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Effect of lanthanum addition on the thiophene hydrodesulfurization activity over Al-MCM-41 supported molybdenum catalysts

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Abstract

A series of Al-MCM-41 modified with 1–7% lanthanum were used as supports to prepare the Mo/La–Al-MCM-41 catalysts containing 10 wt.% molybdenum. The supports and catalysts were characterized with XRD, BET, XPS, TPD, TEM and SEM, and their catalytic activities were tested for thiophene hydrodesulfurization. The La addition did not cause any significant collapse of the structure and morphology of Al-MCM-41 samples, and increased the acidity of Al-MCM-41 samples. The Mo/La–Al-MCM-41 catalysts showed higher thiophene HDS activity than non-modified catalysts. The La-modified catalysts showed an enhanced butene selectivity but a decreased tetrahydrothiophene selectivity, indicating that the La–Al-MCM-41 supports contained a larger amount of acid sites.

Keywords: La addition; Al-MCM-41; Thiophene hydrodesulfurization; Acidity

1. Introduction

There has been a great deal of research and numerous publications on the synthesis, characterization, and properties of the material labeled M41S since Mobil researchers disclosed this surprising material [1,2]. Because of the possibility of its catalytic application, many researchers have tried to introduce transition and nontransition metal ions, such as Co, Zn, Al, Cr, Fe, Ti, V, Mn, Zr, etc., into the silica-based MCM-41 framework and have used them as effective catalysts or supports for various kinds of reactions [3–6].

Al-MCM-41 supported Mo-based catalysts are being widely used as catalysts in a variety of reaction systems and industrial processes [7,8]. Song and Reddy [9] investigated the hydrodesulfurization (HDS) of dibenzothiophene (DBT) over CoMo/Al-MCM-41 at both high and low metal loading. They found that Al-MCM-41 supported catalysts with a high metal loading was substantially more active than its γ-Al_2O_3 supported counterpart in DBT conversion.

In the previous research, several approaches have been tried to increase the HDS activity on the alumina supported Mo-based catalysts, for example use of the additives P [10], B [11], F [12], and W [13], use of increase in the metal loading [14]. To control the acidity of catalysts, modification of Mo-based catalysts with lanthanum has been investigated [15,16]. Moreover, lanthanum oxides are known to increase the dispersion of supported active components and thermal stability of silica [17] or alumina supports [18,19]. However, information on the effect of such lanthanum compounds on HDS over Al-MCM-41 supported Mo-based catalysts is limited. In this work, lanthanum was added into Al-MCM-41 by post-synthesis method, La–Al-MCM-41 supported Mo catalysts were synthesized, and the catalysts were used for thiophene HDS reaction. The effects of lanthanum addition on the catalyst activity and product selectivity were investigated, respectively. Characterizations were made with XRD, BET, NH_3-TPD, XPS, TEM, SEM and elemental analysis.

2. Experimental

2.1. Preparation of Al-MCM-41

Al-MCM-41 materials were prepared according to the procedures reported [20]. Cetyltrimethylammonium chloride (25% CTACl, Aldrich) was dissolved in distilled water. The

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silica source, Ludox HS-40 (DuPont) was added dropwise to the template solution with vigorous stirring at 70 °C in a water bath. The aluminum source, pseudoboehmite (78.2% Al_2O_3, Vista), was added into the hydrogel. The molar composition of mixture gel was 1.0 CTACl:1.0 Na_2O:4.0 SiO_2:400 H_2O, and the Si/Al ratio was taken to be 20. The pH of mixture was maintained at 10 with 30 wt.% acetic acid after heating at 100 °C for 2 days, and this pH adjustment was repeated twice more. The product was filtered, washed, dried in air and calcined at 550 °C for 10 h.

