Heterogeneous Catalysis

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Hydrodesulfurization of 4,6-Dimethyldibenzothiophene over Noble Metals Supported on Mesoporous Zeolites**

*Yinyong Sun and Roel Prins**

The reduction of the sulfur content in gasoline and diesel fuel has been a subject of intense investigation in recent years because the sulfur level must in many countries be reduced to 10 ppm by the year 2010 for environmental reasons, while for fuel-cell applications the sulfur content should be below 0.1 ppm.[1] To reach this low level, even highly refractory molecules such as 4,6-dimethyldibenzothiophene (4,6-DM-DBT) must be desulfurized. However, because of steric hindrance by the methyl groups adjacent to the sulfur atom, desulfurization of 4,6-DM-DBT mainly takes place after the molecule has first been hydrogenated.[2] Therefore, the hydrogenating ability of the catalyst is of critical importance for deep hydrodesulfurization (HDS). Recent studies have shown that noble-metal-supported catalysts[3] have much better hydrogenation performance than conventional metal sulfides in HDS, and may be used in the second reactor of a deep HDS process.

Not only the active catalyst, but also the support plays an important role in the catalytic performance of catalysts. Acidic supports can increase the conversion of dibenzothiophene (DBT) and of 4,6-DM-DBT.[4] One explanation for this is that they enable dealkylation and isomerization reactions of the alkyl substituents, which may transform refractory components into more reactive species and thus accelerate HDS.[4b,d] Moreover, acidic supports may also improve the catalytic activity of the catalyst particles. Since partial electron transfer can occur from the metal particles to acidic sites of the support, the resulting electron-deficient metal particles[5] are deemed to have a better resistance to sulfur poisoning by decreasing the interaction with H_2S.[5b,6] Another explanation for this improvement is the creation of a second hydrogenation pathway by spillover of hydrogen atoms from the metal particles to the aromatic sulfur-containing molecules that are adsorbed on acidic sites in the vicinity of the metal particles.[7] While the metal particles become poisoned by sulfur, they can still dissociate hydrogen molecules, and thus the hydrogenation pathway involving spillover would still be possible.[8]

It is well known that zeolites possess strong acidity, high stability, and a regular pore array, and are for these reasons applied in many industrial catalytic reactions. However, their small pore size means that relatively large molecules such as 4,6-DM-DBT cannot enter the pores; they can only react on the outer surface of the zeolites and cannot reach many active centers. A support with strong acidity and relatively large pores would, therefore, be preferred. The recent discovery of mesoporous zeolites with their hierarchical porosity and strong acidity opens the possibility of using them as supports in HDS.[9] However, until now their use as a support in HDS has not been reported.

Herein we report on Pt, Pd, and Pt-Pd catalysts supported on mesoporous Na-ZSM-5. The catalytic activity and selectivity of these catalysts were studied in the HDS of 4,6-DM-DBT, and the hydrocarbon products as well as the hydrogenated intermediates were analyzed. Compared with conventional Na-ZSM-5- or γ-Al_2O_3-supported catalysts, the mesoporous Na-ZSM-5-supported catalysts exhibited much better catalytic performance for hydrodesulfurization.

The powder XRD patterns of mesoporous Na-ZSM-5 (MNZ-5) and Na-ZSM-5 (NZ-5, see Figure S1 in the Supporting Information) show well-resolved peaks which are characteristic of the ZSM-5 zeolite structure. MNZ-5 exhibited a type IV N_2 adsorption/desorption isotherm (see Figure S2a in the Supporting Information) typical for mesoporous materials. In contrast, NZ-5 showed a type I isotherm, which is typical of microporous materials. Moreover, a uniform pore distribution centered at around 4.9 nm was observed for MNZ-5 (see Figure S2b in the Supporting Information). The detailed sorption data of both samples are listed in Table 1. The BET special surface area and mesoporous volume for MNZ-5 are $579\,m^2\,g^{-1}$ and $0.44\,cm^3\,g^{-1}$, respectively, much higher than those of NZ-5.

