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Unique catalytic properties of Pt and tungstophosphoric acid supported on MCM-41 for the reduction of NO_x in the presence of water vapour

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Pt and tungstophosphoric acid supported on MCM-41 type materials show a pronounced increase in the activity during the catalytic reduction of NO_x with propene in the presence water vapour.

To combine the advantages of zeolites[1–4] and oxide based systems,[5,6] we studied the potential of transition metal containing mesoporous molecular sieves with the MCM-41 type structure for the catalytic reduction of NO_x.[7,8] As the acid sites of these materials are only weakly acidic,[9] we also impregnated the catalysts with tungstophosphoric acid ($H_3PW_{12}O_{40}\cdot 6H_2O$) in order to generate strongly acidic sites.[10]

Siliceous mesoporous molecular sieves with the MCM-41[8] type structure, synthesised with C_{16}TMABr,[11] were impregnated with aqueous solutions of $PtCl_4$ (Pt/MCM-41),[12] of $H_3PW_{12}O_{40}$ (HPW/MCM-41) and of $PtCl_4$ and $H_3PW_{12}O_{40}$ (Pt + HPW/MCM-41). For comparison Pt/SiO_2 (Degussa Aerosil 200) and Pt/γ-Al_2O_3 (170 m^2 g^{-1}), also prepared by impregnation, were used. The metal and tungstophosphoric acid loading of all catalysts investigated are summarised in Table 1.

The characterisation of the support (MCM-41) was carried out by XRD, N_2 BET and IR spectroscopy.[9] The siliceous MCM-41 type material showed four Bragg reflections (*d*-spacing: 39 Å) and a sharp step in the N_2 isotherm at $p/p_0 \approx 0.4$. The dispersion of the metal, determined by volumetric H_2 chemisorption after reduction for 2 h at 773 K in H_2 (heating rate 15 K min^{-1}), was 64% for the Pt/MCM-41 catalyst. The BET surface areas of Pt/MCM-41 and Pt + HPW/MCM-41 were 1000 and 470 m^2 g^{-1}, respectively.[10]

Catalytic properties were studied in a reaction system using a chemiluminescence NO_x analyser and a gas chromatograph (TCD and FID) to determine the concentrations of the reactants and products. The concentrations of the reactants were 1010 ppm NO, 1010 ppm C_3H_6, 4.9 vol% O_2, 0–8 vol% H_2O (balance He). The reactions reported were carried out at 573 K and at a space velocity of 11 000 h^{-1} ($w/F = 6 \times 10^{-2}$ g s cm^{-3}), the activity reported was measured after 2 h on stream. Before the reaction all catalysts were activated in He at 773 K for 1 h. TPD indicated that at this temperature H_2O was completely removed from the Pt + HPW/MCM-41 catalyst.

A comparison of the activity and selectivity (determined at the temperature of maximum NO_x conversion) is given in Table 1. The use of siliceous mesoporous molecular sieves as the Pt support improved the activity and the selectivity towards N_2 formation compared to Pt supported on dense SiO_2.[6] After the co-impregnation of MCM-41 with Pt and tungstophosphoric acid the activity decreased to a level comparable to Pt/SiO_2 and Pt/Al_2O_3, while MCM-41 based catalysts containing tungstophosphoric acid only showed a significantly lower activity. The main product of these reactions, however, was N_2O, which is characteristic for Pt group metals supported on oxides.[13] Transition metals supported on zeolites, such as Fe/ZSM5, show generally a higher N_2 yield, but are only active above 650 K.[14]

The conversions of NO_x over Pt/MCM-41 and Pt + HPW/MCM-41 at 573 K as a function of the water vapour concentration are compared in Fig. 1. At this temperature, the activity and selectivity of the catalysts in the absence of water vapour were almost identical. With increasing H_2O vapour concentration the activity of Pt + HPW/MCM-41 increased, until a maximum was reached at 2.0 vol% H_2O, where the NO_x conversion was 25% (relative %) higher compared to the water-free reaction conditions. A further increase led to a decrease in the activity; however, even at 8.5 vol% water vapour the activity was 10% higher compared to the water-free reaction conditions. In contrast, for Pt/MCM-41 a continuous decrease in the activity with increasing H_2O concentration was observed.