2.2. Preparation of La–Al-MCM-41

La–Al-MCM-41-Post was prepared by introducing lanthanum to Al-MCM-41-Pre by post-incorporation method. Al-MCM-41-Pre was heated to remove water in a vacuum oven at 100 °C for 10 h. Lanthanum nitrate hexahydrate (99.99%, Aldrich) in absolute ethanol (99.8%, Merck) was added to Al-MCM-41-Pre in a propylene bottle and the mixture was stirred vigorously for 30 min. The mixture was filtered, washed and dried at 110 °C in air, and calcined at 550 °C for 10 h. The lanthanum contents were 1, 5 and 7 wt.%, respectively.

2.3. Molybdenum impregnation

The 10 wt.% molybdenum was loaded with ammonium-heptamolybdate (99.9%, Aldrich) by incipient wetness method. All the catalysts were dried at 70 °C in vacuum and calcined at 500 °C for 5 h.

2.4. Characterization

The surface area and pore size distribution of the supports were measured by the nitrogen adsorption–desorption method (ASAP 2000, Micromeritics).

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer with Cu Kα radiation at 40 kV and 45 mA between 1.2° and 10° (2θ) with a scanning rate of 1°/min.

The acidic property of samples was analyzed by TPD (temperature programmed desorption) of chemisorbed ammonia. A 0.02 g sample was placed in a quartz tubular reactor and pretreated in a helium flow, heated to 500 °C with 10 °C/min, and remained at 500 °C for 2 h. The samples were cooled to 100 °C and ammonia pulse was injected. After physisorbed ammonia was purged with helium, TPD was carried out.

The sample was dissolved in ethanol and became colloid in the ethanol. The powders in the colloidal solution were deposited on a grid with a holy carbon copper film. After drying the compounds were transferred to a PHILIPS-F20 instrument with 160 kV of acceleration voltage for transmission electron microscopy (TEM) test.

The SEM micrographs of the calcined samples were obtained in a field emission SEM XL30S-FEG PHILIPS. The samples were deposited on a sample holder with an adhesive carbon foil and sputtered with gold.

X-ray photoelectron spectra (XPS) were obtained using a VG ESCA 2000 spectrograph with C radiation (9 kV, 18.5 mA). The binding energy (BE) of La $3d_{5/2}$ was corrected using the 103.3 eV signal of Si $2p_{3/2}$ in the same sample as the standard. The sensitivity factors used for the calculation of composition are 7.708 and 0.283 for La and Si, respectively.

2.5. Thiophene hydrodesulfurization

Thiophene HDS reaction was carried out at 400 °C in a stainless steel microflow reactor operated at 20 atm. The liquid thiophene flow rate was 0.035 ml/min, the mole ratio of hydrogen to thiophene was 15. Before starting the reaction, each catalyst was sulfided in situ at 400 °C for 2 h with a flow of H_2S (10 vol.%)/H_2 mixture at 30 ml/min. The steady state was achieved after 1 h of run time. Reaction products were analyzed by using a gas chromatography equipped with TCD and the OV-101 packed column.

3. Results and discussion

After calcinations of Al-MCM-41 samples and La–Al-MCM-41 samples with different lanthanum contents, their XRD spectra were obtained to confirm the hexagonal structure of MCM-41-like and the results are shown in Fig. 1. The well-defined MCM-41 XRD patterns may be indexed on the basis of four Bragg peaks [21], a prominent peak for $h\,k\,l$ = 1 0 0 as well as weaker peaks for $h\,k\,l$ = 1 1 0, 2 0 0 and 2 1 0, which can be distinguished in hexagonal lattice symmetry, characteristic of MCM-41 structure. As shown in Fig. 1, these four characteristic peaks were observed in the all of the four samples, which were similar to those of MCM-41. The XRD reflections characteristic of a hexagonally ordered structure were preserved after the Al-incorporated MCM-41 and even La-modified Al-MCM-41 materials, suggesting that the addition of ions did not result in a major collapse of the sample structure.

