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Effect of Pt Particle Size on H/D Exchange of Methane over Alumina- and Zeolite-supported Catalysts

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Deuterium exchange in methane was studied over a series of Pt/Al_2O_3 and Pt/mazzite catalysts. The reaction proceeds by a simple stepwise mechanism with CH_3D being the primary product. Large and small metal particles located in zeolite and alumina catalysts have different catalytic activity with respect to deuterium exchange in methane. The rate of reaction per Pt atom was the same on the catalysts investigated for particles >15–20 Å and considerably lower than the rate of reaction on samples with smaller Pt clusters. The activity of small clusters of Pt (diameter <15–20 Å) depended on the nature of the support.

Alumina and mazzite zeolites modified by platinum are known to be effective catalysts for isomerization of alkanes.[1–3] Mazzite is a large-pore molecular sieve with one-dimensional porosity. The effective diameter of the channels in mazzite is *ca.* 7.4 Å.[3,4] The activity, selectivity and stability of these systems depend on the location, dispersion and electronic properties of the supported metal.

Various methods[2,5–9] are used nowadays to characterise metal dispersion and particle size in supported catalysts: chemisorption of probe molecules such as H_2 and CO, electron microscopy, EXAFS, *etc.* The admission of CO to highly dispersed catalysts could result in the agglomeration of primary metal clusters even at room temperature, restricting the application of this method.[5] The most reliable data are obtained from chemisorption of H_2, electron microscopy and EXAFS information on the first-shell coordination number.

For metal-containing zeolites additional problems arise. The determination of the dispersion of platinum in supported catalysts by H_2 adsorption is usually based on the assumption of 1 : 1 stoichiometry of chemisorption relative to the number of accessible metal atoms. However, this hypothesis is questionable for zeolites with high metal dispersion.[7,8]

Recently the state of the metal in some supported catalysts has been characterised by using catalytic test reactions. Benzene hydrogenation is a useful tool for estimating the dispersion of platinum in supported Pt/Al_2O_3 catalysts.[10] Sachtler and co-workers[11–13] proposed methylcyclopentane transformations for testing the acidity and the state of the metal in Pt-containing zeolite catalysts. Ring-opening hydrogenolysis of methylcyclopentane is predominantly a metal-catalysed reaction, whereas ring enlargement requires support acidity. *n*-Pentane isomerization on Pt/L zeolites is a linear function of the particle size of platinum cluster.[14] Meanwhile, zeolites are characterised by a system of pores and channels the diameter of which is very close to the size of the catalytic test molecules. This is why some of the Pt clusters located in small cavities might be unable to catalyse transformations of large molecules.

Deuterium exchange in methane is recognised as a valuable probe for estimating the surface composition of alloys[15] and supported bimetallic catalysts. Kemball and co-workers[16] showed that the metal composition of Pt–Ir alloys strongly influences the selectivity of the exchange. For silica-supported Pt–Ru catalysts a linear dependence between the turnover frequency of methane exchange and the content of Pt in the bimetallic catalysts was found.[17] The main advantage of using deuterium exchange in methane for determining metal dispersion in porous systems is due to the small molecular size of CH_4 and D_2, which allows them to penetrate into the channels of most zeolites. We have performed some exchange experiments with H_2–D_2. Under the experimental conditions used the reaction kinetics were too fast to be measured with accuracy.

In the present study the deuterium exchange in methane is examined over a series of alumina-supported platinum catalysts and Pt-containing mazzite zeolites with different sized Pt particles.

Experimental

Catalyst Preparation

The alumina-supported Pt catalysts were prepared by anionic exchange of the hydroxy groups of Al_2O_3 with $PtCl_6{}^{2-}$ anions in a solution of H_2PtCl_6. After exchange these samples were calcined in air (723 K) and reduced in a flow of pure hydrogen (823 K). This treatment yielded catalysts with a dispersion of *ca.* 90%. By increasing the calcination temperature it was possible to obtain catalysts with a lower dispersion than 90%. The measurements of dispersion were carried out by hydrogen chemisorption.

