Characterisation and catalytic properties of MCM-41 and Pd/MCM-41 materials

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Pure silica MCM-41 mesoporous molecular sieve material was synthesised and characterised by in situ synchrotron XRD, TEM, TGA/DTA and DRIFTS techniques. In situ energy dispersive XRD (EDXRD) confirmed the exact nature of the pore diameter of MCM-41 and the change in crystal structure on calcination. The IR band at 1057 cm^{-1} of as-synthesised MCM-41 was shifted by 14 cm^{-1} on heating to 673 K due to increased condensation of silanol groups to form Si–O–Si bridges. Calcined MCM-41 materials were used to support Pd, and the catalytic activities for 1-hexene and benzene selective hydrogenation were investigated. The Pd/MCM-41 catalyst showed high activity in hydrogenation of 1-hexene at an inlet reaction temperature of 298 K, but did not show any activity in hydrogenation for benzene. TEM results for the reduced Pd/MCM-41 catalysts revealed that the average Pd particle size was around 2–2.5 nm and these particles were located in the pores of MCM-41 and showed good distribution. TPR measurements showed that about 70% of palladium oxide (PdO) loading in the calcined catalysts was reduced at sub-ambient temperature.

Keywords: MCM-41, in situ synchrotron XRD, diffuse reflectance FTIR, Pd/MCM-41, selective hydrogenation of 1-hexene

1. Introduction

A new class of mesoporous silica tube-like materials designated as MCM-41 was reported in 1992 [1–3]. MCM-41 materials possess a hexagonal arrangement of uniformly sized unidimensional mesopores. An exciting property of these materials is the possibility of controlling the internal diameter of the mesopores between 2 and 10 nm by varying the chain length of the micellar surfactant template [3,4]. Their high thermal and hydrothermal stability, uniform size and shape of the pores, and large surface areas, make them of interest as sorbents and catalysts [1–4].

MCM-41 materials were prepared by others [5,6 and references therein], where a small percentage of silicon has been substituted by Al, Ti, V, Mn, Cr, B and Fe. The valence states, bond lengths and coordinates of the metal ions were studied by X-ray adsorption spectroscopy (XAS) [5]. Titanocene has been grafted onto MCM-41 to prepare Ti-containing MCM-41 [5]. Others incorporated Cu(II) into pure silica MCM-41 via ion-exchange [7]. Most of these mesoporous solids exhibited interesting redox catalytic properties.

MCM-41 has been used as a support for catalyst preparation, which brought a significant improvement when compared to conventional and commercial catalysts. As an example, Ni/HMCM-41 catalyst used for oligomerization of propene showed higher activity and selectivity than catalysts based on medium-pore zeolites [8]. Also, NiMo/MCM-41 catalysts were prepared to study the hydrocracking vacuum gasoil reaction [9]. Recently, Beck and Vartuli [10] reviewed the synthesis, characterisation and application of mesoporous molecular sieve materials.

The work reported here had the following goals: (a) to examine the structure of MCM-41 material carefully during heat treatment (calcination) and (b) to determine catalytic performance of a series of Pd/MCM-41 catalysts, prepared by an incipient wetness technique, for selective hydrogenation of 1-hexene and benzene.

2. Experimental

Synthesis. For this study, pure silica MCM-41 mesoporous molecular sieve synthesis procedure was based on the procedure described in ref. [4], and involved mixing sodium silicate and cetyltrimethylammonium bromide template. Ammonium exchange with an excess of 2 M NH_4Cl solution was carried out on calcined pure silica MCM-41. The product was filtered, washed with deionized water and dried at 393 K, and used as a support for Pd catalyst preparation. A series of Pd/MCM-41 catalysts were prepared using an incipient wetness technique, by impregnating the MCM-41 material with an aqueous solution of the desired amount of $Pd(NH_3)_4Cl_2$. The resulting solid was dried overnight at 393 K and portions were calcined at 593 K in air for 3 h. The catalyst series was prepared with loadings of 0.25, 0.50, 1.0 and 2.0 wt% Pd. The dry and calcined catalysts were designated as Pd-MCM/D and Pd-MCM/C respectively.

