Low temperature CO oxidation over iron-containing MCM-41 catalysts

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Different MCM-41 samples containing framework iron were prepared and tested in CO oxidation showing unprecedented high activities after reduction in hydrogen above 773 K.

Low temperature CO oxidation has a great academic and applied interest. Supported platinum,[1] tin–platinum,[2] and gold[3] containing catalysts were studied in this reaction. Hopcalite[4] ($CuMn_2O_4$) and Co_3O_4[5] based catalysts are the most active noble-metal-free catalysts used in CO oxidation. Iron containing catalysts, such as MFI type ferrisilicates, show high activity only above 673 K.[6] A recent study indicated that nanosized iron oxide is highly active above 523 K.[7] Recently, some attempts were also made using combinatorial approaches to find new catalyst compositions containing no noble metals.[8] Mixed oxides with general formula $Al_1Mn_{6.7}Co_{93.3}O_x$ showed the highest activity. Consequently, there is a great interest to develop noble metal free catalysts for low temperature CO oxidation.

Based on results of Sn–Pt/SiO_2[9] and Au/MgO catalysts[10] we have proposed a new mechanism for CO activation with the involvement of "metal ion–metal nano-cluster" ensemble sites.[11] Over Sn–Pt/SiO_2 catalysts *in situ* formation of surface Sn^{4+}, while on Au/MgO catalysts ionic forms of gold ($Au^{\delta+}$), were detected by different spectroscopic methods.[9,12] According to this concept a metal ion stabilized in the neighbourhood of a supported metal nanocluster interacts with the lone pair of the oxygen atom of a chemisorbed CO molecule. The result of this interaction is the perturbation of the CO molecule leading to its high reactivity even at low temperatures.

The aim of this study is to demonstrate that "metal ion–metal nanocluster" ensemble sites formed in a metal ion environment can oxidize CO at relatively low temperature.

MCM-41 materials with spherical and irregular morphology were synthesised as described earlier.[13,14] Further details are given in the notes.† Characteristic features of samples prepared are given in Table 1.

CO oxidation has been studied in the temperature range 297–673 K using Temperature Programmed Oxidation (TPO) technique.† Details of TPO and FTIR techniques used can be found elsewhere.[9,15]

Fig. 1 shows the influence of different thermal treatment procedures on the activity of a Fe-MCM-41 catalyst. The treatment in oxygen at 623 K gave rise to very low activity. Further increase of the temperature of calcination had no influence on the activity. Omitting the calcination step and reducing the sample at 673 K in H_2 resulted in a more active catalyst. However, this catalyst had an unstable behaviour having both increasing and decreasing parts in the TPO curves. On the other hand the reduction at 773 or 873 K provided a highly active and stable

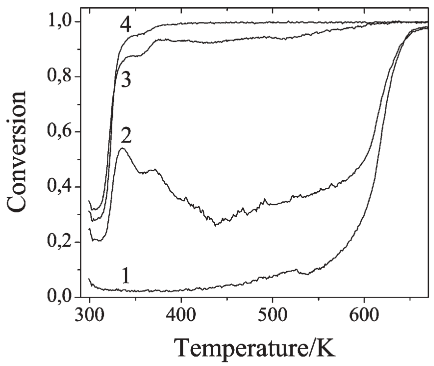

Fig. 1 The influence of the pretreatment procedures on the catalytic properties of Fe-MCM-41(20)(A). 1—oxygen at 623 K; 2—H_2 at 673 K; 3—H_2 at 773 K; 4—H_2 at 873 K.

