Novel highly active FSM-16 supported molybdenum catalyst for hydrotreatment†

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FSM-16 (Folded Sheet Silica) supported catalysts could accommodate 12 wt% Mo (18% MoO_3) as a monolayer with higher dispersion than any other silica support; these catalysts showed outstanding HDS and HYD activities compared to γ-Al_2O_3, amorphous silica, and other mesoporous silica supported catalysts.

Hydrotreating is an important unit operation in petroleum refining.[1] Its importance is further emphasized by the stringent sulfur specifications of petroleum products needing ultra low sulfur fuels in the range 10–15 ppm.[2] On board fuel cells also require fuels with sulfur as low as 0.1 ppm. Calculations revealed that in order to produce such a low sulfur fuel, seven times more active catalysts are needed. Many approaches such as method of preparation of catalysts, variation of promoters or variation of supports are employed towards this end. Among these, variation of the support is an important one.[3–5]

Many materials have been tested as supports for Mo with Co or Ni as promoters, some of which are SiO_2, Al_2O_3, MgO, ZrO_2, TiO_2, carbon, mixed oxides such as TiO_2–ZrO_2, ZrO_2–Al_2O_3, TiO_2–Al_2O_3, ZrO_2–SiO_2, SiO_2–Al_2O_3, TiO_2–SiO_2 *etc.* Zeolites such as NaY, USY, β-zeolite have also been employed as supports. In recent years mesoporous materials[3,4,6,7] such as MCM-41, SBA-15,[8,9] and HMS[10] have been studied with great interest as supports for hydrotreating catalysts due to their high surface area, stability, and well defined pores with narrow size distribution. FSM-16 materials, which are analogous to MCM-41 (hexagonal, p6mm) materials, have gained much attention because of their high surface areas and pore volumes. To our knowledge there is no detailed report on FSM-16 supported molybdenum catalysts for hydrotreatment. Herein, we are reporting for the first time the outstanding activities of FSM-16 supported molybdenum catalysts promoted with cobalt and nickel for hydrotreating reactions.

The FSM-16 material is prepared by a method similar to that used by Inagaki *et al.*[7] A typical synthesis procedure is as follows: 30 g of kanemite was dispersed in 300 ml of water and then stirred for 3 h at 300 K. Then the suspension was filtered out to obtain wet kanemite paste. All of the kanemite paste was dispersed in 480 ml of an aqueous solution of 2-hexadecyltrimethylammonium chloride (0.125 mol l^{-1}) and then stirred at 343 K for 3 h. The suspension was kept stirring at 343 K for 3 h while keeping the pH value at 8–9. After cooling, the solid product was filtered out, washed with water, dried in air and calcined at 823 K to yield mesoporous silicate, FSM-16. A nitrogen adsorption/desorption isotherm of FSM-16 (BET SA: 885 m^2 g^{-1}) and Mo/FSM-16 catalysts showed a typical reversible IUPAC type IV hysteresis loop with the average pore diameter *ca.* 3.0 nm. A series (2–16 wt%) of FSM-16 supported molybdenum catalysts, promoted with nickel or cobalt were prepared by an incipient wetness impregnation method, characterized by low temperature oxygen chemisorption (LTOC)[11] on catalysts sulfided at 673 K and catalytic activities were evaluated for hydrodesulfurization (HDS) of thiophene and hydrogenation (HYD) of cyclohexene. The reactions were carried out at 673 K on catalysts sulfided at the same temperature for 2 h in a flow of a CS_2–H_2 mixture in a fixed bed reactor operating at atmospheric pressure. The first order rates were evaluated according to the equation $x = r(W/F)$ where r is the rate in mol h^{-1} g^{-1}, x the fractional conversion, W the weight of catalysts in grams, and F the flow rate of the reactant in mol h^{-1}.

The oxygen uptakes at 195 K, HDS, HYD activities are shown in Fig. 1. It can be seen that oxygen chemisorption increases with molybdenum loading and is maximum at 12 wt% Mo. This can be taken as completion of a MoS_2 monolayer on the FSM-16 surface. This observation is also

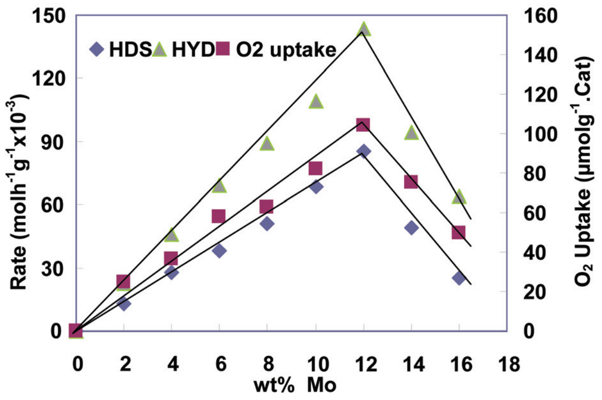

Fig. 1 Effect of Mo loading on hydrodesulfurization reaction rate and oxygen chemisorption on FSM-16 supported catalysts.