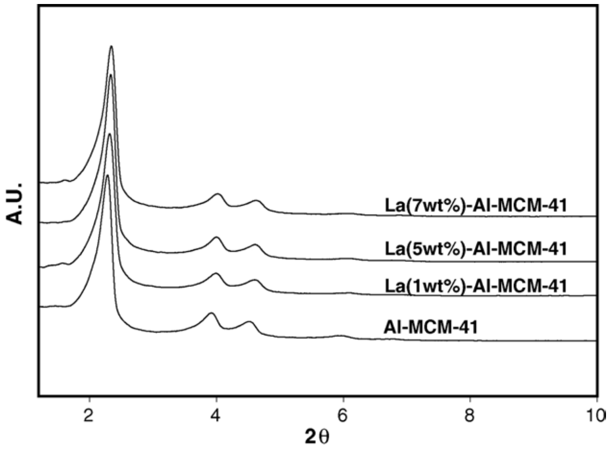


Fig. 1. X-ray diffraction patterns of calcined Al-MCM-41 and La-modified Al-MCM-41 samples.

Table 1
Results of $d_{1\,0\,0}$ spacing, unit cell parameter (α_0), pore diameter (d_p), pore volume (V_p) and BET surface area (S_{BET}) of M′–M-MCM-41 (M′ = La and M = Al) samples

Sample	La (wt.%)	$d_{1\,0\,0}$ (Å)	α_0 (Å)	d_p (Å)	V_p (cm^3/g)	PWT[a] (Å)	S_{BET} (m^2/g)
Al-MCM-41	0	38.72	44.70	35	0.75	9.7	946
La–Al-MCM-41	1	38.05	43.94	34	0.78	9.94	913
La–Al-MCM-41	5	38.38	44.32	34	0.82	10.32	961
La–Al-MCM-41	7	38.55	44.51	34	0.84	10.51	985

[a] PWT: pore wall thickness = $\alpha_0 - d_p$.

Table 2
Binding energies of Si 2p$_{3/2}$, Al 2p$_{3/2}$ and La 3d$_{5/2}$ electrons and La/Si ratios of the samples at the external surface (from XPS) and in the bulk (from elemental analysis)

Sample	La (wt.%)	Si 2p$_{3/2}$ (eV)	Al 2p$_{3/2}$ (eV)	La 3d$_{5/2}$ (eV)	La/Si$_{surf}$	La/Si$_{bulk}$
Al-MCM-41	0	111.8	83.4	–	–	–
La–Al-MCM-41	1	111.9	83.7	839.4	0.646	0.00649
La–Al-MCM-41	5	112.1	83.8	839.6	0.651	0.0332
La–Al-MCM-41	7	112.3	83.8	839.8	0.664	0.0471

The $d_{1\,0\,0}$ values are given in Table 1 along with the corresponding unit cell parameter (α_0) of different samples, calculated from the peak with $h\,k\,l = 1\,0\,0$ using the equation $\alpha_0 = 2d_{1\,0\,0}/\sqrt{3}$. There is nearly no change observed in the unit cell parameters and pore diameters of all the La-modified Al-MCM-41 samples relative to that of Al-MCM-41 sample.

It has been also observed that the BET surface area, pore volume and pore diameter changed little with the La-content (Table 1).

Even at the lowest La-content the sample La–Al-MCM-41 still exhibited very strong signals of La 3d$_{5/2}$ electrons with binding energies of 839.4 eV. A second signal around 863.7 eV appears in the XPS spectra of the sample with strong intensity to stand out from the background, indicating that the lanthanum units responsible are hosted on the external surface of La–Al-MCM-41 samples.

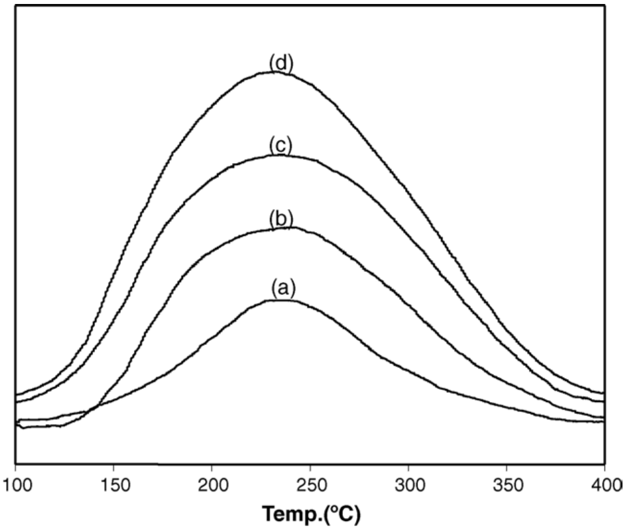


Fig. 2. NH$_3$-TPD spectra of (a) Al-MCM-41 (Si/Al = 20), and (b–d) La–Al-MCM-41; (b) 1 wt.% La, (c) 5 wt.% La, (d) 7 wt.% La.

