

Deep Hydrodesulfurization over W-Based Catalysts Supported by Siliceous MCM-41

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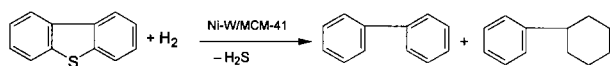
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A deep HDS catalyst, exhibiting considerably high activity in desulfurizing dibenzothiophene and a high-sulfur gas oil, was prepared by depositing Ni–W species over siliceous MCM-41.

The increasing concerns of global air environment have stimulated the demand for cleaner and cleaner engine fuels. Conventional hydrodesulfurization (HDS) catalysts, mainly including Mo- or W-based catalysts supported by γ -Al₂O₃, are active to convert thiophene and benzothiophenes, but not active enough to desulfurize efficiently the most refractory sulfur-containing polyaromatic compounds, e.g. dibenzothiophene (DBT) and its alkyl-substituted derivatives.¹ Consequently, deep HDS becomes of great research interest at present, aiming at removing DBT and its derivatives.

Since the discovery of mesoporous MCM-41, great efforts have been done to develop its supported catalysts for a variety of reactions, including hydrodesulfurization of petroleum fractions.^{2–7} It is interesting to note that almost all the researches have focused on Al-containing MCM-41, probably hoping that its strong acidity may help to crack the polyaromatic sulfur-containing compounds so as to improve the HDS activity. Nevertheless, no great improvement in HDS activity has been achieved on this type of support.



Recently, we found that Ni–W/MCM-41 showed excellent performance in desulfurizing DBT. The evaluation by a high sulfur content gas oil confirmed that this series of catalysts exhibited considerably high activity in hydrodesulfurization.

Ammonium metatungstate hydrate (H₂₆N₆O₄₁W₁₂), Ni(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O were of commercial GR grade (Dalian Chemical Reagents Co.). Dibenzothiophene was synthesized according to the method in the literature.⁸ Decalin was the product of Shanghai Chemical Reagents Co. and used as solvent without further purification. Siliceous MCM-41 was synthesized by following the procedure reported in the previous paper.⁹ From its N₂ adsorption isotherm, the structural parameters of the synthesized MCM-41 was evaluated: BET specific surface area 1046 m²/g, pore size 46 Å, and pore volume 1.00 cm³/g.

The catalysts were prepared by a co-impregnation method. A 20 wt% WO₃ loading level was chosen for preparing this series of catalysts. The content of cobalt or nickel was determined by varying the atomic ratio of Co/W in the range of $x = 0$ –1.0. The catalysts were denoted as Co–W(x) or Ni–W(x).

HDS reaction was carried out in a fixed-bed stainless steel tubular reactor having a dimension of 8.0 mm in internal diameter. Catalysts were pelleted and then crashed and screened to 20–35 meshes. The catalyst particles (0.3 g) were mixed with quartz sand (30–50 mesh) to a constant volume 1.5 cm³ before being charged into the reactor. The HDS activities of the prepared catalysts were evaluated using two feeds: 0.5wt% DBT in decalin and a gas oil (2.83 wt% S).

The catalysts were presulfided before HDS reaction by means of a mixture of H₂S/H₂ (10 vol% H₂S) at atmospheric pressure and 400 °C for 6 h. The reaction conditions for the HDS reaction were temperature 260–380 °C, total pressure 5.0 MPa, H₂/feed ratio 1200 Nm³/m³, and WHSV 12 h^{–1} (2 h^{–1} for gas oil). The liquid products were analyzed by a GC (HP 6890 plus), and the sulfur contents in gas oil were determined by an XRF analyzer (RSR 3400 X).

Figure 1 shows the variation of DBT conversion with temperature for W-based catalysts during HDS of dibenzothiophene. It is indicated that most of these two series of catalysts gave nearly complete conversion of DBT. Moreover, the HDS activities for both catalysts series were accelerated with increasing the content of the promoters until the atomic ratio of Ni/W or Co/W reached 0.75. The optimal atomic ratio for Ni–W/MCM-41 or Co–W/MCM-41 is in the vicinity of 0.75, higher than the conventional γ -Al₂O₃ supported catalysts. It is believed that a high dispersion of WS₂ and the promoters on the surface of the supports is essential to form a monolayer or tiny Co–W–S crystal-

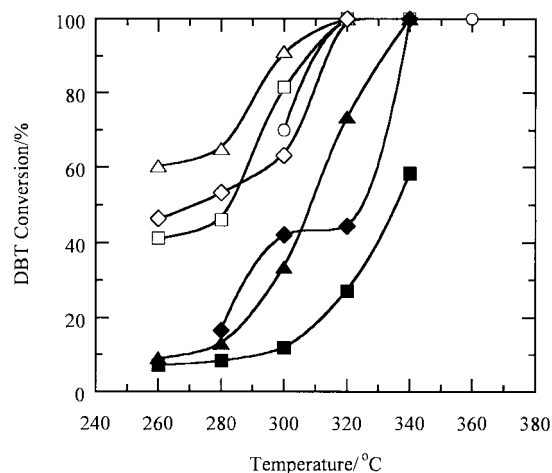


Figure 1. Variation of DBT conversion with reaction temperature during hydrodesulfurization. (○) Ni–W(0.25), (□) Ni–W(0.50), (△) Ni–W(0.75), (◇) Ni–W(1.00), (■) Co–W(0.50), (▲) Co–W(0.75), (◆) Co–W(1.00).