The isomerization of 2-methyl-2-pentene (2M2P) is a good model reaction to evaluate the acidity of solid acids.[10] The molar ratio of *trans*-3-methyl-2-pentene (*trans*-3M2P, obtained by shift of a methyl group) to *trans*- and *cis*-4-methyl-2-pentene (*trans*- and *cis*-4M2P, respectively, obtained by shift of an H atom) in the product reflects the acidity of solid acids. The higher the molar ratio is, the stronger the acidity is. Table 1 shows that MNZ-5 resulted in a higher conversion in the isomerization of 2M2P than did NZ-5; this observation may be attributed to the high BET surface area of MNZ-5. The analysis of the Na content in the two zeolites showed that only 90 % of the Al atoms were charge-compensated by Na cations, so that about 10 % protons existed in NZ-5 and MNZ-5, thus suggesting that they are indeed acidic supports. γ-Al_2O_3, on the other hand, gave a lower conversion

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[*] Dr. Y. Sun, Prof. Dr. R. Prins
Institute for Chemical and Bioengineering, ETH Zürich
8093 Zürich (Switzerland)
Fax: (+41) 44-632-1162
E-mail: prins@chem.ethz.ch

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Table 1: Textural parameters and acidity evaluation of various supports.

Supports	BET area [$m^2 g^{-1}$]	Mesopore volume [$cm^3 g^{-1}$]	Mesopore diameter [nm]	Conversion [%][a]	Molar ratio[b]
γ-Al_2O_3	220	0.60	5.7	21	0
NZ-5	375	0.09	–	25	0.20
MNZ-5	579	0.44	4.9	40	0.33

[a] Conversion of 2M2P at 423 K. [b] Molar ratio of *trans*-3M2P to *trans*- and *cis*-4M2P.

than NZ-5 and MNZ-5, and no *trans*-3M2P was detected, thus indicating that γ-Al_2O_3 has a relatively weak acidity.

Figure 1 shows the catalytic activity of Pt catalysts on various supports in the HDS of 4,6-DM-DBT. The HDS conversion represents the yield of all desulfurized hydrocarbon compounds. HDS conversion reached 63 % for Pt/MNZ-5 at high weight time, 31 % for Pt/NZ-5, and 30 % for Pt/γ-Al_2O_3 (Table 2). The removal of sulfur by Pt/MNZ-5 was twice that of Pt/NZ-5 and Pt/γ-Al_2O_3.

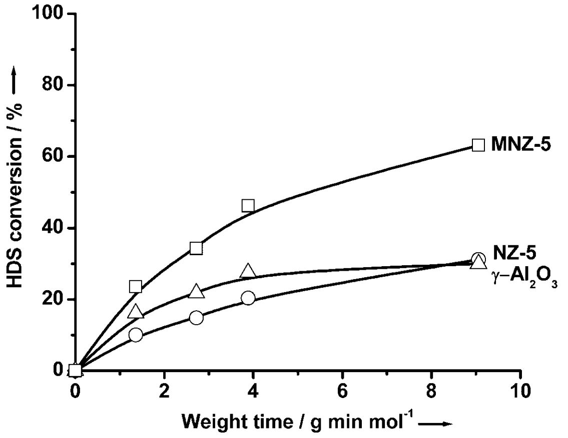


Figure 1. Conversion in the HDS of 4,6-DM-DBT over Pt catalysts on various supports.

Table 2: Metal dispersion, estimated particle size, and performance of various catalysts.

Catalyst	Dispersion [%]	Particle size [nm]	HDS conv. [%][a]
Pt/γ-Al_2O_3	74	1.3	30
Pt/NZ-5	37	2.6	31
Pt/MNZ-5	35	2.7	63
Pd/γ-Al_2O_3	73	1.3	21
Pd/NZ-5	27	3.5	3
Pd/MNZ-5	25	3.8	86
Pt-Pd/γ-Al_2O_3	37	2.5	46[b]
Pt-Pd/NZ-5	24	3.9	3[b]
Pt-Pd/MNZ-5	23	4.0	73[b]

[a] At weight time = 9 g min mol^{-1}. [b] At weight time = 2.7 g min mol^{-1}.