The mazzite used in this work was synthesized and activated by the Centre de Recherche of ELF in Solaize according to the process described in ref. 3. After these treatments the Si : Al ratio in the framework was *ca.* 20 and the Si : Al total ratio was *ca.* 12. The introduction of Pt into mazzite was performed by cationic exchange with $Pt(NH_3)_4Cl_2$ solution. Calcination (723–823 K) and reduction at 823 K yielded the 1PtMaz sample which had a high metal dispersion. The other Pt/Mazzite samples were prepared by treating 1PtMaz with water vapour at 823 K ($P_{H_2O} = 33$ mbar). Varying the duration of this treatment (2–4 h) yielded samples with different metal dispersions. In the case of Pt/mazzite catalysts, the size of the metal particles and the dispersion were determined by transmission electron microscopy (TEM, Zeiss CEM 902, resolution 8 Å). Additional information on metal dispersion in zeolites was extracted from analysis of EXAFS data.[18]

Catalyst Characterisation

Pt/Al_2O_3 *Catalysts*

The dispersion of Pt in Pt/Al_2O_3 samples was measured using data on hydrogen chemisorption (Table 1). A Maccay model assuming that the shape of the particles can be approximated by a semicubooctahedron, as developed for surface clusters by Bellamy *et al.*,[19] was used for the calculation of average particle sizes, bulk Pt metal is known to

Table 1 Content and dispersion of Pt in alumina-supported catalyts

sample	Pt content (wt.%)	dispersion (%)[a]	average particle size/Å[b]
Al_2O_3	—	—	—
$1Pt/Al_2O_3$	0.3	3	∞
$2Pt/Al_2O_3$	0.3	7	∞
$3Pt/Al_2O_3$	0.3	10	>150
$4Pt/Al_2O_3$	0.3	25	57.5
$5Pt/Al_2O_3$	0.3	60	19.8
$6Pt/Al_2O_3$	0.3	71	14.0
$7Pt/Al_2O_3$	0.37[c]	85	10.0
$8Pt/Al_2O_3$	0.37[c]	91	8.0

[a] From H_2 adsorption. [b] For a model semicubooctahedron. [c] Rate of exchange for these samples were normalized for 0.3 Pt wt.%.

form cubic face-centred crystals. In the model of cubooctahedrons Pt atoms in clusters have a type of coordination that is very similar to Pt atoms in bulk metal. Previous calculations of the average Pt particle diameter from H_2 adsorption data gave values for Pt/Al_2O_3 close to the results obtained from electron microscopy.[20]

Pt/*Mazzite Catalysts*

As already mentioned, the determination of Pt dispersion by hydrogen adsorption may not give reliable results on zeolites. For this reason TEM and EXAFS were used to obtain complementary data on the average particle size and the size distribution.

The TEM measurements allowed determination only of the size of Pt particles which are >8 Å directly from microphotographs; however, the samples might contain smaller metal particles. Therefore the average particle size obtained from TEM could be overestimated, especially for highly dispersed systems. For 1PtMaz only particles smaller than 24 Å were observed. For 4PtMaz treated with wet hydrogen, particles with diameters from 8 to 40 Å were found. The histograms of particle size for 1PtMaz and 4PtMaz are shown in Fig. 1. The average particle size was evaluated from the histograms using the expression:

$$d_{av} = \Sigma\ N_i d_i / \Sigma\ N_i$$

where d_i is the particle diameter measured from TEM photographs and N_i is the number of particles with diameter d_i. The average particle sizes calculated from the histograms for 1PtMaz and 4PtMaz are listed in Table 2.