lite structures so as to achieve a very high HDS activity. Since the MCM-41, with extremely high specific surface area and mesopores of 46 Å, provides enough surface space and easy access to accommodate the Co–W pairs, higher HDS activity is expected when the Co/W or Ni/W atomic ratio is close to unit.

It is also shown that Ni–W/MCM-41 showed higher HDS activity than Co–W/MCM-41 in DBT hydrodesulfurization. Since Ni–W sulfides are more active in hydrogenation than Co–W sulfides,¹⁰ it is reasonable to assume that the difference in HDS activities may be attributed to the difference in hydrogenation abilities of the promoters, and that both the routes of hydrogenation followed by desulfurization and of hydrogenolysis play important roles in the HDS reaction networks of DBT over Ni–W/MCM-41 catalysts. The relative selectivity of cyclohexylbenzene (CHB) and biphenyl (BP), as shown in Figure 2, confirms this assumption. It is indicated that Co–W catalysts mainly take the route of hydrogenolysis during DBT hydrodesulfurization.

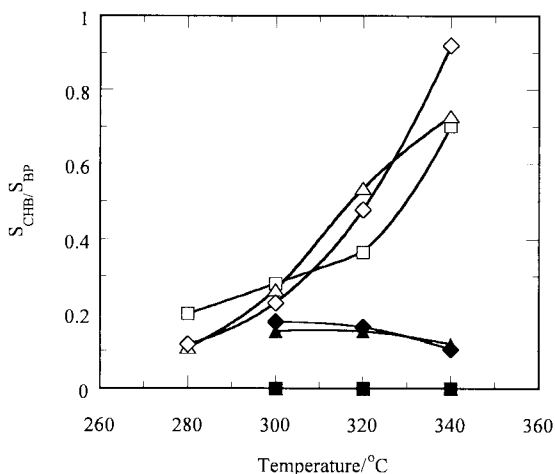


Figure 2. Variation of $S_{\text{CHB}}/S_{\text{BP}}$ with reaction temperature during hydrodesulfurization. (□) Ni-W(0.50), (△) Ni-W(0.75), (◇) Ni-W(1.00), (■) Co-W(0.50), (▲) Co-W(0.75), (◆) Co-W(1.00).

To evaluate the catalysts under industrial circumstances, the HDS of a high sulfur-containing gas oil was performed on both series of catalysts. The HDS conversions as a function of reaction temperature are shown in Figure 3. As expected, the Ni–W/MCM-41 with an atomic ratio of 0.75 exhibited the highest HDS activity, suggesting that the removal of sulfur from DBT and its derivatives is essential in HDS of high sulfur-containing petroleum fractions or in deep HDS. Preliminary investigation on the life of Ni–W(0.75) catalyst indicated that there was no deactivation after 48 h in HDS of the gas oil. On the other hand, it can be seen that the difference of HDS activities for the gas oil is smaller than that for DBT hydrodesulfuriza-

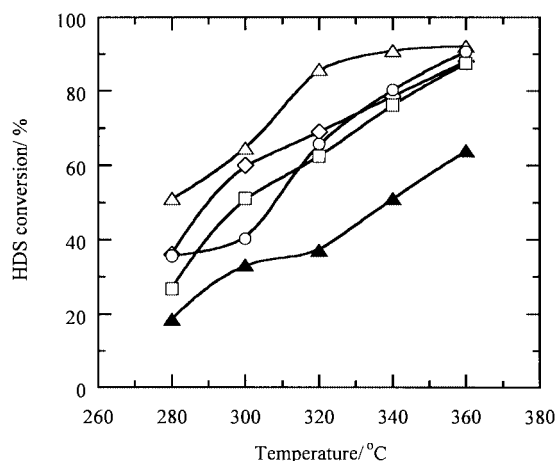


Figure 3. Variation of HDS conversion with reaction temperature during hydrodesulfurization of a gas oil. (○) Ni-W(0.25), (□) Ni-W(0.50), (△) Ni-W(0.75), (◇) Ni-W(1.00), (▲) Co-W(0.75).

tion, indicating that all the catalysts may be highly active to desulfurize the less refractory sulfur-containing compounds which predominate in the gas oil.

In summary, siliceous MCM-41 is a promising support for preparing deep HDS catalysts. Ni–W/MCM-41 with an atomic ratio of 0.75 shows the highest HDS activity for either DBT or gas oil.

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References and Notes

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