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Influence of nanoscale distribution of Pd particles in the mesopores of MCM-41 on the catalytic performance of Pd/MCM-41

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Abstract

Two different nanoscale Pd particle distributions in MCM-41, i.e. in the mesopores and on the external surface, were obtained by using a siliceous MCM-41 and a silylated MCM-41 (S-MCM-41) as the starting support materials, respectively. The electron density of Pd in Pd/S-MCM-41 was lower than that in Pd/MCM-41. Pd/S-MCM-41 exhibited much better selective hydrogenation performance but a lower hydrogenolysis activity than Pd/MCM-41. These differences are related to the different Pd particle distributions in MCM-41 and S-MCM-41, demonstrating that the performance of noble metal catalysts is tunable by simply controlling the nanoscale metal particle distribution in the pores.

Key words: Pd; MCM-41; Nanoscale distribution; Selective hydrogenation; Hydrodesulfurization; Hydrodeoxygenation.

1. Introduction

Noble metals (e.g. Pd and Pt) are well-known hydrogenation catalysts. They are also promising for a variety of important reactions for the removal of hetero atoms such as hydrodesulfurization (HDS) and hydrodeoxygenation (HDO) [1,2]. The support has an important influence on the catalytic performance of noble metal catalysts [3,4]. In many cases, the improved catalyst performance can result by using a nonuniform catalyst activity distribution within the support [5]. This is particularly true for the supported noble metal catalysts which usually possess high activity. *For example, egg-shell catalysts give higher selectivities for consecutive reactions where the intermediate is the desired product, since side reactions are suppressed [6,7].* If the reactants contain poisons, an egg-yolk distribution maybe favorable so that the poison can be captured at the edge of the catalyst body, where few active sites are present [7]. The desired metal profile can be obtained by controlled impregnation with one component, or by successive or competitive impregnation with two or more [6,7]. It should be noted that these nonuniform distributions are usually used on an industrial scale, or in other words the millimeter scale [8].

Previously, Quintanilla et al. [9] reported that the silylation of Pd/SiO₂ catalysts increased the selectivity toward alcohols in the reduction of aromatic ketones. They suggested that the silylation yielded a more hydrophobic support, on which the aromatic alcohol adsorbs more weakly than the ketone, which decreases the amount of alcohol adsorbed on the metal and thus suppresses the consecutive reduction of the alcohol. In their case, silylation reactions were carried out with the catalyst but not the support. In the present work, instead of the post-silylation, a siliceous MCM-41 and a pre-silylated MCM-41 were used as the starting support materials for the preparation of Pd catalysts. *Our aim is to study the influence of nanoscale distribution of Pd in the mesopores of MCM-41 on the catalytic performances of Pd/MCM-41 in a variety of selective hydrogenations, the HDS of dibenzothiophene (DBT), and the HDO of dibenzofuran (DBF)*.

2. Experimental

2.1. Catalyst preparation

The sodium-free siliceous MCM-41 (denoted as MCM-41) was prepared following the procedure reported elsewhere [10]. The prepared MCM-41 (1 g) was then dispersed in 52.5 mL of 4.7 wt.% solution of trimethylchlorosilane (Sinopharm Chemical Reagent Co., Ltd) in dry toluene. The mixture was stirred for 3 h at 110 °C. The solid was filtered and washed with dry toluene, and finally dried in air for 12 h at ambient temperature. This silylated MCM-41 was detonated as S-MCM-41.

Pd/MCM-41 and Pd/S-MCM-41 were prepared by incipient wetness impregnation of MCM-41 and S-MCM-41 with an aqueous solution of PdCl₂ in diluted HCl and a toluene solution of Pd(OAc)₂, respectively. After impregnation, the samples were dried in an oven overnight at 120 °C and then calcinated in air at 400 °C for 5 h, so as to obtain the oxide precursors and to remove organic groups. The loading of Pd was 0.5 wt.%. The catalyst precursor was then pelleted, crushed, and screened to 20 ~ 40 meshes. It was charged in a trickle bed stainless-steel tubular reactor (8.0 mm i.d.). Prior to the reactions, the precursor was reduced at 300 °C and 1.0 MPa in a 75 NmL·min⁻¹ H₂ flow for 1 h.

2.2. The hydrogenation, HDS, and HDO reactions

After the precursor had been reduced in the reactor, the temperature and the total pressure were adjusted to the desired values listed in Table S1 in supplementary data, which also summarizes the conditions of each reaction. The reaction products were analyzed off-line by an Agilent-6890N gas chromatograph equipped with an HP-5 column and a flame ionization detector. Mass spectra were recorded on a GC-MS instrument (Agilent-7890A GC/7000B MS).

