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Silica gel- and MCM-41-supported MoS_2 catalysts for HDS reactions

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MCM-41- and silica gel-supported MoS_2 catalysts were prepared. MCM-41 was synthesized and impregnated with precursor, then activated to obtain the active phase. The sol–gel method was used for providing the SiO_2 support as well as for including the catalyst precursors in one single step of preparation. Such catalysts have applications particularly in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) processes. A comparison of the activities of the catalysts was made. The catalytic activity results showed the method of preparation used in this study was successful in producing very efficient catalysts for the HDS of dibenzothiophene (DBT).

A higher selectivity for direct C–S bond cleavage was observed for the MoS_2 catalyst supported on SiO_2 by the sol–gel method. X-ray diffraction studies showed that the catalysts were poorly crystallized with a very weak intensity of the (002) line of 2H-MoS_2.

KEY WORDS: MoS_2; catalysts; MCM-41; sol–gel; HDS reaction.

1. Introduction

It has been a challenge to process petroleum residues because of the large sizes and structural complexity of their molecules, high boiling point range, and high contents of sulfur, nitrogen and metals. At the same time, it has become clear that crude oils in many existing reserves are heavier and have higher sulfur contents than those already recovered [1]. As a consequence, there is a growing interest in research and development for converting heavy feedstocks (petroleum residues and heavy oils) into lower-boiling products of high quality with a low sulfur content. Therefore, hydrodesulfurization (HDS) of heavy petroleum feedstocks to produce distillate fuels, particularly diesel fuels and gasoline (either directly or via subsequent fluid catalytic cracking), has become an important research subject.

Earlier research has shown that certain sulfur compounds are easier to convert and the reactivities of the one- to three-ring sulfur compounds decrease in the order thiophenes > benzothiophenes > dibenzothiophenes [2,3]. It was also shown that under mild conditions, conventional catalysts are not effective for converting bulky organosulfur compounds, particularly 4-methyl and 4,6-dimethyl substituted benzothiophenes [3,4].

Hence, it has become necessary to explore catalysts for converting bulky sulfur compounds in order to produce environmentally friendly transportation fuels.

Recently, Mobil researchers have produced MCM-41-type mesoporous molecular sieves possessing a hexagonal array of uniform mesopores [5,6] and this material has been studied as a support for different catalysts [7–9]. The pure silica MCM-41 can present a surface area higher than $900\,m^2/g$ with a narrow pore size distribution, which means the diameter can be tuned according to the application [10]. The tailoring of the surface with catalyst and promoters gives a promising catalyst due to the combination of high surface area, controlled pore size and the low activity of the surface of the support [11].

On the other hand, the ease and versatility of the sol–gel method makes it suitable for producing thin films [12,13], powders with definite porosity [14–17], low-density materials [18], and articles with appropriate geometry [19,20]. There have been studies of sol–gel SiO_2 concerned with the use of this material as a matrix embedding finely distributed transition metals as ionic species or metallic and metal oxide particles. Research includes the use of sol–gel SiO_2–metal composites for sensors [21,22], optical waveguides [23,24], electrochromic materials [21,25–27] and, in general, for the multi-faceted interests of the electronic industry.

The inclusion of VIIIB and IB elements in sol–gel SiO_2 immediately led to applications in heterogeneous catalysis. The sol–gel method ensures the availability of SiO_2 with surface features suitable for optimal metal

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dispersion [28,29] and provides extended internal porosity, such as in aero-gel SiO_2 [30,31], to allow easy reactant diffusion inside the bulk. While the variety of strategies for sol–gel SiO_2 preparation accentuates the prospective exploitations of this material, the appropriate SiO_2 reactivity may be crucial for particular alloy-metal phase dispersions [32,33], for promoting photocatalytic activity [34], and for catalyst selectivity.

In this work, a new, easy and cost-effective approach for preparing an active MoS_2 catalyst embedded in SiO_2 matrix prepared by the sol–gel method and with the MCM-41 structure is introduced.

2. Experimental

The MoS_2-supported catalysts were prepared using two different methods: by incipient impregnation of the MoS_2 precursor onto the MCM-41 support and by the sol–gel technique.

