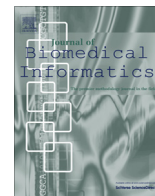




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Effect of MoO₃ on the heat resistant performances of nickel based MCM-41 methanation catalysts

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HIGHLIGHTS

- Several Ni–Mo based MCM-41 catalysts were prepared by the impregnation method.
- The Ni–Mo catalysts showed excellent performances of resistance sintering.
- The addition of MoO₃ can enhance the interaction between the nickel and the support.

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ABSTRACT

Several Ni–Mo based catalysts with Mo content from 1 wt% to 7 wt% were prepared by the impregnation method with MCM-41 as the support. The effect of Mo content on the activity of the catalyst was investigated for syngas methanation in a fixed-bed reactor. The addition of MoO₃ could obviously improve catalytic activity of Ni/M catalyst at low temperature of 250 °C with the CO conversion and the CH₄ selectivity from about 20%, 16% to 100%, about 80%, respectively. Ni–3%Mo/M catalyst showed the best activity with a CO conversion of 100% and a CH₄ selectivity of 94% at 350 °C under 1.0 MPa and 12000 ml/g/h with a 3:1 molar ratio of H₂ to CO. Compared with Ni/M catalyst, Ni–Mo/M catalysts showed higher resistance to sintering and no decrease in the catalytic activity after calcination at 700 °C for 2 h. In the 100 h stability test under atmospheric pressure, the CO conversion and the CH₄ selectivity obtained on Ni–3%Mo/M catalyst maintained at about 100% and 89%, respectively, suggesting an excellent catalytic stability of this catalyst. The catalysts were characterized by N₂ adsorption–desorption, CO chemisorptions, TEM, SEM-EDS, ICP, XRD, H₂-TPR and XPS, and the results showed that electron transfer from MoO₃ to metal nickel was the main cause of activity improvement of Ni–Mo/M catalysts at low reaction temperature of 250 °C. The addition of MoO₃ could obviously improve the heat resistant performance of Ni/M catalyst. The results of TPR, SEM-EDS and XRD showed that the addition of MoO₃ could enhance the interaction between metal nickel and the support in the way of Ni–Mo alloy, which inhibited the catalyst sintering.

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1. Introduction

As a high efficient and clean energy, substitute natural gas (SNG) has attracted increasing attention due to continuous rising prices and exhaustion of natural gas [1]. Generally, SNG is produced via gasification of coal [2] and biomass [3], which produces syngas (the mixture of H₂ and CO), followed by subsequent CO methanation process (CO + 3H₂ → CH₄ + H₂O; ΔH_{298K} = –206.1 KJ/mol), which is a highly exothermic and thermodynamically feasible reaction. Since some metals such as Ni, Ru, Fe and Co, were discovered by Sabatier and Senderens that they could catalyze the methanation reaction in 1902 [4], many methanation catalysts

have been developed. However, Ni based catalysts are still the most favorable choice for the production of SNG due to its relatively high catalytic activity and suitable price [5]. But the syngas methanation reaction is highly exothermic, which easily leads to sintering of active metal and/or the support [6]. The support can significantly affect the dispersion of the active metal and the stability of the catalyst. Thus, the choice of a suitable support is important for the preparation of the catalyst.

Since the invention of MCM-41 mesoporous molecular sieves by the Mobil company, transition metal supported MCM-41 catalysts have been extensively studied due to excellent properties, such as high specific surface area, regular pore structure of nanometer size and adjustable heteroatom content [7]. The nickel based MCM-41 catalyst with high metal loading and good dispersion of active metal could be prepared by the incipient wetness impregnation method with a nickel precursor solution [8]. Wojcieszak et al. [9]

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reported that the nickel based MCM-41 catalyst showed good activity in the hydrogenation of benzene, which prepared via a wet impregnation method. In our previous work [10], the nickel based MCM-41 catalyst showed good activity in the production of SNG via syngas methanation, but poor thermal stability, which was easily sintered after high temperature calcination. Therefore, it is still a challenge to develop methanation catalysts with both high activity and good thermal stability against sintering.

In recent years, bimetallic catalysts have attracted worldwide attention. The interaction between the two metals may provide pathways to higher activity and better anti-sintering performance [11,12]. One explanation for the synergetic interaction between the two metals is physical promotion provided by one of the metals. The other one is electron transfer from one of the metal (or metal oxide) sites to the second metal [13]. As an important catalytic promoter, Mo can improve the dispersion of active metal and the activity of the catalyst in many situations. The addition of Mo could significantly promote the activity, the sulfur resistance and the anti-sintering performance of Ni-based catalyst [14,15]. The sulfur resistance of Mo is a potential advantage for industrial application due to copious amounts of sulfur in the syngas used in commercial operation [16].

The Ni–Mo bimetallic supported catalysts with Ni as the main active component and Mo as the promoter [14,15] were widely investigated. The accession of Mo could promote the reduction of NiO, which improved catalytic activity of the nickel catalyst. For bimetallic catalysts, the synergetic interaction between the two metals has been explained either by physical promotion provided by Mo species or by electron transfer from MoO_x sites to the other metal [17–19]. The coverage of active metal sites by MoO_x species at high metal loadings also needs to be taken into account as a third interaction mechanism [17,19,20]. However, the effect of Mo on the heat resistant performance on the nickel based MCM-41 catalyst, which was used to produce SNG via syngas methanation, was scarcely investigated.

