Synthesis of nanosized platinum cluster in cubic mesoporous material via a direct introduction method

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Platinum-cluster-containing cubic mesoporous material (Pt-MCM-48) has been synthesized by direct introduction of chloroplatinic acid during the synthesis of MCM-48. In addition, we have also studied the incipient wetness impregnation and ion-exchange method to obtain the platinum-containing cubic mesoporous material. The nature of the platinum-MCM-48 catalyst has been characterized by different techniques such as XRD, N_2 adsorption, TEM, XPS, and NMR. The catalyst obtained by direct introduction of platinum in the synthesis gel shows higher activity in the hydrogenation of benzene and toluene.

Keywords: MCM-48, direct incorporation, incipient wetness impregnation, dispersion, hydrogenation

1. Introduction

The development of ordered mesoporous material (M41S) containing different hetero atoms in the pore walls has opened a new possibility for the use of mesoporous molecular sieve materials in the field of catalysis [1–7]. Mesoporous materials have channels with regular pores modulated in some cases from 1.5 to 7 nm and ordered in a hexagonal (MCM-41), cubic (MCM-48), or lamellar (MCM-50) array. They represent a new class of molecular sieve type materials with extremely narrow pore size distribution in the mesoporous region, long range order, high surface area ($>$700 $m^2\,g^{-1}$) and are stable after calcination. Most of the studies in this area deal with the molecular sieve MCM-41 related structure. In contrast, little is known about the cubic-phase MCM-48 [8,9] and the influence of isomorphous substitution on its properties. In terms of the diffusion and catalytic point of view, MCM-48 is the most interesting material in comparison to the one-dimensional channel of MCM-41. MCM-48 has its pore architecture built up of two independent tridirectional channel systems. In the field of catalytic reactions such as aromatization, hydrocracking, and hydrogenation platinum-loaded zeolites are the most effective. The mesoporous aluminosilicate MCM-41 has already been proved to be a suitable support for preparing noble-metal-based catalysts. Inui et al. [10] supported Pt by impregnating H_2PtCl_6 on FSM-16 synthesized from kanemite, which seemed to be identical to MCM-41. The supported platinum was useful for hydrogenation of olefins. However, dispersions of noble metal to the cubic mesoporous system using a hydrothermal method have not been studied yet. This seems due to the less reliable synthesis of MCM-48 compared to MCM-41. According to previous reports [11–15], the synthesis of a cubic mesophase depends on the surfactant concentration, silica source and pH of the gel. Herein we report in detail the synthesis of MCM-48 containing highly dispersed platinum. We have systematically studied the formation of the cubic structure of MCM-48 containing platinum. These achievements certainly open the way for finding more possibilities for the use of MCM-48 as an effective catalyst.

2. Experimental

We attempted the synthesis of this cubic mesoporous material by varying the concentration of surfactant. Using chloroplatinic acid as the platinum source Pt-MCM-48 molecular sieve was successfully obtained from gels with the following molar composition $1SiO_2 : 0.61CTABr : 0.25Na_2O : x PtO : 61H_2O$, where $x = 0.0025$–0.02. The synthesis of highly-dispersed-Pt-containing MCM-48 was carried out under hydrothermal condition. In a typical synthesis platinum salt solution was added to the surfactant solution containing NaOH. The resulting solution was stirred for 30 min. Tetraethylorthosilicate was added dropwise to the above solution containing CTABr, H_2PtCl_6 solution and H_2O under stirring and stirred for another 1 h. The resultant gel was then loaded into a Teflon-lined stainless-steel autoclave and heated at 100 °C for 72 h in static condition. The solid product was recovered by filtration, washed extensively with water and dried at ambient temperature. The occluded organic was removed by heating the materials in air at 550 °C for 10 h. It has been found that the cubic mesoporous phase was formed with surf/Si ratio 0.45–0.61 containing platinum. In presence of platinum with increasing surf/Si ratio above 0.61 the structure was transformed to a lamellar one. A lower ratio of surf/Si leads to the formation of a hexagonal phase at room temperature and converted to

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a lamellar phase after hydrothermal treatment. In addition to the above method, we also studied the incipient wetness impregnation and ion-exchange method. Incipient wetness impregnation was carried out using platinum solutions of appropriate concentrations. The impregnated samples were dried at different temperatures between room temperature and 773 K. For ion exchange 0.1 M solutions were used at various pH values and different exchange times at room temperature. Samples with Si : Al of 40 and a BET surface area 1060 $m^2\,g^{-1}$ were used for impregnation and ion exchange. All methods of platinum incorporation resulted in platinum-containing catalysts. However, the achievable loading was dependent on the preparation method. By direct incorporation via the synthesis gels about 60% of the Pt were incorporated into the final catalyst upto the highest loading investigated.