2.1. MoS_2 supported in MCM-41

MCM-41 was synthesized according to the method described by Cai *et al.* [35]. An amount of 4.0 g of the surfactant tetradecyl trimethyl ammonium bromide (TDTAB) was added to 950 ml of ammonium hydroxide (10.8 wt% solution) and was maintained under stirring and moderate heating until total dissolution of TDTAB was observed. An amount of 20 ml of tetraethylorthosilicate (TEOS) was added to the solution and the slurry obtained was maintained under stirring at room temperature for 20 h. The suspension obtained was filtered and washed with distilled water. The solids were dried at 60 °C for 1 h, and then calcined in air at 550 °C for 4 h.

The impregnation process was carried out in two steps: precursor (ammonium thiomolybdate ($(NH_4)_2MoS_4$)) was dissolved in water, and then the solution was added to the MCM-41 support, a process known as incipient wetness impregnation. Under these conditions the amount of catalyst (MoS_2) represents 23% of the weight of the final product.

The drying process was then carried out at 80 °C for 2 h, followed by pellet formation. The pellets were crushed and sieved in order to obtain a fine and uniform powder.

Activation of the impregnated precursor was made *in situ* at 350 °C before the catalytic activity measurement. The whole process is summarized in figure 1.

2.2. MoS_2 supported in silica gel

An amount of 7 ml of tetraethylorthosilicate (TEOS) (Aldrich, reactive grade) was mixed with 11 ml of ethanol (Baker, reactive grade). Then 0.35 g of $(NH_4)_2MoS_4$ were dissolved in 5.25 ml of distilled water and added to the former solution under vigorous stirring; the molar composition of the system TEOS : water : ethanol was 1 : 10.5 : 6. Then 1.1 ml of glycerin were added and finally 2 ml of HF (Baker) at 45 wt% was added to catalyze the sol–gel reaction. The amount of catalyst (MoS_2) represents 10% of the weight of the final product. Under these conditions gelation occurred within 2 min. The drying process was carried out at room temperature for three days.

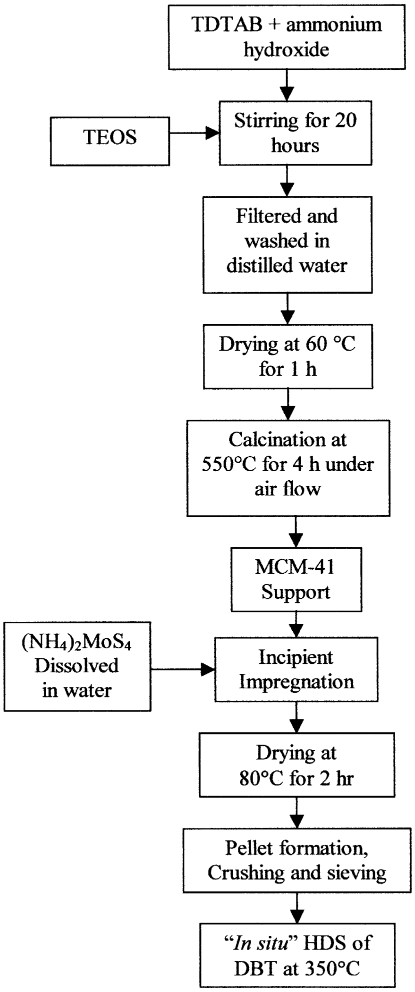

Figure 1. Block diagram showing the process followed to make MoS_2 catalyst supported in MCM-41.

The precursor to MoS_2 conversion was made *ex situ* in a tube furnace at 350 °C for 2 h. The heating rate used to achieve this temperature was 5 °C/min. A gas mixture of $H_2/10\%$ H_2S with a flow rate of 0.75 ml/min was used to provide a sulfiding environment and prevent oxidation. Figure 2 shows the entire process.