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X-ray synchrotron analysis. X-ray powder diffraction patterns for the as-synthesised and calcined MCM-41 samples were obtained on an angular dispersive powder XRD (ADXRD) instrument on beamline station 2.3 at the Daresbury laboratory. The procedure has been illustrated elsewhere [11]. In situ EDXRD spectra of MCM-41 samples were recorded on diffraction station 9.7 at $2\theta = 2.064°$. The sample was heated in situ using a linkaun furnace from 295 to 543 K at 2 K min^{-1} in an air atmosphere. In a second experiment, the same sample was cooled down to room temperature and heated again in situ from room temperature up to 623 K at 5 K min^{-1} in an air atmosphere.

Diffuse reflectance infrared FT spectroscopy (DRIFTS). A Perkin-Elmer 2000 FTIR spectrometer was used in the range 4000–400 cm^{-1} using KBr powder containing ca. 1 wt% of as-synthesised MCM-41. The powder sample was placed in a diffuse reflectance environmental chamber (Grazeby Specac) connected to a temperature controller. The sample was heated in situ from room temperature (298 K) up to 673 K in an air atmosphere. Spectra were recorded 10 min after each preset temperature had been reached.

Transmission electron microscopy (TEM). Calcined MCM-41 and reduced Pd/MCM-41 samples were deposited on a grid with a holey carbon film and transferred to a Jeol JEM-200CX electron microscope operating at 200 kV. The sample was then kept in a vacuum (ca. 5×10^{-7} Torr). TEM images were recorded at magnifications from 50 000 to 100 000 depending on the beam stability of the specimen.

Thermal analysis. TGA/DTA were carried out using a Shimadzu TGA-50 instrument. The sample was heated under an atmosphere of flowing nitrogen at a heating rate of 5 K min^{-1} for all data collections.

Catalysis. A series of Pd/MCM-41 catalysts were tested to study the catalytic performance of selective hydrogenation of 1-hexene and benzene to form hexane and cyclohexane respectively on a flow fixed bed reactor. (Hydrogenation of unsaturated hydrocarbons is an important process for industrial applications, such as saturation of 1-hexene to form hexane and benzene to form cyclohexane. These products are important solvents for use in organic reactions. Cyclohexane can also be used as an intermediate for the manufacture of Nylon-6 and Nylon-66). Prior to the test, each dry catalyst as well as the MCM-41 bed (100 mg) was first reduced in a mixture of H_2 gas (30 cm^3 min^{-1}) and N_2 gas (15 cm^3 min^{-1}) for one hour at 373 K. The reduced catalysts were cooled down under H_2/N_2 flow to 298 K, then 1-hexene or benzene vapour was introduced into the reduced catalyst at atmospheric pressure and at a space velocity of 1800 h^{-1} to study the reaction activity at 298 K. The selective hydrogenation of benzene was also carried out at higher reaction temperatures (up to 353 K). The reaction products were separated and analysed at six minute intervals using a GC-MS. The respective reaction parameters are given in the related figures.

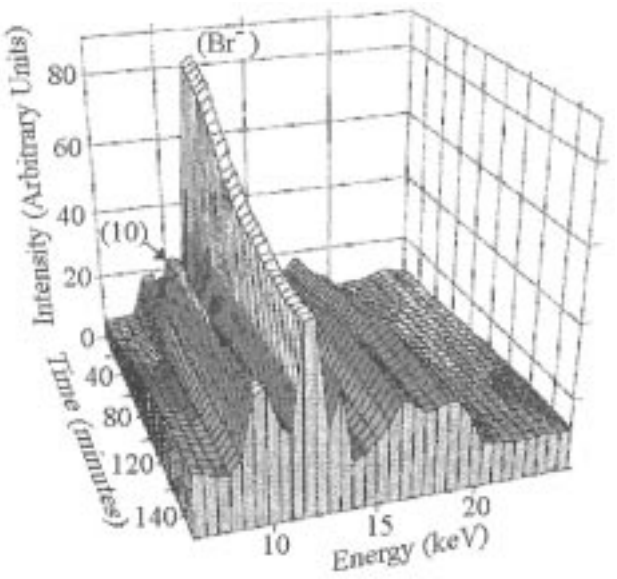

Figure 1. Time-resolved energy dispersive X-ray pattern for as-synthesised MCM-41 heated in situ from 298 to 543 K at a heating rate of 2 K min^{-1}.