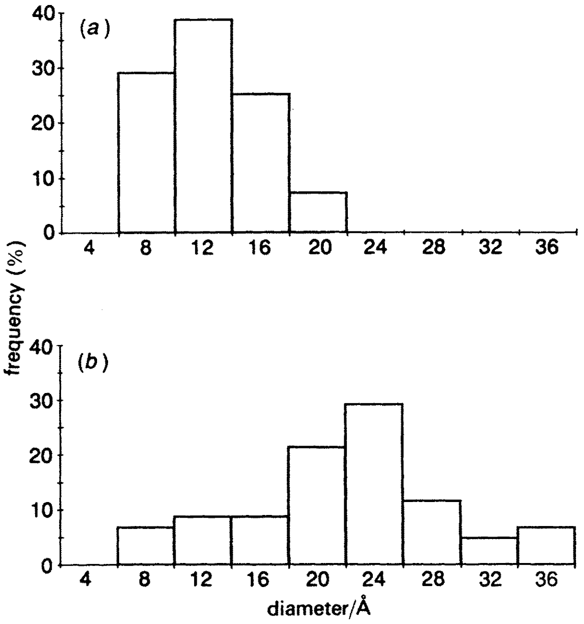


Fig. 1 Histograms of particle size for various Pt/Maz zeolites: (*a*) 1PtMaz, $d_{av} = 12.4$ Å; (*b*) 4PtMaz, $d_{av} = 22.3$ Å

Table 2 Pt content, TEM and EXAFS data for mazzite zeolites

sample	Pt content (wt.%)	average particle size/Å[a]	N_{Pt-Pt}
1PtMaz	0.3	12.4	3.7
2PtMaz	0.3	—	5.1
3PtMaz	0.3	—	6.4
4PtMaz	0.3	22.3	6.9

[a] From TEM. [b] From EXAFS; $\Delta N = 20\%$.

EXAFS experiments were carried out at LURE (Orsay, France) and are described in another article (EXAFS characterisation).[18] The main results concerned the N_{Pt-Pt} coordination number in the PtMaz samples shown in Table 2.

Deuterium Exchange in Methane

Before reaction, the samples were treated at 473 K under an excess of D_2 ($P_{D_2} = 1020$ mbar) in order to avoid the rapid exchange of the hydroxy group of the support with deuterium during the methane exchange reaction.

The exchange reaction was carried out at 460–508 K in a closed batch reactor linked to a mass spectrometer (IQ 200 Leybold). In order to avoid any transport limitation phenomenon, the circulation of gases was ensured by a pump with a flow rate of 2 l min^{-1}. The reactant gas was a mixture of 50–300 mbar of CH_4 and 50–300 mbar of D_2.

Results

No exchange of methane with deuterium was observed on the protonated form of mazzite zeolites and pure alumina at 460–500 K.

Catalytic transformation of methane and deuterium on Pt/alumina and Pt/mazzite catalysts at 460–500 K resulted in the formation of different deuteriomethanes. Typical distributions of the deuteriomethanes on $5Pt/Al_2O_3$ and 3PtMaz are shown in Fig. 2. At the beginning of the reaction only CH_3D was observed as a product. After 10 min CH_2D_2 appeared, followed by CHD_3. Analysis of the distribution suggests that CH_3D is likely to be the primary product and other deuteriomethanes can be considered as secondary products forming from CH_3D on alumina and zeolite catalysts. In this case a simple exchange process is in operation by the following stepwise mechanism:

$$CH_4 \rightarrow CH_3D \rightarrow CH_2D_2 \rightarrow CHD_3 \rightarrow CD_4$$

Assuming that all the hydrogen atoms in the molecule are exchangeable, and knowing that the influence of isotopes is negligible, the course of the reaction according to Kemball[21] can be followed either by means of the deuterium content in the hydrocarbons or by some parameter related to this quantity. Let x_i be the percentage of the deuteriomethane present as isotopic species $CH_{4-i}D_i$ at time t. If a parameter ϕ is defined by

$$\phi = x_1 + 2x_2 + 3x_3 + 4x_4$$

the mean deuterium content at any stage of the reaction is given by $\phi/4$. The exchange rate (per gram of catalyst) was calculated by multiplying $1/4(d\phi/dt)$ by the initial number of CH_4 molecules in the gas phase.