3. Results and discussion

In the case of direct introduction of platinum reduced platinum species were found in the resultant product since during calcination template can act as a reducing agent. The samples obtained by the other methods required reduction of platinum in a flow of hydrogen (60 ml min^{-1}) at 400 °C for 3 h.

An X-ray powder diffraction pattern of a typical calcined material is depicted and indexed in figure 1. The diffractogram of Pt-MCM-48 sample presents eight reflections, which seems to be a minimum requirement for a high quality cubic mesoporous structure. Direct addition of the platinum compound did not affect the formation of mesoporous material. In all cases a cubic structure was identified for Pt-MCM-48 that resembled MCM-48 consisting of pure silica, as described in the literature [16]. No platinum lines were observed in the X-ray diffractogram of Pt-MCM-48 indicating either the clusters are too small for detection, they are inside the pores or they are highly dispersed and amorphous.

Further evidence is provided by the transmission electron micrograph (TEM), which shows the cubic structure with platinum clusters in the material. Figure 2 shows images of the calcined sample obtained by the above method. The good distribution of platinum clusters represented by black dots was observed. Particle sizes obtained with the three preparation methods varied substantially. For *in situ* loading during the synthesis the average particle size was around 4–5 nm. The Pt particles coalesce to form a crystallite after the removal of template by calcination. For the sample prepared by ion exchange and the incipient wetness method, the platinum crystallites are around 10 and 4–20 nm, respectively.

The N_2 adsorption–desorption isotherm is of type IV (figure 3). Prior to the experiment, the samples were degassed at 300 °C for one night. The specific surface area, A_{BET}, was determined from the linear part of the BET plot

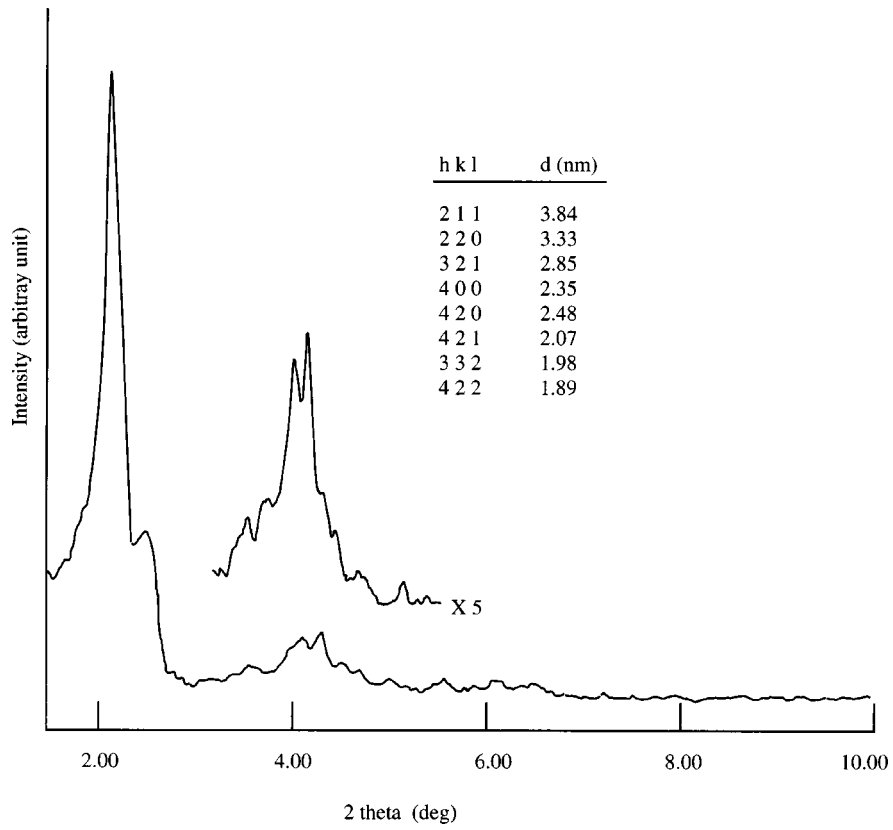

Figure 1. Powder X-ray diffraction pattern of the calcined form of the Pt-MCM-48 sample.

