₃N, which contains net of nickel atoms, the holes in which are filled by Mo₆N octahedral [17].

The results of catalytic measurements performed at different temperatures for the Ni₂Mo₃N/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 Ni₂Mo₃N catalysts.

Catalyst	S _{BET} (m ² /g)	Elemental composition
Ni ₂ Mo ₃ N	10.61	Ni ₂ Mo _{3.09} N _{0.94}
Ni ₂ Mo ₃ N/MCM41	179.12	Ni ₂ Mo _{2.88} N _{1.06} 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
Mo ₂ N/MCM41	Mo 22.9	483	0	8.2	0
Ni ₂ Mo ₃ N + MCM41 ^c	Ni 9.3 Mo 22.9	483	21.0	37.1	7.5
Ni ₂ Mo ₃ N/MCM41	Ni 9.3 Mo 22.9	483	100	100	0
Ni ₂ Mo ₃ N/MCM41	Ni 9.3 Mo 22.9	463	79.2	98.4	0
Ni ₂ Mo ₃ N/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 Ni₂Mo₃N and MCM41 support, in which the Ni₂Mo₃N content is similar to that of the 25 wt% Ni₂Mo₃N/MCM41 catalyst.

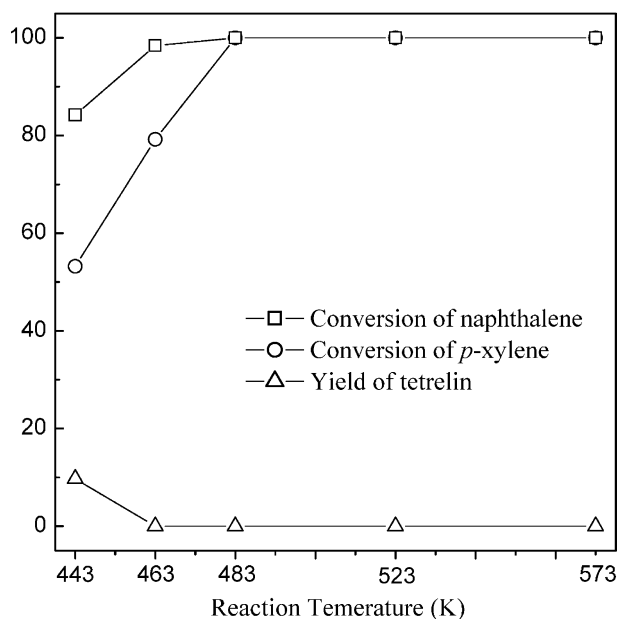


Figure 3. Conversion of *p*-xylene (○) and naphthalene (□) and yield of tetralin (△) at different temperatures.

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 Ni₂Mo₃N/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 Ni₂Mo₃N 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 Mo₂N/MCM41 samples having similar metal loadings. The results demonstrate that the incorporation of Ni into the molybdenum nitride in the form of MCM41-supported Ni₂Mo₃N catalyst resulted in a considerable increase in hydrogenation activity. The MCM41-supported Ni₂Mo₃N 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 Ni₂Mo₃N 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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