Fig. 2 clearly shows that at the very beginning of the exchange kinetics an appreciable amount of CH_3D is formed

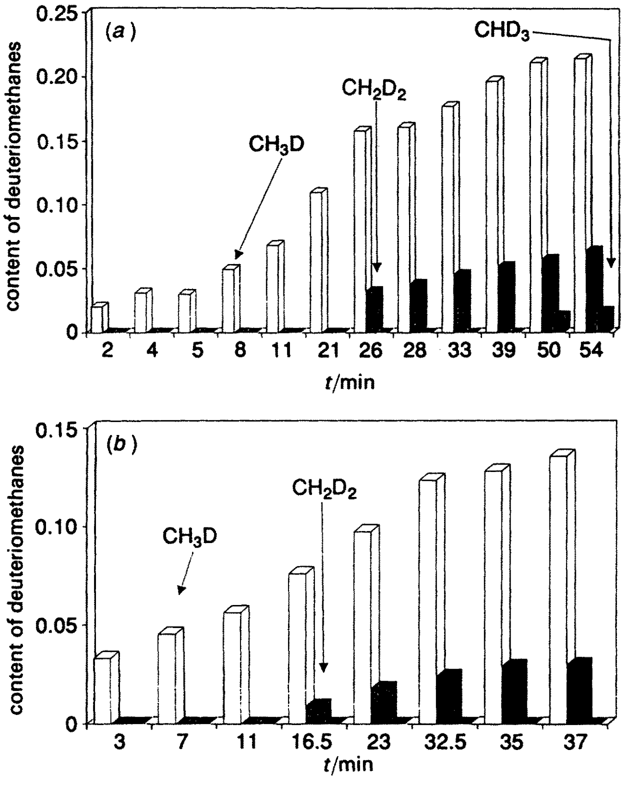


Fig. 2 Distribution of products for the exchange of methane on supported catalysts: (*a*) $5PT/Al_2O_3$, $T = 500$ K, $P_{CH_4} = P_{D_2} = 100$ mbar; (*b*) 3PtMaz, $T = 460$ K, $P_{CH_4} = P_{D_2} = 100$ mbar

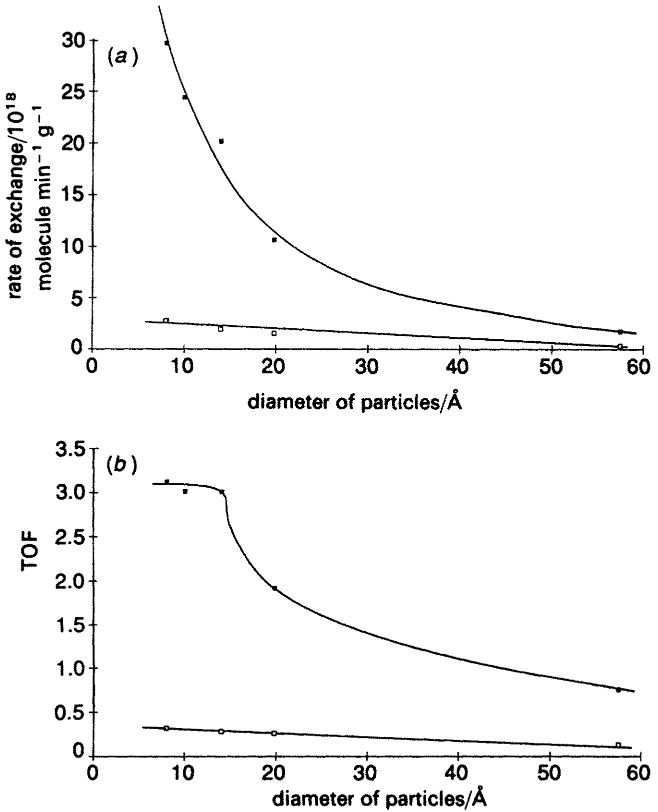


Fig. 3 Rate of deuterium exchange in methane (*a*) and turnover frequency (*b*) on Pt/Al_2O_3 with different particle sizes. $P_{D_2} = P_{CH_4} = 100$ mbar; T/K: □, 460; ■, 500.