3. Results and discussion

3.1. Characterisation

As-synthesised pure silica MCM-41 exhibited a very strong reflection at 3.87 nm and weak reflections at 2.24,

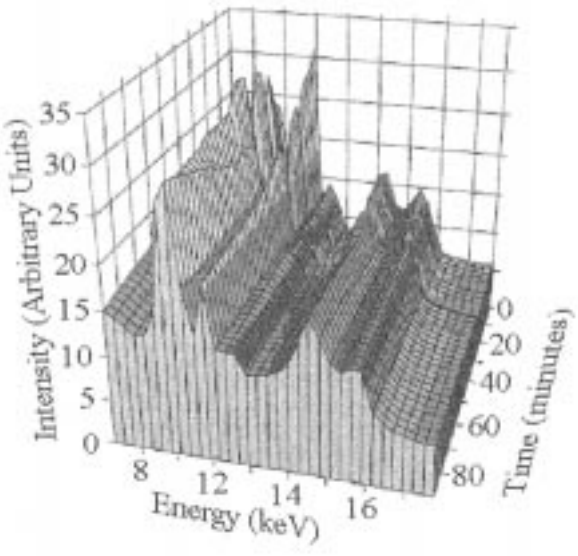

Figure 2. Time-resolved energy dispersive X-ray pattern for MCM-41 heated in situ from 328 to 623 K at a heating rate of 5 K min^{-1}. This was a continuation from the experiment shown in figure 1 after cooling the sample and realignment.

1.94 and 1.46 nm from ADXRD measurements. These four peaks can be indexed on a hexagonal unit cell with $a = 2d_{100}/\sqrt{3} = 4.47$ nm. The calcined MCM-41 sample exhibited a very strong reflection at 3.65 nm and weak reflections which were not resolved (retention of the hexagonal $hk0$ indexing: $a = 4.21$ nm), indicating a lattice contraction of about 0.26 nm upon calcination. These results were similar to those reported previously [3,5].

Figure 1 shows the time-resolved in situ EDXRD results for as-synthesised MCM-41 during heating from room temperature to 543 K at a rate of 2 K min^{-1}. The large peaks at 11.7 and 13.2 keV were assigned to bromine atom fluorescence which is present in the template. As the sample was heated to higher temperatures, the intensity of the peak at 11.7 keV decreased. The experiment was stopped at 543 K and the bromine atom fluorescence peak was still present, indicating that the template had not completely decomposed at 543 K. In a second experiment, the sample was cooled down to room temperature, and during a 140 min interval the X-ray beam was realigned to ensure optimum resolution throughout the experiment. The sample was then heated to 623 K at a rate of 5 K min^{-1} (see figure 2). The intensity of the bromine atom fluorescence peak decreased with increasing temperature due to further removal of the template. The in situ EDXRD revealed that a trace of bromine remained in the sample even after calcination at 623 K. This may be important when considering the heterogeneity of the material [12]. The peak at 8.77 keV due to the hexagonal geometry (100) was shifted to higher energy (9.97 keV), which was attributed to the contraction in the lattice size according to the equation $E = 6.199/d \sin\theta$. The peaks were sharp and well resolved and an accurate lattice parameter, $a = 4.54$ nm, for a hexagonal structure with P1 symmetry was obtained for as-synthesised MCM-41, shifting to 3.99 nm on calcination at 623 K. The change in the lattice size of microporous molecular sieves (example, VPI-5) upon calcination or dehydration in comparison was very low [13].

The TEM image results of the calcined MCM-41 revealed the regular hexagonal array of uniform channels with a diameter of ca. 3 nm.