The activity changed almost instantaneously with the addition of 2.5 vol% water vapour into the gas stream (see Fig. 2). After switching back to water-free reaction conditions the activity immediately returned to the initial value on Pt/MCM-41. On Pt + HPW/MCM-41 it decreased to a constant level, which was 12% above the initial activity, and only after an additional heating for 1 h at 773 K in He could the initial activity be restored.

In contrast to the published results,[3,14,15] this is the first time that a pronounced increase in catalytic activity during the reduction of NO_x with hydrocarbons in the presence of H_2O vapour has been observed. The activity of the Pt + HPW/MCM-41 catalyst is significantly improved in the presence of up to 8.5 vol% water vapour compared to water free reaction conditions, while the activity of Pt/MCM-41 was slightly suppressed in the presence of water vapour.

To elucidate the reason behind these unique catalytic properties, the formation of acidic surface sites resulting from the deposition of tungstophosphoric acid on MCM-41 was

Table 1 Composition and catalytic properties of the catalysts

Sample	Pt (wt%)	Tungstophosphoric acid (wt%)	Max. NO_x conversion (%)	Temp. for max. NO_x conversion/K	Selectivity to $N_2{}^a$ (%)
Pt/MCM-41	1.61	0	62	493	35
Pt + HPW/MCM-41 (0 vol% H_2O)	1.61	30	47	543	36
Pt + HPW/MCM-41 (2 vol% H_2O)	1.61	30	51	553	37
HPW/MCM-41 (0 vol% H_2O)	0	30	22	593	32
HPW/MCM-41 (2 vol% H_2O)	0	30	19	593	35
Pt/SiO_2	1.61	0	51	513	29
Pt/Al_2O_3	1.62	0	46	543	34

[a] *vs.* formation of N_2O (reported at the temperature at the highest NO_x conversion).

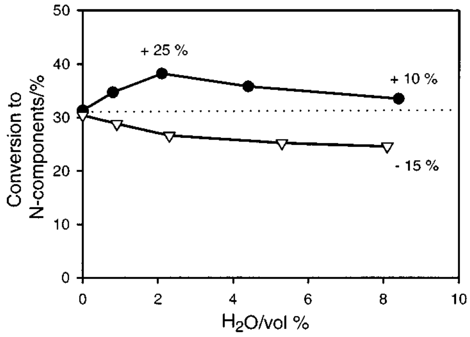

Fig. 1 Activity of (▽) Pt/MCM-41 and (●) Pt + HPW/MCM-41 as a function of water vapour concentration (573 K).

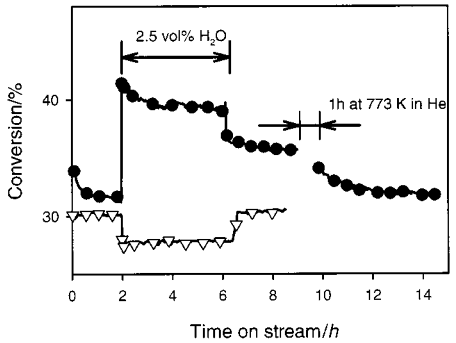

Fig. 2 Changes in activity of (▽) Pt/MCM-41 and (●) Pt + HPW/MCM-41 during a stepwise change of the water vapour concentration between 0 and 2.5 vol% at 573 K.