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supported by similar activity variation for HDS and HYD shown in the same figure. These results indicate that 12 wt% MoS_2 can be accommodated as a monolayer on this support. It can be seen that there exists a correlation between oxygen uptake capacities (anion vacancies) and activity. Since it is well known that the anion vacancies are the seat for HDS as well as HYD and it is also well documented that oxygen chemisorption is associated with anion vacancies, such an observation therefore suggests that oxygen uptakes are related to the catalytic activities through anion vacancies. The wide angle XRD pattern indicated that Mo supported on FSM-16 has no peaks due to MoO_3 up to 12 wt% loading. The MoO_3 peaks appear at higher loadings. These results also support the fact that on this support highly dispersed Mo is present up to 12 wt% Mo. TPR results also indicated that the hydrogen consumption per g of catalyst *vs.* Mo loading exhibits an inflection at 12 wt% Mo. All these results support the proposal that this support accommodates 12 wt% Mo in a highly dispersed form (monolayer). In contrast to γ-Al_2O_3 supported catalysts Mo forms the so-called monolayer at 8 wt% Mo, amorphous SiO_2 supported catalyst at 4 wt% Mo, ZrO_2 at 6 wt% Mo, SBA-15 and SBA-16 at 8 wt% Mo. These results clearly indicate that FSM-16 accommodates more molybdenum in a highly dispersed state than any other silica support.

It is intriguing to see how such a large amount (12 wt% Mo) of Mo can be accommodated on this siliceous support. It is well known in molybdenum chemistry that oxomolybdenum species interact with support surface hydroxyl groups of particular strength. The amount accommodated and strength of interactions are determined by such groups. There appear to be more of this type of active OH groups on this FSM-16 support surface. In other words the mesoporous structure is altering the chemistry of hydroxyl groups on these FSM-16 supported catalysts. Further investigations are in progress to understand this observation.

Comparison of the activities of Mo, CoMo and NiMo catalysts supported on FSM-16 with other supports are shown in Fig. 2. It can be seen that FSM-16 supported Mo, CoMo and NiMo catalysts are 4–5 times more active than γ-Al_2O_3 supported ones, 2–4 times more active than SBA-15 supported catalysts, and 2–2.5 times more active than HMS supported catalysts.

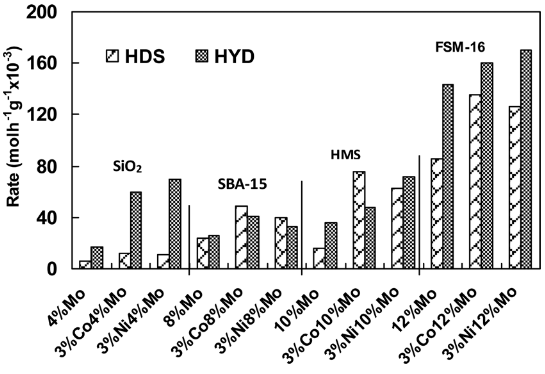

Fig. 2 Comparison of HDS and HYD activities of SiO_2, SBA-15, HMS and FSM-16 supported molybdenum catalysts.

Table 1 Comparison of HDS activity and QTOF values of γ-Al_2O_3, SBA-15, HMS and FSM-16 supported molybdenum catalysts

Catalyst	QTOF/ mol h^{-1} g^{-1} Mo	HDS rate/ mol h^{-1} g^{-1} $\times$ 10^{-3}
12% Mo/FSM-16	0.71	85.5
3% Co–12% Mo/FSM-16	0.91	136
3% Ni–12% Mo/FSM-16	0.84	126
8% Mo/γ-Al_2O_3	0.14	11.2
3% Co–8% Mo/γ-Al_2O_3	0.24	26.8
3% Ni–8% Mo/γ-Al_2O_3	0.17	19.1
4% Mo/SiO_2	0.14	5.6
3% Co–4% Mo/SiO_2	0.17	11.8
3% Ni–4% Mo/SiO_2	0.15	10.6
8% Mo/SBA-15	0.30	24.0
3% Co–8% Mo/SBA-15	0.45	49.1
3% Ni–8% Mo/SBA-15	0.36	39.6
10% Mo/HMS	0.16	16.4
3% Co–10% Mo/HMS	0.58	75.3
3% Ni–10% Mo/HMS	0.48	62.3

The *quasi* turnover frequency (QTOF) is the measure of rate of reaction per g of Mo. QTOF values and rate constants for HDS are shown in Table 1. It can be seen that the QTOF or activity per Mo is greater in the case of FSM-16 catalysts, suggesting that in addition to having a larger number of active sites as indicated by O_2 uptakes, the activity per Mo is also higher. HRTEM observations of sulfided catalysts reflect the changes in morphology of MoS_2. A 12% Mo/FSM-16 image showed MoS_2 crystallites with length 26.3 Å and average stacking of 2–3 layers. These results are also in agreement with the crystallite size obtained from oxygen uptakes (21.2 Å), therefore it is clear that the outstanding activities obtained by MoS_2 are due to the highly dispersed nature of MoS_2 on these supports as evidenced by oxygen chemisorption and HRTEM results.

It is rare to see a silica based support accommodating 12 wt% Mo (18 wt% MoO_3) in highly dispersed form in the oxide and sulfided state and exhibiting outstanding activities. The reported results demonstrate that highly dispersed molybdenum accommodated as a monolayer upto 12 wt% leads to promising activities for HDS of thiophene for Mo, CoMo and NiMo catalysts.

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