Table 1 X-ray and surface characteristics of Fe-MCM-41 samples

Samples[a]	Si/Fe	Fe cont./mmol g^{-1}[h]	d_{100}/nm	SA[b]/m^2g^{-1}	PD[c]/nm	WTH[d]/nm
Fe-MCM-41(45)	44.9	0.360	3.78	727	2.47	1.90
Fe-MCM-41(20)(A)	18.0	0.860	3.84	847	2.27	2.16
Fe-MCM-41(10)	10.0	1.410	3.92	770	2.28	2.24
Fe-MCM-41(20)(B)	23.6	0.667	3.47	1004	2.31	1.70
Fe-MCM-41(20)(C)	20.1	0.778	3.80	1400	2.36	1.72
Fe-MCM-41(38) (imp)[e]	38.1	0.421	3.32	1049	2.30	1.53
Fe–SiO_2 (spherical)[f]	22.8	0.688	[g]	107	—	—

[a] Sample (A) was prepared by the sol–gel method of Unger *et al.*,[13] sample (B) by applying the same procedure with modifying the composition of the synthesis gel, and sample (C), having irregular morphology with hydrothermal synthesis.[13] [b] Specific surface area. [c] Mean pore diameter calculated by BJH method. [d] Wall thickness, WTH = $2/3^{1/2}d_{100}$ – PD. [e] Iron was introduced by impregnation. [f] The same synthesis procedure like in case of Fe-MCM-41(20)(A), but without using template. [g] X-ray amorphous. [h] Related to 1g sample calcined at 1273 K.

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catalyst with $T_{50} < 323$ K. This high activity is unprecedented in CO oxidation using iron-containing catalysts.

The observation that high activity appears only after reduction above 773 K strongly suggests that in Fe-MCM-41 new surface species with metallic character have been formed.

Fig. 2 shows the influence of dehydroxylation on the TPO pattern. As emerges from Fig. 2 after reduction at 523 K the initial conversion was below 10% and the T_{50} value was around 573 K. However, the addition of a dehydroxylation step at 773 K in He increased considerably the activity resulting in T_{50} = 338 K. Results given in Fig. 2 also show that the reduction temperature has more pronounced influence on the activity than the temperature of dehydroxylation.

The increase of the reduction temperature from 523 to 673 K followed by treatment in He at 773 K decreased further the T_{50} value to 323 K. The highest activity was obtained after reduction in H_2 at 773 K followed by treatment in He at the same temperature resulting in about 65% conversion at room temperature and 100% conversion at 338 K.

The catalyst reduced at 773 K is highly active, its initial activity at 300 K is higher than 50%. However, for the catalysts treated in He omitting the reduction step has much lower activity. Consequently, the high temperature reduction is a crucial step in the process leading to a highly active Fe-containing catalyst. Results shown in Fig. 2 indicate that this process can be further enhanced by high temperature treatment in an inert atmosphere. Further studies will be required to elucidate the character of interactions during high temperature treatment in He. It is tentatively suggested that in addition to dehydoxylation partial auto-reduction of Fe^{3+} can take place in samples treated only in He at high temperature.

The results strongly indicate that the activity of Fe-MCM-41 catalysts depends on both the extent of reduction of iron and the amount of surface OH groups in the neighbourhood of the active sites. The former is controlled by the temperature of reduction, while the latter by the temperature of thermal treatment procedures performed either in H_2 or He. It is suggested that high surface concentration of OH hinders the access of reactants and oxygen to iron containing active sites.

In the next series the Si/Fe ratio in Fe-MCM-41 was varied in the range 10–50. The T_{50} values decreased in the following order: Fe-MCM-41(10) (T_{50} = 320 K) > Fe-MCM-41(45) (T_{50} = 313 K) > Fe-MCM-41(20) (T_{50} = 300 K). Consequently, these results indicate that there is an optimum in the iron content in Fe-MCM-41 type catalysts.

In the next set of experiments the following parameters were varied: (i) surface area of Fe-MCM-41, (ii) spherical *vs.* non-spherical particles, (iii) form of iron, *i.e.* 'framework' *vs.* surface iron. As emerges from Fig. 3 both Fe-MCM-41(imp) and Fe–SiO_2(spherical) have much lower activity than Fe-MCM-41(20)(A). This finding indicates that the nano-environment of iron containing sites has a great influence on the catalytic activity. Only iron stabilised in MCM-41 structure resulted in highly active surface species for low temperature CO oxidation. In addition, the results show also that the higher the surface area of spherical Fe-MCM-41(20) the higher the catalytic activity (compare samples (A) and (B)).