investigated by following the adsorption of pyridine using IR spectroscopy. The spectra shown in Fig. 3 were normalised to the structural vibrations of MCM-41 between 2100 and 1770 cm^{-1}, the other experimental details are described in ref. 9. After activation in vacuum ($\approx 10^{-6}$ mbar) at 773 K, pyridine was adsorbed with a partial pressure of 10^{-1} mbar at 423 K on Pt + HPW/MCM-41 and on siliceous MCM-41. Subsequently, the tungstophosphoric acid containing sample was hydrated by the co-adsorption of 9×10^{-1} mbar H_2O. The bands at 1449 and 1600 cm^{-1}, present after adsorption of pyridine on MCM-41 and on Pt + HPW/MCM-41, are assigned to hydrogen-bonded pyridine formed on Lewis acid sites. Brønsted acid sites, indicated by the bands at 1540 and 1614 cm^{-1}, were only present on Pt + HPW/MCM-41. After the co-adsorption of H_2O the concentration of Brønsted acid sites on Pt + HPW/MCM-41 increased by about 75%, while the concentration of Lewis acid sites was not affected by the presence of water vapour.

In recent work[16–18] it was shown that hydrated tungstophosphoric acid supported on SiO_2 forms protonated NO species (*i.e.* NOH^+) upon adsorption of NO and that the adsorbed NO is almost completely decomposed (70–100% NO conversion) into N_2 and N_2O ($\approx 50\%$ selectivity to N_2) in the presence of O_2 and H_2O around 700 K. This reaction was only observed on hydrated tungstophosphoric acid and, therefore, could be the additional reaction pathway accounting for the improved activity of the Pt + HPW/MCM-41 catalyst in the presence of water vapour.

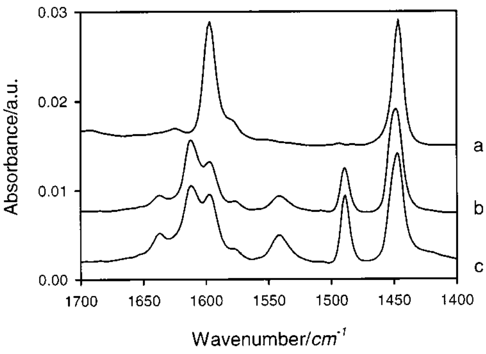

Fig. 3 Difference IR spectra after adsorption of pyridine at 423 K: (a) 10^{-1} mbar pyridine on siliceous MCM-41, (b) 10^{-1} mbar pyridine on Pt + HPW/MCM-41 and (c) 10^{-1} mbar pyridine and 9×10^{-1} mbar H_2O on Pt + HPW/MCM-41.

The reactions reported here however, were carried out at a much lower temperature (573 K), where the NO_x conversion over the Pt-free HPW/MCM-41 catalyst was only 8%. Also, the activity of the HPW/MCM-41 catalyst was not influenced by the presence of water vapour. Therefore, we assume that the direct reaction on tungstophosphoric acid is not the main route contributing to the overall activity in these experiments and that Pt and tungstophosphoric acid are essential to achieve the additional activity observed in the presence of water vapour.

We propose two reaction pathways in order to explain the additional activity observed on the Pt + HPW/MCM-41 catalyst in the presence of water vapour: (i) NOH^+, formed on the hydrated tungstophosphoric acid, disproportionates and the carbonaceous species formed on the Pt clusters react with the O atoms to form CO_2, while N recombines and desorbs as N_2. This reaction mechanism is similar to that described for $C_3H_6/NO/O_2$ reactions, with an additionally proposed reaction pathway for the formation of $N-*$ and $O-*$ on the surface of the hydrated tungstophosphoric acid; (ii) in the other reaction pathway we suppose that C_3H_6 adsorbs on the hydrated tungstophosphoric acid. The C_xH_y species, formed upon adsorption on the Brønsted acid sites, react with $NO-*$ adsorbed on the metal. The presence of highly acidic Brønsted sites on the hydrated tungstophosphoric acid (see Fig. 3) generates additional adsorption sites, which increases the local concentration of hydrocarbons on the perimeter of the metal clusters and thus give rise to the higher activity in the presence of water vapour.

In both mechanisms proposed an additional pathway is described, which is not present on Pt/MCM-41 or on dehydrated Pt + HPW/MCM-41 catalysts. However, at the moment we can not unequivocally decide which of the two routes described is responsible for the catalytic effects observed.

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