Since all the La/Si ratios found by XPS are much higher than those determined by elemental analysis of the bulk (Table 2), it can be stated that the external surface of all lanthanum-containing Al-MCM-41 is full of lanthanum ions. Major amounts of lanthanum ions are dispersed on the surface of the La–Al-MCM-41 samples.

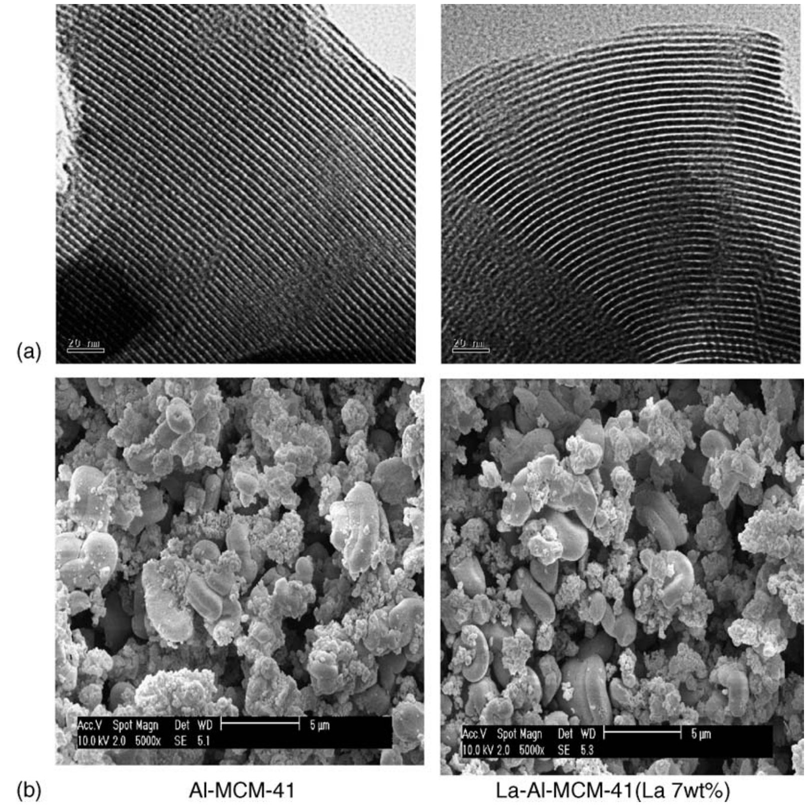
The acidic properties of synthesized Al-MCM-41 and series of La–Al-MCM-41 samples were investigated by ammonia TPD. Fig. 2 shows the profiles of ammonia TPD of samples. It is very obvious that the addition of La increased the acidities of Al-MCM-41 samples.

Fig. 3 shows the TEM (Transmission Electron Microscopy) and SEM (Scanning Electron Microscopy) images of Al-MCM-41 and La–Al-MCM-41 (La 7 wt.%). From Fig. 3, it is found that Al-MCM-41 and La–Al-MCM-41 (La 7 wt.%) have almost same morphology and pore channel structure. It indicates that the introduction of La affect little on the structure of Al-MCM-41, which is consistent with XRD results.

It was found that the dispersion of molybdenum on the La–Al-MCM-41 with different La loadings was almost the same as measured by CO chemisorption.