In the case of Pt/MNZ-5, trimethylcyclopentenylbenzene (TMC) and the 3,3′-dimethylcyclohexylbenzene (3,3′-DM-CHB) and 3,3′-dimethylbicyclohexyl (3,3′-DM-BCH) isomers were found in the final products together with the sulfur-containing intermediates 4,6-dimethyltetrahydrodibenzothiophene (4,6-TH-DM-DBT) and 4,6-dimethylhexahydrodibenzothiophene (4,6-HH-DM-DBT), and the desulfurized products 3,3′-DM-CHB and 3,3′-DM-BCH (see Figure S3 in the Supporting Information). The product yields and selectivities showed that 3,3′-DM-CHB was always the most abundant product, irrespective of the weight time (see Figure S4 in the Supporting Information). The yield and selectivity reached 28 and 41 %, respectively, at high weight time. 3,3′-DM-BCH was the second major product, and had a similar selectivity as TMC. The yield and selectivity of 3,3′-DM-BCH were 17 and 25 %, respectively, and those of TMC were 16 and 24 %, respectively. The selectivity of 3,3′-DM-BP (3 %) was constant throughout the reaction, thus indicating that 3,3′-DM-BP does not hydrogenate further on Pt/MNZ-5 under the HDS conditions. The selectivity of the sulfur-containing molecules 4,6-DM-TH-DBT and 4,6-DM-HH-DBT decreased with weight time. They were observed in small amounts at high weight time, which suggests that these intermediates can be desulfurized easily. The same sulfur-containing intermediates and hydrocarbons were observed with Pt/NZ-5 as with Pt/MNZ-5, but with only a trace amount of TMC. 3,3′-DM-CHB was also the most abundant product and showed increasing selectivity with weight time. The yield and selectivity were 20 and 54 %, respectively, at high weight time. 3,3′-DM-BCH was the second major product, with a yield and selectivity of 7.7 and 20 %, respectively. The selectivity of 3,3′-DM-BP (5 %) was also constant throughout the reaction and the yield was only 4 %. The selectivity of 4,6-TH-DM-DBT and 4,6-HH-DM-DBT decreased with weight time. These results suggested that more active sites were accessible in Pt/MNZ-5 because of the existence of mesopores, although Pt/MNZ-5 had a similar metal dispersion as Pt/NZ-5 (Table 2). The finding that Pt/γ-Al_2O_3 had lower HDS activity than Pt/MNZ-5, even though it possessed mesoporosity and a relatively high metal dispersion, revealed that the acidity was advantageous for the improvement of the HDS activity.

Figure 2 shows the HDS conversion of Pd catalysts on various supports in the HDS of 4,6-DM-DBT. Pd/MNZ-5 exhibited much higher catalytic activity than Pd/NZ-5 and Pd/γ-Al_2O_3: HDS conversion with Pd/MNZ-5 was 86 % at high weight time, but only 3 % for Pd/NZ-5 and 21 % for Pd/γ-Al_2O_3 (Table 2). The sulfur removal by Pd/MNZ-5 was 29 times higher than for Pd/NZ-5 and 4 times higher than for Pd/γ-Al_2O_3. These results indicated that MNZ-5 with mesopores was a better catalyst support in the HDS of 4,6-DM-DBT than was NZ-5 without mesopores, thus proving that mesoporosity in the supports played a positive role in sulfur removal. Pd/MNZ-5 even showed a much higher HDS activity than Pd/γ-Al_2O_3, although it had a much lower metal dispersion (Table 2), further revealing that acidity was beneficial for enhancing the HDS activity. Therefore, the combination of mesoporosity and acidity promotes the efficiency of sulfur removal.

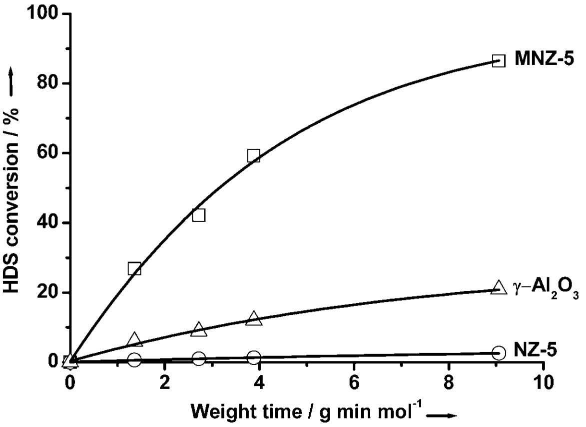
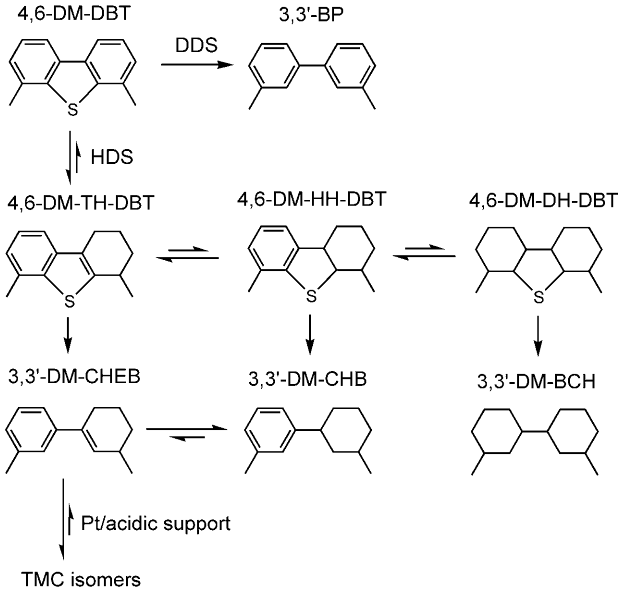