2.3. Characterization

The XRD patterns of the samples were measured on a Rigaku D/Max 2400 diffractometer with nickel-filtered Cu-Kα radiation at 40 kV and 100 mA. Nitrogen physisorption was performed using a Tristar II 3020 adsorption analyzer. *No residual chloride was detected in*

Pd/MCM-41 by means of XRF (Bruker SRS-3400). Transmission electron microscopy images of the supported Pd catalysts and their oxide precursors were taken using a JEM-2100UHR transmission electron microscope.

The FT-IR spectra were recorded on an Equinox 55 spectrophotometer in the range of 400-4000 cm⁻¹. Transmission IR spectra of CO adsorbed on the catalysts (CO-IR) were recorded with the same instrument according to the method described by Hu et al. [11]. The H₂ chemisorption measurement was carried out using a dynamic pulse method on a Chembet-3000 instrument described elsewhere [12], and the H₂ uptakes and metal dispersions of the catalysts were calculated based on the equations given by Aramendía et al. [13].

3. Results and discussion

The XRD patterns of MCM-41 and S-MCM-41 (Figure S1, supplementary data) featured a narrow (1 0 0) peak and separated (1 1 0) and (2 0 0) reflections, indicating that both samples possessed hexagonal structures. In the FT-IR spectrum of S-MCM-41 (Figure S2, supplementary data), the bands corresponding to the C–H stretching vibrations of the methyl (2963 cm⁻¹) and methylene (2925 and 2856 cm⁻¹) groups were detected [9,14], confirming that the methyl groups were grafted onto MCM-41 by silvlation. All these bands disappeared in the spectrum of the oxide precursor of Pd/S-MCM-41 (Figure S2, supplementary data), demonstrating that the methyl groups were burned during calcination. The absence of the methyl groups makes Pd/S-MCM-41 a totally different catalyst than those reported in the previous work [9]. The specific surface area (S_g) , the total pore volume (V_t) , and the pore size (r_p) of MCM-41 all decreased after the silvlation (*Table 1*). The loading of Pd led to a drastic decrease in the S_g and the V_t of MCM-41 (*Table 1*). Except a small decrease in S_g , the V_t and the r_p of Pd/S-MCM-41 were almost identical to those of S-MCM-41 (*Table 1*). Besides, Pd/S-MCM-41 showed a slightly higher H₂ uptake than Pd/MCM-41 (*Table 1*). Based on the calculated metal dispersions (Table 1), the average metal particle sizes of Pd/MCM-41 and Pd/S-MCM-41 were estimated to be 6.9 and 6.4 nm, respectively. In the CO-IR spectrum of

Pd/MCM-41 (Figure 1), the narrow band at 2077 cm⁻¹ can be assigned to the linearly bonded CO species (the L band), while the broad band in the 1750 ~ 1990 cm⁻¹ range is due to bridge bonded CO species (the B band) [15,16]. Both the B band and the L band of Pd/S-MCM-41 shifted to higher wavenumbers (Figure 1). The L/B ratio also increased from 0.29 of Pd/MCM-41 to 0.88 of Pd/S-MCM-41. These results indicate that the electron density of Pd in Pd/S-MCM-41 is lower than that in Pd/MCM-41 [11,17]. Our present data are not sufficient enough to explain the difference, and we will study it further.

The TEM images of the catalysts (Figure 2) reveal that the Pd particles were almost all confined in the well-ordered pores of MCM-41 and distributed along the pore channels, whereas the spherical Pd nanoparticles were exclusively on the external surface of S-MCM-41. The observation of the lattice fringes with an *interplanar* distance of ca. 0.23 nm corresponding to the Pd (1 1 1) plane confirms the reduction of the oxide precursors to Pd (Figure S3, supplementary data). Pd/S-MCM-41 had a narrow particle size distribution and the average size of the Pd nanoparticles measured based on the TEM images was 6.8 nm (Figure S4, supplementary data), which agreed well with the value (6.4 nm) estimated by H_2 chemisorption. Although the Pd particles confined in the pores of MCM-41 were smaller than those on the surface of Pd/S-MCM-41, as evidenced by TEM analysis (Figure 2), the H₂ uptake of Pd/MCM-41 was slightly lower (*Table 1*). One explanation might be that not all the surface metal sites of Pd particles in the pores of MCM-41 are available for H₂ adsorption. In other words, it is likely that only the surface Pd atoms near the pore mouths are able to adsorb H₂. The pore blockage caused by the deposition of Pd particles in the one-dimensional pores of MCM-41 must also be responsible for the significant decrease in the pore volume and the specific surface area of MCM-41 after the loading of Pd (Table 1). The different Pd distribution profiles of Pd/MCM-41 and Pd/S-MCM-41 were already formed in their oxide precursors (Figure S5, supplementary data). Multiple factors may affect the final metal profile, such as the drying conditions and system properties [6], the surface property of the starting

support materials (hydrophobic for S-MCM-41 and hydrophilic for MCM-41), *the Pd salts used for catalyst preparation*, as well as the significantly different heats of vaporization of impregnation solvents (2427.8 $J \cdot g^{-1}$ for water and 397.7 $J \cdot g^{-1}$ for toluene). To clarify this question, further studies are needed.