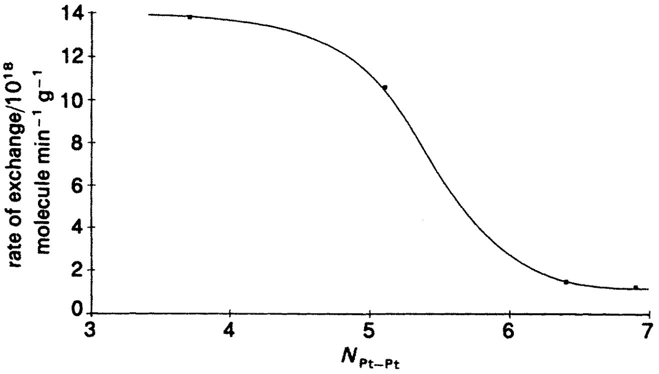


Fig. 4 Dependence of rate of the exchange on N_{Pt-Pt} in mazzites. $P_{D_2} = P_{CH_4} = 100$ mbar.

(*ca.* 4%). This was observed for all the catalysts studied and corresponds to the exchange of deuteriated hydroxy groups. Experiments performed in the absence of deuterium in the gas phase led to the conclusion that similar amounts of CH_3D could be measured, resulting from the reaction:

$$CH_4 + T{-}OD \rightarrow CH_3D + T{-}OH \quad \text{(where T is Al or Si)}$$

The partial orders of reaction were investigated for the $8Pt/Al_2O_3$ sample. The partial order of reaction assuming CH_3D to be the primary product with respect to deuterium was found to be -1 and close to 0.8 with respect to methane. These results are in agreement with the data of Kemball for Pt containing catalysts[21] and the results of Dalmon[22] and Frennet,[23] who studied the deuterium exchange in methane on Ni catalysts.

The dependence of the rate of exchange and turnover frequency (rate of exchange per Pt surface atom) on the particle size was compared at 460 and 500 K for alumina-supported catalysts (Fig. 3). The dependence of the rate of the exchange on N_{Pt-Pt} measured by EXAFS for mazzite catalysts at 460 K is shown in Fig. 4.

No marked change in selectivity of exchange was found as a function of metal particle size in the catalysts studied.

Discussion

We first examine the mechanism of the exchange reaction. As already mentioned, the order of appearance of the reaction products (Fig. 2) indicates that stepwise exchange is takes place preferentially. In our case (0.3% Pt, reaction temperature 460 K) we did not find any remarkable contribution from multiple exchange or dependence of the selectivity to different deuteriomethanes on metal dispersion in the alumina- and zeolite-supported catalysts.

Our results can be compared with the data of Ponec and co-workers,[24] who also investigated deuterium exchange in methane on Pt/alumina catalysts which contained a large amount of Pt (6–10%) and found a contribution from multiple exchange at above 523 K. A decrease in the reaction temperature to 473 K was observed by these authors to be accompanied by a significant decrease in the contribution of multiple exchange, in agreement with our observations.