Methods of *in situ* infrared spectroscopy were used to prove the partial reduction of iron in Fe-MCM-41 type catalysts. Fig. 4 shows the FTIR spectra of chemisorbed CO at RT on Fe-MCM-41(20)(A) after reduction at 773 K. The build up of surface species has a strong pressure dependence. At low CO pressure (p_{CO} = 20 mbar) there are only two IR bands: an intensive broad asymmetric band at 2170 cm^{-1} and a weak band around 2080 cm^{-1}. The broad band has a shoulder around 2165 cm^{-1}. Upon increasing the CO partial pressure to 50 and 100 mbar additional bands appear at 2048 and 2128 cm^{-1}. Further increase in p_{CO} resulted in no additional IR bands.

The band around 2048 cm^{-1} unambiguously indicates the formation of metallic iron. In Fe/Al_2O_3 and Fe/SiO_2 catalysts the band around 2050 cm^{-1} was assigned as CO adsorbed on reduced iron.[16] It has to be emphasized that the band at 2048 cm^{-1} was not observed on Fe-MCM-41(20) reduced at 573 K. In ref. 11 upon extending the reduction temperature to 873 K the intensity of the band at 2050 cm^{-1} became more pronounced. There are additional references confirming that the band around 2050 cm^{-1} can be assigned to linear CO adsorbed on metallic iron.[17] It is assumed that the particle size of the iron nano-clusters formed after high temperature reduction is very small as no metallic iron was detected by powder XRD.

The exposure of the Fe-MCM-41 sample to CO + O_2 mixture resulted in pronounced alteration in the FTIR spectra as shown in Fig. 4/D. Due to the presence of oxygen the band at 2048 cm^{-1}

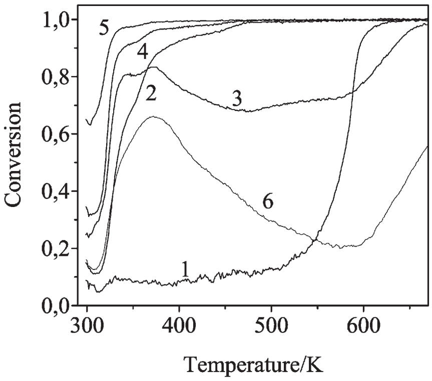

Fig. 2 The influence of the temperature of dehydroxylation (catalyst: Fe-MCM-41(20)(B)). 1—H_2: 523 K; 2—H_2: 523 K, He: 773 K; 3—H_2: 673 K; 4—H_2: 673 K, He: 773 K; 5—H_2 773 K; 6—He 773 K.

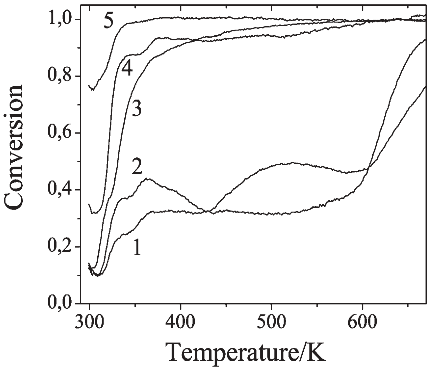

Fig. 3 Influence of different structural variables on the catalytic activity: 1—Fe–SiO_2(spherical); 2—Fe-MCM-41(imp); 3—Fe-MCM-41(20)(C); 4—Fe-MCM-41(18)(A); 5—Fe-MCM-41(24)(B). (For abbreviations see Table 1.)