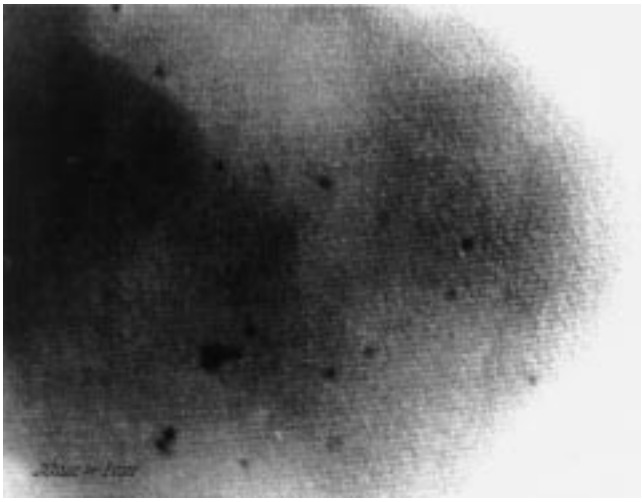

Figure 2. TEM image of Pt-MCM-48 after calcination (Si/Pt = 200).

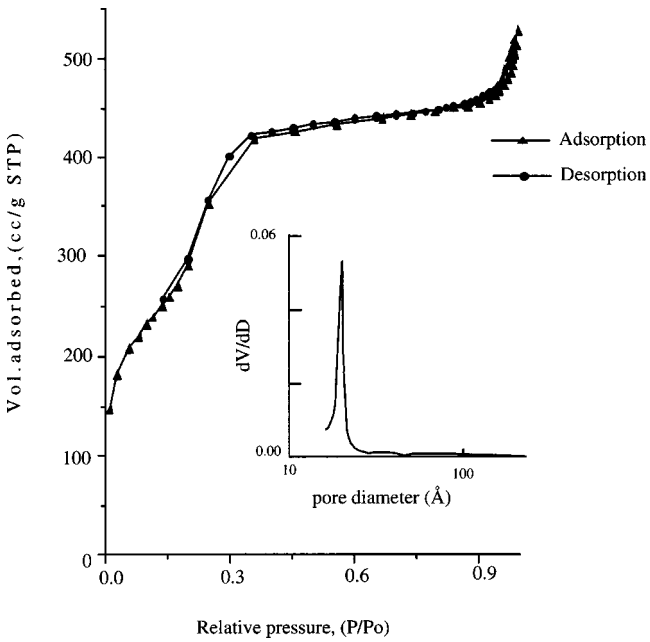

Figure 3. N_2 adsorption–desorption isotherm with insert showing the BJH pore size distribution.

($p/p_0 = 0.05$–0.30). The mesopore size distribution (PSD) was calculated using desorption branches of the N_2 adsorption isotherm and the Barrett–Joyner–Halenda (BJH) formula. The p/p_0 coordinate of the isotherm inflection point depends on the pore size. The sharpness in this step suggests a uniform size pore system (shown in figure 3). The average pore diameter of the sample determined was 35.2 Å and BET surface area was 1025 $m^2\,g^{-1}$.

The location of platinum particles may be deduced from the analysis of XPS spectra shown in figure 4. The Pt 4f and 4d core levels are suitable for the XPS study of Pt-containing materials. Unfortunately, the 4d lines are rather broad and unsuitable for the purpose of identification of the metal oxidation state and line shape analysis. According to figure 4(a), the Pt $4f_{7/2}$ and $4f_{5/2}$ binding energies

