

MCM-41 as a Support for Small Platinum Particles: A Catalyst for Low-temperature Carbon Monoxide Oxidation

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MCM-41 is loaded with platinum *via* different pathways, resulting in highly active oxidation catalysts.

MCM-41 was discovered in 1992 by Mobil Corporation scientists.¹ As a result the catalytic properties of MCM-41 type materials containing heteroelements in the walls of the pores have been investigated as oxidation catalysts by several groups,^{2,3,4} as well as the properties of the pure aluminosilicates as acidic catalysts.⁵ However, MCM-41 has only recently been studied as a support, supporting NiMo in a hydrocracking reaction.⁶ This is surprising since MCM-41 has excellent properties as a catalyst for these applications: it is thermally stable up to 1300 K and has surface areas of $\leq 1500 \text{ m}^2 \text{ g}^{-1}$. We therefore attempted to synthesise Pt-containing MCM-41 samples by different pathways and studied their catalytic performance using CO oxidation in air as a test reaction.

In addition to the conventional methods for incorporation of platinum, we also studied the direct introduction of platinum during the synthesis of the MCM-41 by incipient wetness impregnation and ion exchange. In a typical synthesis the platinum salt was added to 12.3 g of hexadecyltrimethylammonium chloride solution (Aldrich, aq. solution, 25 mass%) and stirred for 1 h. 1.54 g of Aerosil 200 (Degussa) was then rapidly added, followed by dropwise addition of a solution of 2.24 g sodium water glass (Woellner) in 12.3 g of water. The resulting mixture was stirred for a further 1 h before being placed in a preheated oven at 363 K for 3 d using sealed polypropylene bottle reaction vessels. The resulting solid was filtered and thoroughly washed, dried at 363 K overnight and then calcined at 823 K for 5 h. As platinum precursors three differently charged compounds were used, the neutral $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ complex, the positively charged $[\text{Pt}(\text{NH}_3)_4]^{2+}$ as the nitrate, and the negatively charged $[\text{PtCl}_6]^{2-}$ as the potassium salt. Nominal loadings were varied between 1 and 5% by mass.

Incipient wetness impregnation was carried out using solutions of $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ of appropriate concentrations. The impregnated samples were dried at different temperatures between room temperature and 673 K. For the ion exchange 0.1 mol dm^{-3} solutions of $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ were used at different solution-to-solid ratios, various pH-values and exchange times at room temperature. Exchange under reflux was also attempted, but the results were not satisfactory due to partial structural collapse of the MCM-41 after prolonged heating. For both methods of impregnation, samples with Si:Al of 17 and a BET surface area of around $500 \text{ m}^2 \text{ g}^{-1}$ were used.

All methods of platinum incorporation resulted in platinum containing catalysts. However, the achievable loadings, as analysed by X-ray fluorescence, were dependent on the preparation method. Ion exchange resulted in a maximum loading of around 1 mass% which is appreciably lower than the maximum loading, assuming 100% exchange and one platinum atom per aluminum atom. Probably not all the aluminum atoms in the material create an ion exchange site. Using direct incorporation *via* the synthesis gel, about 80% of the $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ was incorporated into the final catalyst up to the highest loading investigated. With $[\text{Pt}(\text{NH}_3)_4]^{2+}$ as the precursor 30–50% incorporation was achieved. The incorporation of $[\text{PtCl}_6]^{2-}$ was dependent on the loading: for high nominal loadings around 5 mass% about 50% were incorporated while at

nominal loadings of 1 mass% only 15% of the platinum was found in the final catalyst.

The samples were reduced in a flow of hydrogen (60 ml min^{-1}) at 673 K to reduce the Pt. However, CO-adsorption monitored by IR-spectroscopy revealed that a major fraction of the Pt is already in the oxidation state zero prior to reduction in H_2 , as evidenced by the absorption band around 2080 cm^{-1} . During the calcination, an autoreduction of the Pt-complexes probably occurs. Moreover, in the case of samples loaded *in situ* during the synthesis, reducing conditions are present during the calcination since the template can act as a reducing agent at elevated temperatures.

The addition of platinum compounds to the synthesis mixture for MCM-41 did not affect the formation of the mesoporous material. In all cases samples containing the hexagonal phase were obtained with at least three well resolved peaks in the X-ray diffraction pattern [(100), (110), (200)]. In the wide-angle region very broad peaks corresponding to the Pt(111), (200) and (220) reflections could be identified (Fig. 1).