According to the data of Frennet *et al.*[23] the following reaction scheme could be considered

$$Pt{-}Pt + D_2 \rightarrow 2PtD \quad (1)$$

$$Pt{-}Pt + CH_4 \rightarrow PtCH_3 + PtH \quad (2)$$

$$PtCH_3 + D_2 \rightarrow PtD + CH_3D \quad (3)$$

or

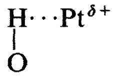
$$PtCH_3 + PtD \rightarrow Pt\text{–}Pt + H_3D \qquad (4)$$

which includes adsorption of deuterium on the Pt clusters and reaction of gaseous methane with Pt–Pt pairs, leading to the formation of surface methyl groups. The surface methyl species may react with deuterium to form deuteriomethanes. The slowest step of the transformation seems to be activation and dissociation of methane molecules by free Pt atoms [eqn. (2)].[21] The partial negative order with respect to deuterium strongly suggests that deuterium species occupy the adsorption sites for CH_4. The positive order with respect to methane indicates that those sites not occupied by deuterium are partially filled by CH_4 and are responsible for methane activation and dissociation. Our observations on the partial order of the reaction are in good agreement with known data on the kinetics of exchange of saturated hydrocarbons with deuterium.[21–24]

The widespread use of hydrogen to measure metal dispersion and particle size in zeolites is based on the assumption that each hydrogen atom is adsorbed on one accessible Pt atom of the metal clusters. However, the stoichiometry of the adsorption can vary for different metal-supported zeolites and the data on H_2 chemisorption can be misleading, even in a qualitative sense. Recently Sachtler[7,8] and Dwyer[9] observed that small Pt clusters have a low ability to adsorb hydrogen, so that particles sizes measured from data on H_2 adsorption are usually higher than those determined by electron microscopy.

For alumina-supported Pt catalysts a good correlation between the data on dispersion measured by electron microscopy and by H_2 adsorption is usually found.[25]

For zeolites one of the factors that restricts the application of H_2 chemisorption seems to be the formation of the following bridged structures



$$\underset{\displaystyle O}{\overset{|}{H}}\cdots Pt^{\delta+}$$

The interaction between protons of the hydroxy groups and metal particles results in partial electron transfer from the Pt clusters, and these particles cannot adsorb molecular hydrogen at room temperature.

The resolution of transmission electron microscopy is *ca.* 8 Å. That is why the average particle diameter obtained from TEM data could be overestimated for mazzites with channel diameters of *ca.* 7.4 Å and these samples may contain a significant concentration of Pt clusters smaller than 8 Å which cannot be seen by TEM.

The low EXAFS Pt–Pt coordination numbers ($N_{Pt-Pt} \approx$ 4–7 in the samples, in bulk metal $N_{Pt-Pt} = 12$) (Table 2) found in mazzites suggest that the Pt particles are located preferentially in the zeolite channels. The calculation of Pt particle diameters assuming a cubooctahedral shapes for metal clusters even for $N_{Pt-Pt} = 6$–7 indicates that their diameter is $<$9–10 Å, which is comparable with the diameter of mazzite channels (7.4 Å). Analysis of the distribution of Pt atoms between metal particles located on the external surface and in the zeolite bulk demonstrated that 60–80% of the Pt atoms are in the mazzite channels.[18]

Having considered three techniques (H_2 adsorption, TEM and EXAFS) which are usually applied to measure metal particle sizes in supported-metal catalysts, we have chosen EXAFS as being especially convenient for estimating the metal dispersion in zeolites.

If we consider now the evolution of the exchange rate with particle size on alumina-containing catalysts two different domains can be distinguished [Fig. 3(*a*)]: (i) For diameters $>$15–20 Å the reaction rate increases very slowly with increasing metal dispersion and turnover frequency (the rate of exchange per Pt surface atom) is independent of the particle size, as shown in Fig. 3(*b*). Obviously for such relatively large particles the influence of support is likely to be small and the observed activity reflects that of bulk platinum. (ii) For diameter $<$15–20 Å, on Pt/Al_2O_3 a significant increase of the reaction rate with decreasing of the particle size is apparent. These results emphasise the predominant role of the support on the catalytic properties of small Pt particles.