Figure 3 shows the TGA curve for as-synthesised MCM-41 in N_2(g). Three distinct stages of weight loss were observed, 298–418 K (due to desorption of water), 418–673 K (due to decomposition of the template) and above 673 K (due to water loss via condensation of silanol groups to form siloxane bonds). The MCM-41 sample showed a weight loss above 50% due to water and organic matter which indicated that the majority of the template was removed by heating to 653 K. These results are in good agreement with those reported by Chen et al. [4].

Figures 4A, 4B show the in situ DRIFT spectra of as-synthesised MCM-41 heated from room temperature to 673 K. The broad band between 1000 and 1250 cm^{-1}

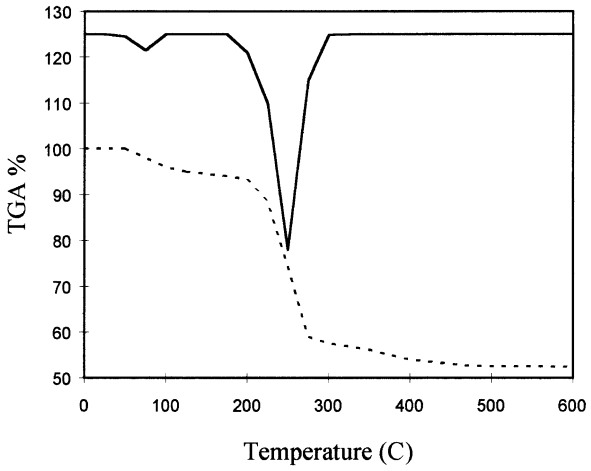

Figure 3. Simultaneous thermal analysis of as-synthesised MCM-41, TGA (- - -) and DTA (——).

of as-synthesised MCM-41 (see figure 4A) consists of a main peak at 1057 cm^{-1} and three shoulders at 1040, 1140 and 1220 cm^{-1}. These features may be assigned to the asymmetric stretching of Si–O–Si bridges which is related to the transverse optic (TO) and longitudinal optic (LO) splitting of the in-phase mode, AS1, and the out-of-phase mode, AS2 [14]. At 298 K, the shoulder at

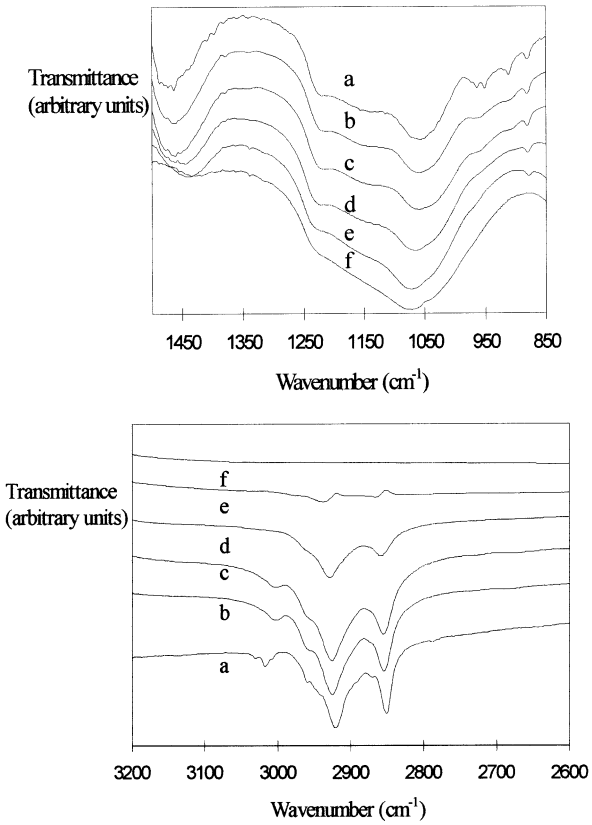

Figure 4. (A) Infrared spectra of as-synthesised MCM-41 at (a) 298 K, (b) 393 K, (c) 473 K, (d) 523 K, (e) 573 K, (f) 673 K. (B) Infrared spectra of as-synthesised MCM-41 (annotation as in (A)).