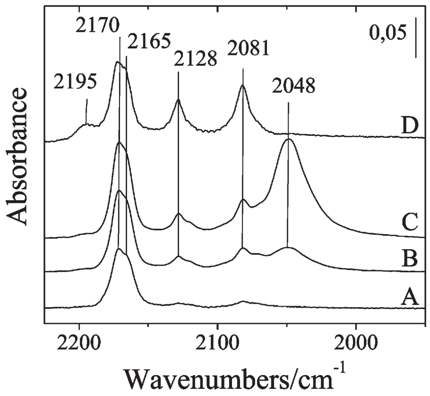

Fig. 4 FTIR spectra of adsorbed CO at RT on Fe-MCM-41(20)(A). A—p_{CO} = 20 mbar; B—p_{CO} = 50 mbar; C—p_{CO} = 100 mbar; D—p_{CO} = 100 mbar, p_{O2} = 50 mbar.

entirely disappeared and a new band appeared at 2195 cm^{-1}. The letter has been assigned to CO adsorbed on Fe^{3+} sites.

Based on literature data[18] the following further assignments were made: *band around 2080 cm^{-1}*: CO adsorbed on Fe^{2+} in the silicate matrix; *band around 2128 cm^{-1}*: fingerprint of iron ions with a mean oxidation number between 2 and 3; *band around 2170 cm^{-1}*: Fe^{2+} cations stabilised in the neighbourhood of Fe^{3+}.

The results of the activity test indicate that iron modified MCM-41 is highly active in low temperature CO oxidation. FTIR results showed unambiguously the partial reduction of iron in hydrogen above 773 K.

Based on the results obtained in this study we propose that there are at least four structural elements involved in the activity control: (i) the concave surface accommodating iron in the MCM-41 channels, (ii) the extent of reduction of iron, (iii) a proper balance between ionic and metallic forms of iron, and (iv) low surface coverage of silanol groups.

In summary, new types of iron containing catalysts were prepared and tested in CO oxidation using a temperature programmed oxidation technique. The Fe-MCM-41 samples after high temperature treatment in H_2 and He showed high activity with a T_{50} value around 320 K. This activity is much higher than the activity of iron-oxide containing catalysts prepared earlier.[6,7] Results of FTIR measurements provided an exact proof that after high temperature reduction in H_2 the Fe-MCM-41 sample contained both metallic and ionic forms of iron. It was shown for the first time that supported iron containing catalysts having both ionic and metallic forms of iron are active in low temperature CO oxidation. The results provided further proof that "metal ion–metal nanocluster" ensemble sites have a crucial role in CO activation.

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Notes and references

† *Experimental:* Modifying the procedure of Unger *et al.*[13], C_{16}TMABr, water, ethanol and TEOS were mixed in the desired proportion. $Fe(NO_3)_3.9H_2O$ (Fluka) was added and stirred for 30 min. Conc. ammonia was poured into this solution causing immediate gel precipitation. In a second synthesis procedure the composition of the synthesis gel was modified, in consequence of using diluted ammonia. This second procedure resulted in better ordered Fe-MCM-41 samples with higher surface area. The template removal was carried out at 770 K in N_2 and air. Further details on the synthesis can be found elsewhere.[14] Fe-MCM-41(20)(imp) was prepared by impregnation of 2 g Si-MCM-41 with methanolic solution of dried $Fe(NO_3)_3$ (80 g l^{-1}), stirring for 24 h under N_2 atmosphere followed by filtering, washing with methanol, drying and calcining at 373 K and 773 K, respectively. *Catalytic tests:* TPO technique has been used.[9] The amount of catalyst: 0.100 g, total flow rate 70 ml min^{-1}, P_{CO} = 16 Torr, P_{O2} = 16 Torr, heating rate 10 K min^{-1}. Catalysts characterisation and catalytic tests were performed in a multipurpose, ASDI RXM 100 equipment (Advanced Scientific Designs, Inc.). Before testing, the catalysts were reduced in H_2 and/or dehydroxylated in He. MS method was used for product analysis. The temperature required to achieve 50% conversion (T_{50}) was used to compare the activity of catalysts. *FTIR studies: FTIR measurements. In situ* infrared spectra were recorded at room temperature using Nicolet Impact 400 FTIR instrument. In the spectral region 4000–1100 cm^{-1} the resolution was 1 cm^{-1}. The description of the cell and the high vacuum apparatus used can be found elsewhere.[15]

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