Figure 2. Conversion in the HDS of 4,6-DM-DBT over Pd catalysts on various supports.

To further demonstrate the efficiency of sulfur removal for noble-metal catalysts supported on mesoporous zeolites, the catalytic performance of the bimetallic Pt-Pd/MNZ-5 catalyst was studied. The results showed that the bimetallic catalysts were much more active than the monometallic catalysts, thus proving that a chemical synergism existed between the noble metals present and that alloying had taken place. HDS conversion with Pt-Pd/MNZ-5 reached 73 % at low weight time (2.7 g min mol^{-1}), but only 3 % for Pt-Pd/NZ-5 and 46 % for Pt-Pd/γ-Al$_2$O$_3$ (Table 2). The sulfur removal was twice that of Pt-Pd/γ-Al$_2$O$_3$ and 24 times higher than that for Pt-Pd/NZ-5.

On the basis of the obtained results, we propose a new reaction scheme for the HDS of 4,6-DM-DBT on noble-metal catalysts (Scheme 1). 3,3′-DM-CHEB was introduced in the scheme, because of the observation of TMC isomers, which should be produced by the isomerization of 3,3′-DM-CHEB. The isomerization occurred when Pt was combined with an acidic support. However, when Pd or Pt-Pd was used, no isomerization was observed, probably because of their strong hydrogenation ability. To demonstrate the contribution of acidity on the formation of TMC isomers, 500 Pa piperidine was added to destroy the acidity during the HDS of 4.6-DMDBT over Pt/MNZ-5. As a result, TMC isomers were not observed, thereby proving that acidity is the main factor for the formation of the TMC isomers. Therefore, in the proposed reaction scheme, 3,3′-DM-CHEB was considered as an intermediate to form 3,3′-DM-CHB or TMC isomers.



Scheme 1. Reaction pathway of the HDS of 4,6-DM-DBT on noble-metal catalysts.

In conclusion, the catalytic performance of noble-metal catalysts supported on mesoporous zeolites in the HDS of 4,6-DM-DBT was investigated for the first time. Sulfur removal by these catalysts was much more efficient than those on microporous zeolites and γ-Al$_2$O$_3$. A new reaction scheme for the HDS of 4,6-DM-DBT was proposed on the basis of the obtained results. Further improvement in the catalytic performance can be expected by tuning the acidity and pore size of the mesoporous zeolites. This study proves that mesoporous zeolites are ideal candidates of supports for deep HDS.

Experimental Section

The mesoporous Na-ZSM-5 (MNZ-5) and conventional Na-ZSM-5 (NZ-5) zeolites were prepared according to published procedures.[9i,j] γ-Al$_2$O$_3$ was obtained from Condea. The noble-metal catalysts were prepared by incipient wetness impregnation of the calcined support with an appropriate aqueous solution of [Pt(NH$_3$)$_4$](NO$_3$)$_2$ (Aldrich, 99 %) and/or [Pd(NH$_3$)$_4$](NO$_3$)$_2$ (Alfa, 5 wt % in Pd). After impregnation, the catalysts were dried in air at ambient temperature for 3 h, then in an oven at 393 K for 4 h, and finally calcined at 773 K for 4 h (at a heating rate of 1 K min^{-1}). According to the above procedures, monometallic 0.5 wt % Pt, 0.5 wt % Pd, and bimetallic 0.25 wt % Pt/0.25 wt % Pd were prepared. Further experimental details are given in the Supporting Information.

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