1220 cm^{-1} can be assigned to the AS2 mode and the peak at 1057 cm^{-1} to the AS1 mode. The peak at 1057 cm^{-1} was shifted by 14 cm^{-1} on heating to 673 K. This shift may be attributed to the strengthening of coulombic interactions within the amorphous silica network which resulted from a greater number of Si–O–Si bridges from the increased condensation of silanol groups [14]. Also, this shift is assigned to the shrinkage of the pore structure on heating from 4.54 to 3.99 nm which was observed by in situ EDXRD results (see figures 1 and 2). Infrared bands were also observed at 720–740 and 1400–1500 cm^{-1} from aliphatic C–H bending and at 2800–3100 cm^{-1} from aliphatic C–H stretching vibrations of the template (see figure 4B). The C–H vibrations from the template decreased with increasing temperature and disappeared at 673 K indicating that all the template had been removed. The water bending band at 1645 cm^{-1} and broad band at 3400 cm^{-1} associated with hydrogen-bonded silanol groups were also reduced with increasing temperature.

3.2. Catalytic activity

Pd was chosen as the active material because of its particular suitability for hydrogenation of olefins and cost-effectivity. Figure 5 shows the performance of a dried Pd/MCM-41 catalyst series for 1-hexene hydrogenation at room temperature (298 K) as a function of time-on-stream. The conversions were calculated to allow a ready comparison between the dry Pd catalyst series. The 0.5, 1.0 and 2.0 wt% Pd-MCM/D catalysts showed 100% hexene conversion over 60 min with 100% selectivity towards hexane as the final product, while the 0.25 wt% Pd-MCM/D catalyst showed about 80% conversion with 97% selectivity towards hexane and about 3% selectivity towards the mixture of the cis- and trans-2-hexene isomers. Similar catalytic performance was obtained for the calcined Pd (Pd-MCM/C) catalyst series as shown in figure 5. The pure calcined MCM-41 showed no hydrogenation activity at room temperature (298 K). The conventional hydrogenation catalyst Pt/SiO_2 gave good conversion rates, although side products such as cis- and trans-isomers were formed [15].

1% Pd-MCM/D and 1% Pd-MCM/C catalysts were chosen for the selective hydrogenation of benzene to form cyclohexane. Similar pretreatments were applied as before to reduce the catalyst samples. Both catalysts showed no hydrogenation activity at an inlet reaction temperature of 298 K. Increasing the reaction temperature to 343 K also showed no activity (see figure 6). At an inlet reaction temperature of 353 K, both catalysts showed similar activity with conversions of 10% (see figure 6). The outlet reaction mixtures were analysed with GC-MS and showed a mixture of benzene (unreacted), cyclohexane (completely saturated), 1-cyclohexene and 1,3-cyclohexadiene (partially saturated).

These results showed that the inlet reaction temperature of 373 K was just beginning to initiate the hydrogenation of benzene, and higher temperatures would be necessary to obtain higher conversions. By contrast, room temperature would be enough to initiate the hydrogenation of 1-hexene. The pure MCM-41 showed no activity for hydrogenation of benzene either at room temperature or at higher temperatures (up to 353 K).

Borghard et al. [16] studied the hydrogenation of benzene using 1% Pd/MCM-41–Al_2O_3 catalysts, with Pd/SiO_2 and Pd/ZSM-5 catalysts being tested for comparison. At a reaction inlet temperature of 373 K, H_2/benzene molar ratio 100 : 1, and at atmospheric pressure, it was found that Pd/MCM-41–Al_2O_3 showed higher activity to form cyclohexane than Pd/SiO_2 and Pd/ZSM-5 catalysts. The Pd dispersion is higher on the MCM-41 material than the SiO_2 and ZSM-5 materials.