2.3. Catalytic activity

The HDS of dibenzothiophene (DBT) was carried out in a Parr model 4522 high-pressure bath reactor. An amount of 1 g of catalyst of each sample along with the dissolved reagent (5 vol% of DBT in decaline) was

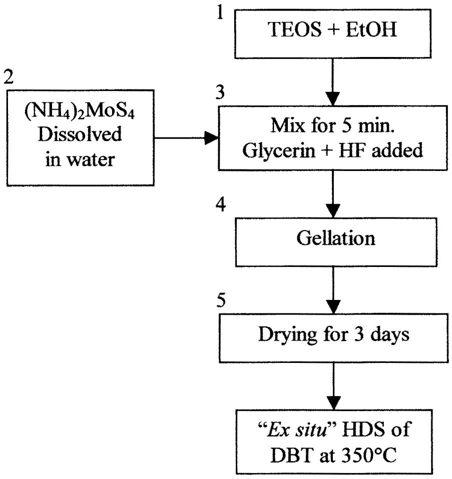

Figure 2. Block diagram showing the process followed to make MoS_2 catalyst supported in silica gels. Steps 1–5 at room temperature.

placed in the reactor, then pressurized to 3.1 MPa with hydrogen and heated to 623 K at a rate of 10 K/min. After the working temperature was reached, sampling for chromatographic analysis was performed during the course of each run to determine conversion versus time dependence. Reaction runs averaged about 5 h. The reaction products were analyzed using a Perkin Elmer model Auto-system chromatograph with a 6 ft long, $\frac{1}{8}$ in packed column containing OV-3 as separating phase.

The selectivity for a given product was calculated as the weight percentage of the product in the product mixture. There are three main products from the HDS reaction of DBT: biphenyl (BIP), phenylcyclohexane (PCH) and dicyclohexane (DCH). In this case, the variation of selectivity for the main reaction products (BIP, PCH and DCH) was analyzed for MoS_2 catalysts subjected to changes in preparation. The mean standard deviation for catalytic measurements was ±2.5%.

2.4. Catalyst characterization

Characterization of catalysts was performed on samples obtained before and after the catalytic tests. For those after the catalytic test, samples were separated from the reaction mixture by filtration, then washed with isopropanol to remove residual hydrocarbons and dried at room temperature before analysis.

Specific surface area determination was carried out using a Quantachome model AUTOSORB-1, by nitrogen adsorption at 77 K using the BET isotherm. Samples