The line broadening of the peaks was used to determine particle sizes, applying the Scherrer formula and assuming strain free crystallites. In addition, transmission electron micrographs were taken from several selected samples in order to check the X-ray analysis and to obtain information on the distribution of the Pt-crystallites in the samples. Particle sizes obtained with the three preparation methods varied substantially. For the *in situ* loading during the synthesis the final average particle size was around 6 nm for the $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ precursor, calculated from the X-ray line broadening. TEM (Fig. 2) revealed that the smaller (4 nm) crystallites were located in the pores of MCM-41 and the larger crystallites were on the external surface or at defects of the MCM-41 particles. The average particle size of the Pt-crystallites obtained from the charged precursors were higher at up to *ca.* 10 nm. The fact that the neutral precursor results in the formation of the smallest particles could be explained in terms of the model of MCM-41 formation put forward by Monnier *et al.*⁷ During the synthesis

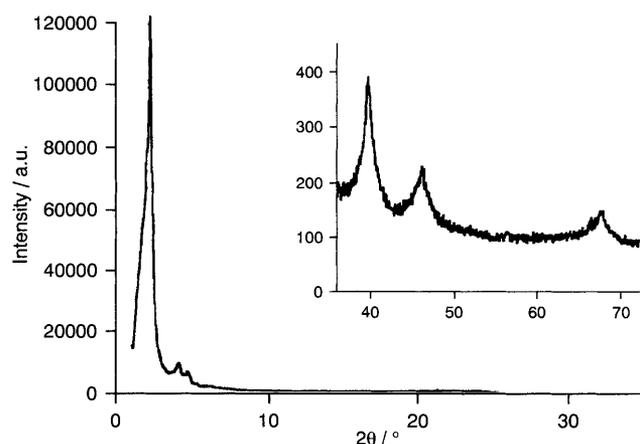


Fig. 1 X-Ray diffraction pattern of Pt-MCM 41, prepared by *in situ* loading with *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, 5 mass%

the neutral complex is located in the hydrophobic part of the composite and the individual Pt species are fairly well separated. When the template is removed by calcination, only the Pt-particles within one pore coalesce to form a crystallite. This Pt-dispersion is then very stable. At 823 K no further coalescence of the crystallites occurs.

For the samples prepared by ion exchange the Pt-crystallites are around 10 nm, with little or no change with the exchange conditions. The incipient wetness impregnation results in a

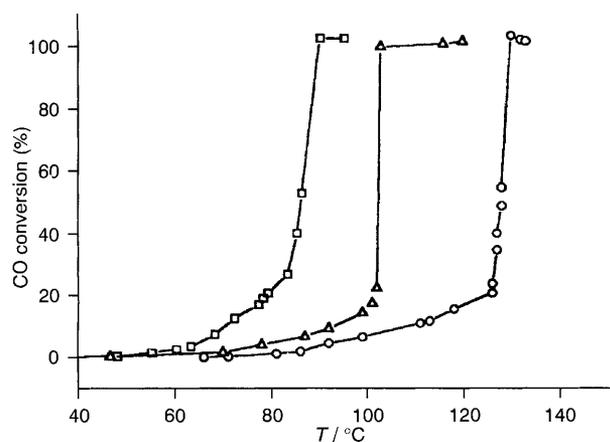


Fig. 3 Activity of Pt-MCM 41, CO conversion vs T , \square incipient wetness, \triangle ion-exchange, \circ *in situ*

bimodal crystallite size distribution, with Pt-particles of *ca.* 20 nm and very small particles of *ca.* 2 nm. The ratio between these two sizes of Pt particles varies with varying loading: At higher loadings above 4 mass% the amount of the 2 nm particles is almost constant and independent of the loading. With increasing loading only the fraction of large particles, which are not located in the mesopores, increases. However, if the loading is reduced to 2 mass% the amount of smaller crystallites also decreases and larger particles still exist even at these relatively low loading levels.

As a first catalytic test the oxidation of CO with synthetic air in an open flow reactor at a gas hourly space velocity of 25 000 h^{-1} was investigated. In Fig. 3 the performance of three catalysts, typical for each synthesis pathway, are compared. All catalysts are clearly very active in this reaction since the temperatures at which full conversion is reached are remarkably low. Many different catalysts for each synthesis pathway have been analysed. As in the case with the Pt-crystallite sizes, the strongest influence on the catalytic performance is the general method of preparation, *i.e.* *in situ* incorporation vs. ion exchange vs. incipient wetness. The catalysts can clearly be divided into three classes according to their method of preparation where the catalytic activity is markedly different for each case. The least active catalysts are obtained by the ion exchange procedure, corresponding well to the relatively large average Pt-crystallite size. All ion exchanged catalysts reach 50% conversion at around 400 K with deviations of only around ± 5 K for different conditions during the ion exchange. The catalysts prepared by the *in situ* incorporation of the Pt-species reach 50% conversion at around 375 K, again with only little deviations within this group. However, the temperatures for 50% conversion are systematically lower for the materials prepared with the neutral Pt-complex by about 5 K as compared to the charged species, again in agreement with the smaller Pt-crystallite sizes. The best performance was achieved over the samples prepared by incipient wetness, where 50% conversion was reached at temperatures as low as 360 K. Here the very small Pt-particles of around 2 nm most probably play the predominant role in reaching the high conversions.

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