Our catalytic performance results were due to the fact that the $Pd(NH_3)_4Cl_2$ (i.e. Pd^{2+}) on the surface of the MCM-41 support (in the case of dried catalysts) and PdO (i.e. Pd^{2+}) on the surface of the MCM-41 support (in the case of calcined catalysts) were reduced complete-

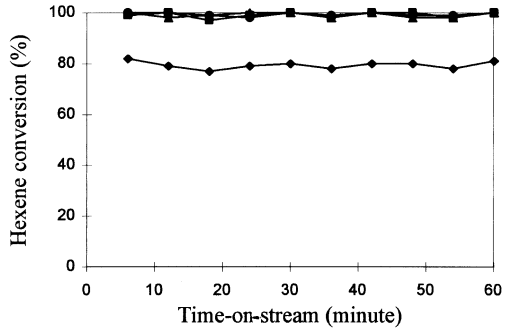

Figure 5. Plot of conversion versus time-on-stream for the selective hydrogenation of 1-hexene catalyzed at an inlet reaction temperature of 298 K by: 0.25% Pd-MCM/D (◆), 0.5% Pd-MCM/D (●), 1.0% Pd-MCM/D (■) and 2.0% Pd-MCM/D (▲).

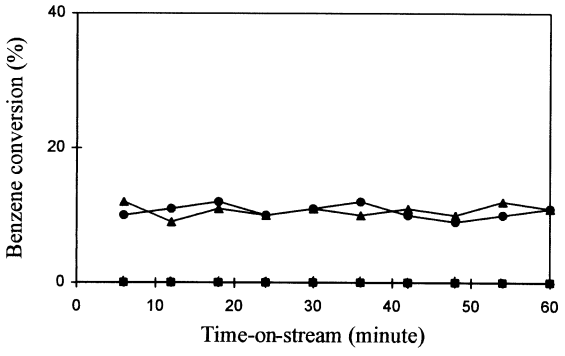

Figure 6. Plot of conversion versus time-on-stream for the selective hydrogenation of benzene catalyzed by: (■) 1.0% Pd-MCM/D, $T = 343$ K; (◆) 1.0% Pd/MCM/C, $T = 343$ K; (●) 1% Pd-MCM/D, $T = 353$ K; and (▲) 1% Pd-MCM/D, $T = 353$ K. T is an inlet reaction temperature.

ly to the Pd metal during the pretreatment in a flow of H_2/N_2 gas mixture at 373 K. Our temperature-programmed reduction (TPR) measurements for the calcined Pd (Pd–MCM/C) catalyst series (in a flow of 6% H_2/Ar gas mixture at heating rate 5 K min^{-1}) showed that about 70% of the PdO contained in the catalysts were reduced at sub-ambient temperature and the other 30% of PdO were reduced within 298–323 K [17], while the pure MCM-41 showed no reduction up to 873 K. The pretreatment of the dried and calcined Pd catalysts in the reactor in a flow of H_2/N_2 gas mixture at 373 K for one hour was more than enough therefore, to reduce the whole $Pd(NH_3)_4Cl_2$ and PdO on the surface of the supports to Pd metal. The above activity results showed that the Pd species were well dispersed on the surface of the MCM-41 for both dried and calcined catalysts.

TEM results for the reduced Pd/MCM-41 catalysts revealed that the average Pd particle size was around 2–2.5 nm and these particles were located in the pores of MCM-41 and showed good distribution, which was in agreement with the activity results. These small Pd particles probably formed the active sites for hydrogenation and played the predominant role in reaching the higher conversions. The higher performance of Pd/MCM-41 catalysts for selective hydrogenation of 1-hexene was also attributed to its high surface area and also to its mesoporous structure which favours a high distribution of Pd metal.

4. Conclusions

Careful material preparation and characterisation is needed in order to take advantage of these properties. In this work we have carried out such a synthesis and characterisation of MCM-41,and have examined the activity of Pd/MCM-41 for two hydrogenation reactions.

Our characterisation studies indicate there is a lattice contraction of MCM-41 on calcination which is accompanied by a loss in silanol density via condensation of Si–OH groups. Selective catalytic hydrogenation of 1-hexene using Pd on a MCM-41 mesoporous support was achieved at 298 K. No activity was detected at this temperature in the case of hydrogenation of benzene, however. TEM results showed that the Pd metal particles in the reduced Pd/MCM-41 catalysts were located in the pores of MCM-41 with good distribution.

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