In this paper, several Ni–Mo catalysts with Mo content from 1 to 7 wt% were prepared via an impregnation method by adding MoO₃ into the nickel based MCM-41 catalysts and the catalytic behavior of the catalyst for the production of SNG via syngas methanation with a 3:1 molar ratio of H₂ to CO was investigated and discussed. The effect of Mo on the structure and catalytic activity of the catalyst was studied by various characterization means, such as X-ray diffraction (XRD), nitrogen adsorption–desorption measurements, inductive coupled plasma emission spectrometer (ICP), CO chemisorptions, transmission electron microscopy (TEM), scanning electron microscopy–energy dispersive spectrometer (SEM-EDS), H₂ temperature-program reduction (H₂-TPR) and X-ray photoelectron spectra (XPS).

2. Experimental

2.1. Catalyst preparation

2.2.1. MCM-41 preparation

MCM-41 materials were synthesized to the procedure of Liu et al. [21]. Cetyltrimethyl ammonium bromide (CTABr, C₁₆H₃₃(CH₃)₃NBr, 99% pure, Merck) and tetraethylorthosilicate (TEOS, C₈H₂₀O₄Si, 99% pure, Merck) were used as the surfactant and the silica source, respectively. The surfactant (CTABr) was dissolved in the deionized water with vigorously stirring at 40 °C. Then the silica source (TEOS) was slowly added into the solution and the pH value of the solution was adjusted to 11. The resulting gel with a molar composition of TEOS:CTABr:NaOH:H₂O of 1:0.12:0.2:100, was aged at room temperature for 2 h under vigorously stirring, transferred into an autoclave and crystallized statically at 120 °C

for 24 h. After being cooled to room temperature, the resulting solid was centrifuged, washed with deionized water and dried at 100 °C overnight. The MCM-41 support was obtained by calcination in air (6 h at 550 °C, heating rate = 1 °C min⁻¹) to remove the template.

2.2.2. Ni–Mo/MCM-41 catalyst preparation

The Mo based MCM-41 catalysts with different Mo content (1° wt%, 3° wt%, 5° wt%, 7° wt%) were prepared by the incipient wetness impregnation with (NH₄)₆Mo₇O₂₄·4H₂O (99% pure, Merck) as the molybdenum precursor and MCM-41 as the support under vacuum overnight [22]. After impregnation, the samples were dried at 120 °C for 12 h and calcined in air at 550 °C for 4 h (heating rate = 1 °C min⁻¹). The Ni–Mo based MCM-41 catalysts were prepared by the same procedure with Ni(NO₃)₂·6H₂O (99% pure, Merck) as the nickel precursor and the Mo based MCM-41 catalyst as the support and calcined in air at 550 °C for 4 h (heating rate = 1 °C min⁻¹). The nickel content of all the catalysts was 10 wt%. The catalysts were designated as Ni–xMo/M, in which x represented the molybdenum weight content. For comparison, the nickel based MCM-41 catalyst with 10 wt% nickel content was also prepared by the same procedure and MCM-41 as the support. And the catalyst was designated as Ni/M.

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2.2. Evaluation of catalyst performance

The evaluation of Ni/M and Ni–Mo/M catalysts for syngas methanation was carried out in a continuous flow fixed-bed reactor with a stainless steel tube (length: 40 cm, inner diameter: 10 mm). 500 mg catalyst (sieve fraction 100 mesh) was filled in the tubular reactor and reduced in situ at 500 °C (except for special instruction) for 2 h in a continuous flow of pure H₂ (50 ml/min). Ultimately, it was tested over a temperature range of 250–650 °C and a pressure range of atmospheric pressure to 1.0 MPa. The mixed reactant gas consisted of H₂/CO/N₂ with a molar ratio of 3:1:1, in which N₂ was added as an internal standard gas for GC analysis. The weight space velocity was selected to be 12000 ml/g/h. The outlet gases were cooled by a cold water trap and analyzed on-line by the gas chromatograph (Techcomp, GC7890T) with a TDX-01 column using the thermal conductivity detector. To calculate the CO conversion and the CH₄ selectivity, the outlet gases were collected after half an hour of steady-state operation at each temperature. The calculation formulas were described as follows:

$$\text{CO conversion} : X_{\text{CO}}(\%) = (\text{moles of CO reacted}) \times 100 / (\text{moles of CO supplied}) \quad (1)$$

$$\text{CH}_4 \text{ selectivity} : S_{\text{CH}_4}(\%) = (\text{moles of CH}_4 \text{ prepared}) \times 100 / (\text{moles of CO reacted}) \quad (2)$$

$$\text{CH}_4 \text{ yield} : Y_{\text{CH}_4}(\%) = X_{\text{CO}} \times S_{\text{CH}_4} / 100 \quad (3)$$

2.3. Characterization

The porous structure of the catalyst was investigated using an ASAP 2020 (Micromeritics) instrument and the pore size distribution was calculated by the Barret-Joyner-Hallender (BJH) method using the desorption branch. XRD patterns were recorded on a Rigaku D-MAX2500-PC using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) at 50 kV and 100 mA. The metal compositions of the samples were analyzed by ICP. H₂-TPR experiment was carried out on a TP-

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