The hydrodesulfurization of thiophene was carried out using different samples with a same active metal Mo-content, as shown in Fig. 4. The Mo/La–Al-MCM-41 catalysts showed higher conversion than the Al-MCM-41 counterpart, and the activity was improved with lanthanum contents. With time on stream all of the catalysts showed similar tendency in activity from start of reaction until 7 h reaction. But the activity of Mo/La–Al-MCM-41 with higher La amounts (7 wt.%) decreased rapidly after 5 h. The higher acidity of this catalyst resulted in the higher amount of coke deposit during the reaction.

Fig. 5 shows the effect of La loading on the product selectivity for thiophene HDS. In a HDS reaction of thiophene,



Al-MCM-41 La-Al-MCM-41(La 7wt%)

Fig. 3. TEM (a) and SEM (b) images of Al-MCM-41 and La–Al-MCM-41 (La 7 wt.%).

the major product is butene due to hydrogenolysis and the by-product is THT (tetrahydrothiophene) due to hydrogenation without desulfurization. This indicates that La-promoted Mo/Al-MCM-41 catalysts slightly enhanced the HDS reaction through the desulfurization pathway, attributed to a larger amount of acid sites on the La–Al-MCM-41 supports.

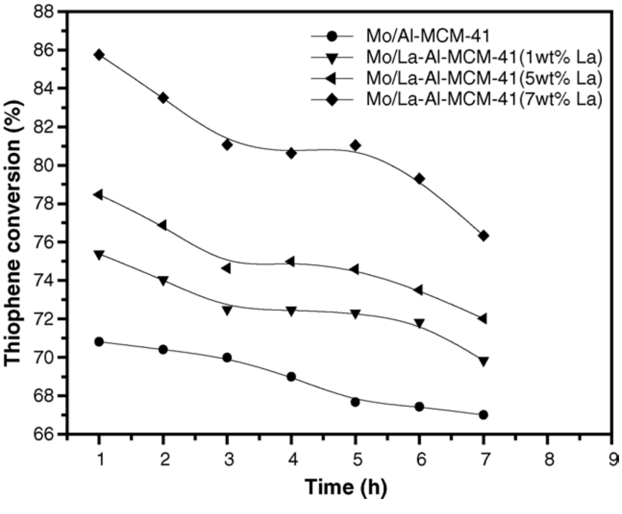


Fig. 4. HDS activity over supported Mo catalysts with time on stream (reaction temperature: 673 K, reaction time: 8 h, H_2/thiophene = 15, W/F = 5.71 gcat - min/cc thiophene).

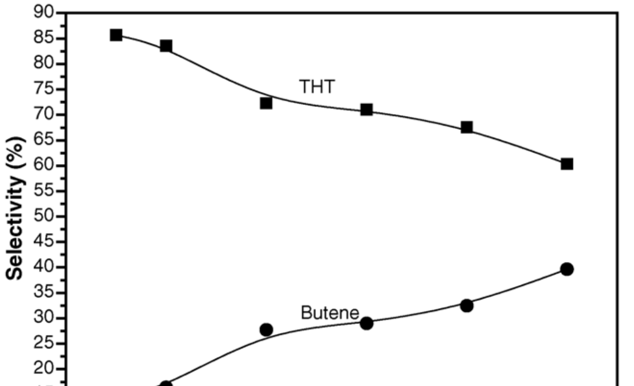


Fig. 5. Variation of product selectivity as a function of La loading: (reaction temperature: 673 K, reaction time: 8 h, H_2/thiophene = 15, W/F = 5.71 gcat - min/cc thiophene, reaction time: 1 h).

4. Conclusion

A series of La-modified Al-MCM-41 mesoporous materials with various compositions were prepared and characterized with XRD, N_2 sorption, XPS, TPD, TEM and SEM. The La addition did not result in any appreciable collapse of the structure and morphology of Al-MCM-41 samples. The acidities of Al-MCM-41 sample were increased by La addition.

La-modified Mo/Al-MCM-41 catalysts showed higher activity for thiophene HDS than the non-modified counterparts due to the improved acidity of modified supports. A larger amount of acid sites on the La–Al-MCM-41 supports was also confirmed by the different selectivity between THT and butene in thiophene HDS.

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