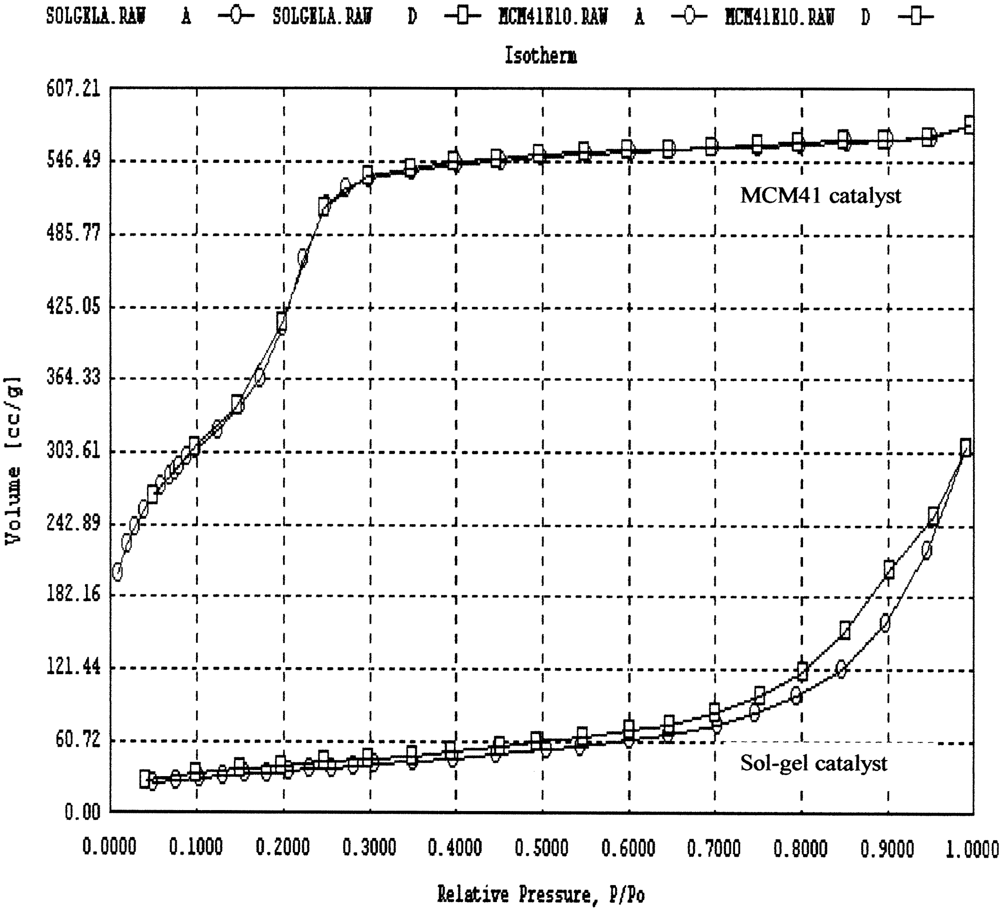

Figure 3. Isotherms of N_2 adsorption/desorption for sol–gel and MCM-41 supports.

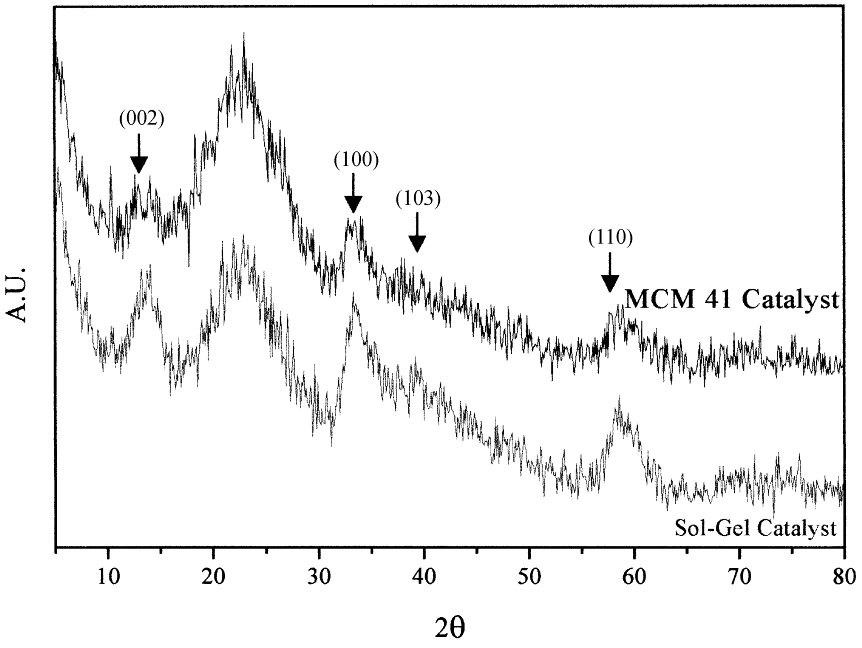

Figure 4. XRD patterns for catalysts after reaction test.

were degassed under flowing argon at 473 K for 2 h before nitrogen adsorption. The mean standard deviation for surface area measurements was about 2%.

X-ray diffraction (XRD) studies were carried out using a Phillips X Pert MPD diffractometer, equipped with a curved graphite monochromator, using CuKα radiation.

3. Results and discussion

Isotherms of N_2 adsorption/desorption for sol–gel and MCM-41-supported catalysts are shown in figure 3. As can be observed, the support prepared by the sol–gel method has a low surface area of approximately 130 m^2/g, and the dominant pores are macropores. For the MCM-41 structure, however, the surface area is 950 m^2/g, and it contains only well-defined mesopores of 25 Å.