The results of the selective hydrogenation of phenylacetylene (PA), naphthalene (NP), and p-chloronitrobenzene (p-CINB) over Pd/S-MCM-41 and Pd/MCM-41 are listed in Table 2. The product selectivities of these hydrogenation reactions are summarized in Table S2 in supplementary data. Since the two catalysts possessed similar H₂ uptakes (Table 1), the conversion of the substrate can be used as a measure of the intrinsic activity of the catalyst. It should be mentioned that the molecular sizes of all the reactants and products of the reactions involved in our present work are smaller than the pore sizes of Pd/MCM-41 and Pd/S-MCM-41, which means that the configurational diffusion of these molecules in the catalysts can be ruled out. The H_2 /Oil ratios of all the reactions (Table S1, supplementary data) were also high enough to eliminate the external mass-transfer limitations. Pd/S-MCM-41 behaved much better than Pd/MCM-41 in these typical selective hydrogenation reactions (Table 2). The lower electron density of Pd particles in Pd/S-MCM-41 than in Pd/MCM-41 (Figure 1) could explain their higher activity in the hydrogenation of NP and p-CINB [3,18], but it is hardly true for the hydrogenation of PA. In the hydrogenation of acetylenic substrates, the formation of electron-deficient Pd particles is expected to result in a sharp decrease in the turnover frequency [3]. Additionally, all the products listed in *Table 2* are the intermediates of consecutive hydrogenation reactions. For such reactions at high conversion levels, an increase in the conversion is usually accompanied by a decrease in the yield or the selectivity of the intermediates, which is contradictory with our observations. Considering the different metal distribution profiles, we suggest that the pore diffusion accounts for the different catalytic behavior of Pd/MCM-41 and Pd/S-MCM-41. Since the Pd nanoparticles were confined in the mesopores of MCM-41, they may suffer from more severe resistance to

diffusion in the nanodimensional pores than the Pd particles on the outer surface of S-MCM-41, leading to the decrease in the conversion of the substrates and the selectivity of the intermediate products [19]. The situation is more complicated for the hydrogenation of *p*-CINB. The selectivity of *p*-chloroaniline (the desired product) increased from 43.4% over Pd/MCM-41 to 99.2% over Pd/S-MCM-41 (*Table 2 and Table S2 in supplementary data*), indicating that the dechlorination was nearly completely suppressed. This demonstrates that Pd/S-MCM-41 possesses a low hydrogenolysis activity because the dechlorination of *p*-CINB to aniline follows a hydrogenolysis mechanism [20,21]. The dechlorination reaction and the hydrogenation of the nitro group are parallel reactions. Hence, the high *p*-chloroaniline selectivity over Pd/S-MCM-41 cannot only be attributed to the elimination of pore diffusion.

The higher selective hydrogenation activity and the lower hydrogenolysis activity of Pd/S-MCM-41 compared with the catalytic performance of Pd/MCM-41 was confirmed by the HDS of DBT and the HDO of DBF. DBT undergoes HDS by two parallel pathways (Scheme S1, supplementary data): direct desulfurization (DDS) and hydrogenation (HYD). Since the hydrogenation of BP to CHB is negligible in the presence of sulfur-containing compounds (Figure S6, supplementary data), the yield of BP can be used as a measure of the DDS pathway activity. Pd/S-MCM-41 showed a higher HDS activity than Pd/MCM-41 at 300 °C. The increase in the HDS activity was due to the increase in its HYD pathway activity, whereas the yield of BP decreased (Figure 3). Because the DDS of DBT to BP mainly follows the hydrogenolysis mechanism [22], the lower BP yield is an indication of the lower hydrogenolysis activity of Pd/S-MCM-41. Since C-O bond is stronger than C-S bond, the direct hydrogenolysis of DBF to BP was not observed over the two catalysts at temperature as high as 340 °C. The conversion of DBF over Pd/S-MCM-41 was about 16% higher than over Pd/MCM-41, and the increase in the DBF conversion was mainly due to the significant increase in the yield of 2-cyclohexylphenol (CHPOH) and a slightly increase in the yield of 2-cyclohexylcyclohexanol (CHCHOH), whereas the yields of all the deoxygenation products

(CHB and BCH) decreased (Figure 3). According to the HDO network of DBF over noble metals (Scheme S2, supplementary data) [23,24], Pd/S-MCM-41 is more active in the selective hydrogenation of the first aromatic ring of DBF, but has difficulties in the successive hydrogenation and deoxygenation reactions. It is generally accepted that hydrogenolysis is catalyzed by metals [25]. The Pd particles in Pd/S-MCM-41 was more ionic or electron-deficient than those in Pd/MCM-41 (Figure 1), which can be one of the reasons to account for its lower hydrogenolysis activity.