The interaction between platinum and the support in alumina-supported Pt catalysts is likely to be electron transfer, leading to a positive charge on the Pt clusters. This transfer could be ascribed to the bonding of the platinum atoms with hydrogen atoms of acidic hydroxy groups. The interaction would affect platinum atoms in direct contact with hydrogen and the next-nearest neighbours. This effect has already been described in the literature.[2,5,13]

In the exchange reaction studied, positively charged Pt atoms may (i) stabilise the CH_3 species which are electron donors and (ii) destabilise absorbed deuterium atoms, the reducing the poisoning effect of deuterium. The suggestion of destabilisation of Pt–D species on small metal particles in mazzites is confirmed by the known data[7–9,13] on the low capability of small Pt clusters in zeolites to adsorb hydrogen. These two effects favour a higher $PtCH_3$ species concentration per Pt surface atom on smaller particles than on larger ones and therefore a higher rate of exchange.

The influence of the support on the rate of CH_4–D_2 exchange is also clearly revealed when comparing the activity of alumina and mazzite zeolites. As seen from Fig. 4, Pt/Maz samples are markedly more active than Pt/Al_2O_3 samples. The higher activity of mazzite may be first due to the fact that the size of the metal clusters is smaller in mazzite ($<$9 Å $\approx$ diameter of distorted mazzite channels) than in alumina (average particle size $\geqslant$9 Å, Table 1). Secondly, different interaction mechanisms between supports and metals could be taken into account. Besides bonding between platinum atoms in small metal clusters with hydrogen atoms of the support, resulting in positively charged Pt atoms in alumina and mazzite zeolites, in mazzite zeolites superacid hydroxy groups could also affect the platinum atoms. A greater electron deficiency would confer on these atoms a large reactivity and would therefore cause a higher rate of exchange on Pt/Maz than on Pt/Al_2O_3. The argument concerning chemical bonding of Pt atoms and superacid hydroxy groups of zeolites has already been used by Sachtler[7,8,13] for explaining the low capability of small Pt clusters to adsorb hydrogen at room temperature.

Another marked difference between Pt/Al_2O_3 and Pt/Maz catalysts concerning deuterium exchange in methane deals with the different localisation of Pt clusters on alumina and in mazzites. On alumina the Pt particles are located on the surface and in mesopores of the catalysts whereas in mazzite, according to EXAFS data, most of the particles are likely to be in channels. It was recently suggested[13] that single Pt atoms in zeolites can be effective in alkane deuterium exchange reactions involving a stepwise mechanism. Our results are not in contradiction with this assumption. However, in our opinion isolated monatomic Pt species are not the only sites responsible for the dramatic acceleration of stepwise methane deuterium exchange on zeolites. Some type of polyatomic clusters, *e.g.* Pt_4 tethrahedra ($N_{Pt-Pt} = 3$, $d =$ 5.5 Å) or two-dimensional rafts could also possess significant activity in this reaction.

The treatment of mazzites with water to obtain samples with larger particles resulted in sintering and the formation of clusters with sizes comparable with the diameter of the channels (7.4 Å). After such treatment some of the mazzite channels are probably blocked by large metal particles. This is the fourth reason why activity of the mazzites decreases dramatically with increasing N_{Pt-Pt} up to 6–7.

The high sensitivity of the rate of exchange to the concentration of small Pt particles allows this reaction to be used for the investigation of the state and localisation of supported metals in the catalysts. Another advantage of deuterium exchange in methane is related to the similarity of methane to higher hydrocarbons which are the usual reactants of catalytic reactions on zeolites and alumina. The data on CH_4–D_2 exchange might also provide some information on the extent of C—H bond activation on Pt-supported catalysts.

Conclusion

The results obtained show that the reaction of methane with deuterium on alumina-supported catalysts and Pt zeolites proceeds by simple stepwise exchange. For Pt/mazzite and alumina-supported Pt catalysts it was shown that the rate of exchange depended strongly on the metal particle size, the nature of the metal–support interaction and the localisation of the metal clusters. In the one-directional channel system of mazzite zeolites, the blockage of the structure by Pt particles could also be considered.

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