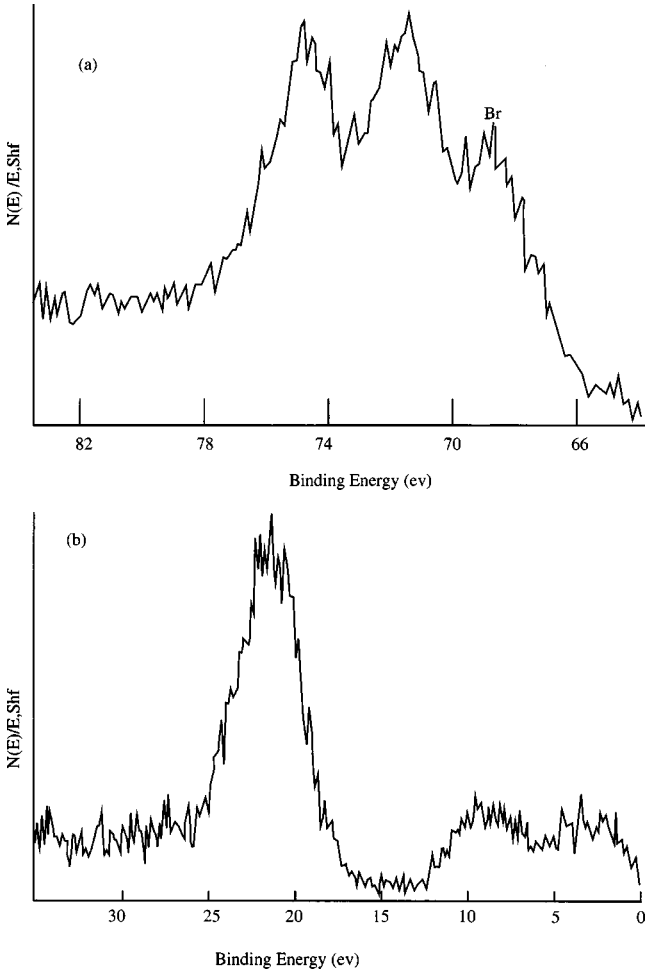

Figure 4. XPS spectra of platinum-loaded MCM-48: (a) 4f electrons, (b) valence band region.

are 72.0 and 74.8 eV, respectively. The binding energy was then compared with the platinum foil ($4f_{7/2}$ and $4f_{5/2}$ are 71.0 and 74.1 eV, respectively) under the same condition. The Pt $4f_{7/2}$ and $4f_{5/2}$ core level binding energies indicate an apparent positive chemical shift with respect to the sputtered Pt films ($4f_{7/2}$ and $4f_{5/2}$ are 71.3 and 74.6 eV, respectively) [17] and platinum foil. Such a positive shift was also postulated for highly dispersed platinum on silica [18]. Figure 4(b) represents the XPS spectra of the valence band region (binding energy 0–10 eV). In this region, the principal contributions to the photoelectron spectra suffered extensive molecular (orbital) or solid (band) involvement. The accumulation of states observed in the region 5–10 eV probably does not represent the atomic states. The structure in the 5–10 eV region may be interpreted either as a surface state or as a bonding state representing Pt–support bonding [18]. In either case, this structure is due to very small platinum crystallites having large fraction of atoms as surface atoms located along metal–support interfaces.

The ^{29}Si MAS NMR spectrum of the as-synthesized sample was dominated by the line at -101.5 ppm (Q3) and a comparatively low portion of Q4 signal. As there was no change in the intensity Q4 signal substitution can-

not be predicted. ^{1}H–^{29}Si CP MAS NMR of Si-MCM-48 and Pt-MCM-48 shows a marked increase in the relative intensity of the Q3 line (−101 ppm), in comparison with ^{29}Si MAS spectra. It confirms that the silicon atoms are attached to the hydroxyl group [19]. The Q3 : Q4 ratio of ^{29}Si MAS spectra of Pt-MCM-48 is identical with that of ^{29}Si MAS spectra of Si-MCM-48, confirming the dispersion of platinum species.

As a first catalytic test the hydrogenation of benzene and toluene was carried out in a pulse microreactor with the flow rate of hydrogen always being 50 ml/min. 20 mg of catalyst was heated at 500 °C for 3 h. This was followed by the injection of the 0.5 μl of the aromatic into the catalyst bed. The reactants and products were analyzed by an on-line gas chromatograph. The results of hydrogenation of aromatics indicate that the activities of the catalyst mainly depend on the method of synthesis. This classification of the catalyst may be due to the difference in size of the platinum crystallites. It has been found that the catalyst obtained by direct incorporation of Pt in the synthesis gel shows 50% conversion at 200 °C for benzene and 30–35% conversion of toluene. The catalyst obtained by the impregnation method also shows better activity (35% conversion at 200 °C for benzene) and in the case of the ion-exchange sample at 200 °C 10–12% conversion of benzene has been found. The investigation concerning different parameters of hydrogenation reaction is still going on.

4. Conclusion

In conclusion, it has been proven that it is possible to synthesise the cubic mesoporous material containing noble metal in a very selective way. The Pt-MCM-48 produced shows higher activity in hydrogenation of benzene and toluene and the activity of the catalyst depends on the method of synthesis.

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