4. Conclusions

In summary, we realized the control of nanoscale distribution of Pd particles in MCM-41 by impregnation of a siliceous MCM-41 with a solution of PdCl₂ in diluted HCl and a silylated MCM-41 with a toluene solution of Pd(OAc)₂. The Pd particles were almost all confined in the mesopores of MCM-41, whereas spherical Pd nanoparticles were exclusively on the surface of S-MCM-41. The electron density of Pd in Pd/S-MCM-41 was lower than that in Pd/MCM-41. Compared with Pd/MCM-41, Pd/S-MCM-41 exhibited much better selective hydrogenation performance but a lower hydrogenolysis activity. The different catalytic performances of the two catalysts can be related to their different metal particle distribution profiles and different average electron densities of Pd.

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Table 1. The structural properties of MCM-41, S-MCM-41, Pd/MCM-41, and Pd/S-MCM-41.

Sample	Specific surface area	Total pore volume	Pore size	H ₂ uptake	Pd dispersion
Sample	$(m^2 \cdot g^{-1})$	$(\mathrm{cm}^3 \cdot \mathrm{g}^{-1})$	(nm)	$(\mu mol \cdot g^{-1})$	(%)
MCM-41	1028	0.88	3.4	-	-
S-MCM-41	746	0.70	3.0	-	-
Pd/MCM-41	676	0.66	3.2	3.8	16.2
Pd/S-MCM-41	687	0.69	2.9	4.1	17.5

Table 2. The performances of Pd/S-MCM-41 and Pd/MCM-41 in the selective hydrogenation of phenylacetylene, naphthalene, and *p*-chloronitrobenzene.

Reaction	Conversion (%)		Selectivity (%)		
	Pd/S-MCM-41	Pd/MCM-41	Pd/S-MCM-41	Pd/MCM-41	
	85.2	58.1	64.6	54.2	
$\overset{H_2}{\longrightarrow} \overset{H_2}{\longrightarrow} H_$	^b 93.4	79.2	99.7	99.4	
$\underset{CI}{\overset{NO_2}{\longrightarrow}} \underset{CI}{\overset{H_2}{\longrightarrow}} \underset{CI}{\overset{NH_2}{\longrightarrow}} $	c 43.3	36.7	99.2	43.4	

^a Reaction conditions: 1.0 MPa, 80 °C, H₂/Oil 500, and WHSV 288 h⁻¹.

^b Reaction conditions: 4.0 MPa, 200 °C, H₂/Oil 500, and WHSV 82 h⁻¹.

^c Reaction conditions: 1.0 MPa, 100 $^{\circ}$ C, H₂/Oil 500, and WHSV 82 h⁻¹.

Figure captions

Figure 1. The CO-IR spectra of Pd/MCM-41 and Pd/S-MCM-41.

Figure 2. The TEM images of Pd/MCM-41 and Pd/S-MCM-41.

Figure 3. The product compositions of the HDS of DBT (5.0 MPa, 300 °C, H_2/Oil 1500, and WHSV 54 h^{-1}) and the HDO of DBF (5.0 MPa, 340 °C, H_2/Oil 1500, and WHSV 18 h^{-1}) over Pd/MCM-41 (open) and Pd/S-MCM-41 (filled).

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Figure 1. The CO-IR spectra of Pd/MCM-41 and Pd/S-MCM-41.



Figure 2. The TEM images of Pd/MCM-41 and Pd/S-MCM-41.



Figure 3. The product compositions of the HDS of DBT (5.0 MPa, 300 $^{\circ}C$, H₂/Oil 1500, and WHSV 54 h^{-1}) and the HDO of DBF (5.0 MPa, 340 $^{\circ}C$, H₂/Oil 1500, and WHSV 18 h^{-1}) over Pd/MCM-41 (open) and Pd/S-MCM-41 (filled).

Impreganating a siliceous MCM-41 with PdCl₂ in diluted HCI (Pd/MCM-41) electivity Selectivity Impreganating a silylated MCM-41 with Pd(OAc)₂ in toluene (Pd/S-MCM-41) Conversion A CORRECTION OF Selectivity

Highlights

- Pd nanoparticles were confined in the mesopores of a siliceous MCM-41 (Pd/MCM-41).
- Pd nanoparticles were on the external surface of a silylated MCM-41 (Pd/S-MCM-41).
- The electron density of Pd in Pd/S-MCM-41 was lower than that in Pd/MCM-41.
- Pd/S-MCM-41 behaved much better than Pd/MCM-41 in selective hydrogenation reactions.
- Pd/S-MCM-41 possessed a lower hydrogenolysis activity than Pd/MCM-41.

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