X-ray powder diffractograms are shown in figure 4. As can be seen, both samples show diffraction peaks that are associated with the different crystalline planes of MoS_2. These peaks are less intense for the MCM-41 sample. In particular, the (002) reflection is less intense for the MCM-41 sample than for the silica gel one; this agrees with the activity results and means that there is greater hydrogenation in the case of the MCM-41 sample and direct hydrodesulfurization in the case of

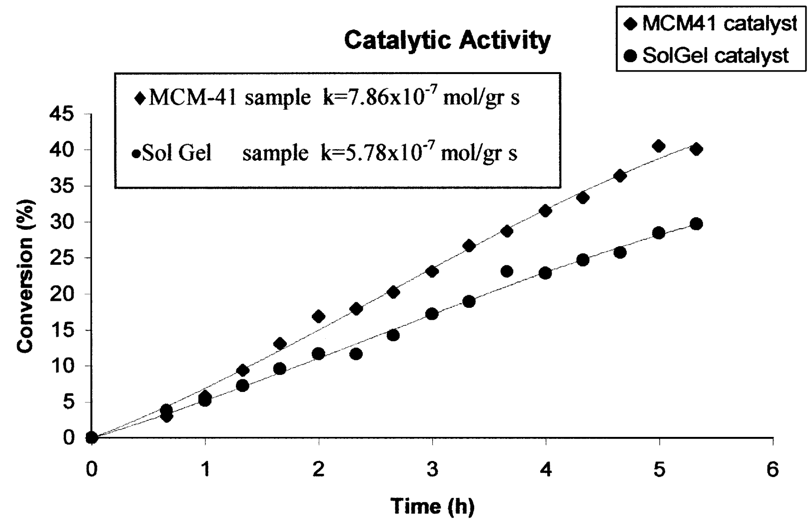

Figure 5. Catalytic activity for MCM-41-supported (◆) and silica gel-supported (●) MoS_2 catalysts.

Table 1
Data for HDY/HDS ratio calculation after 5 h of reaction time

MoS_2 from:	DCH (%)	PCH (%)	BIP (%)	HYD/HDS
MCM-41	3.7	32.3	64.0	0.56
Sol–gel	2.4	24.6	73.0	0.37

the silica gel sample, as can be seen in table 1. The broad peak around 22° corresponds to silica from silica gel and MCM-41.

Figure 5 shows the conversion rate and initial HDS rate constants for MCM-41- and silica gel-supported catalysts. As can be observed in both cases the k values are of the same order of magnitude: $k = 7.86 \times 10^{-7}$ mol/g s for the MCM-41 sample and $k = 5.78 \times 10^{-7}$ mol/g s for the sol–gel one. Moreover, in both cases the activity results are comparable with that obtained for unsupported MoS_2 catalysts that are similarly prepared ($k = 4 \times 10^{-7}$ mol/g s). Table 1 summarizes the data for the HDY/HDS ratio calculation after 5 h of reaction time. The HDY/HDS ratio was calculated using $(\mathrm{DCH} + \mathrm{PCH})/\mathrm{BIP}$.

In spite of the lower surface area shown by the silica gel-supported catalyst the results for the initial HDS rate constants are of the same order of magnitude. Moreover, the amount of active catalyst phase is much less in the case of silica gel than MCM-41 and the moles of DBT converted per second per unit catalyst surface area is higher for the silica gel-supported catalyst. That is, the silica gel-supported catalyst has a rate constant of 4×10^{-9} moles per second per unit surface area while the MCM-41-supported catalyst has a rate constant of 8.27×10^{-10} moles per second per unit surface area.

The two catalysts have the same chemical composition of the SiO_2 support, the same SiO_2 crystal structure and essentially the same MoS_2 crystal structure (except for the feature discussed above). The major difference between the two catalysts is the method of manufacture and this could be the key to the difference in activity. In the case of MCM-41, the MoS_2 active phase is incorporated by impregnation to the previously prepared support; in the case of silica gel, the MoS_2 active phase is incorporated during the preparation of the support. This suggests that better and more uniform dispersion of active phase is obtained in the case of silica gel. This also is in agreement with the results discussed in the previous paragraph.

4. Conclusion

A new, easy and cost-effective approach for preparing an active catalyst embedded in SiO_2 matrix prepared by the sol–gel method and with the MCM-41 structure is introduced.

The processes to obtain the final supported MoS_2 catalysts are quite different and it is clear that the sol–gel process requires very few steps and room temperature conditions, while the MCM-41 route requires a great deal of energy. The number of moles of DBT converted per second per unit of catalyst surface area is higher in the case of silica gel support. This has a direct impact on the cost-efficiency and highlights the importance of the sol–gel process, which could be a much better option in the manufacture of these supported catalysts.

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