Copper active sites for the selective reduction of nitrogen monoxide by propane on Cu-MFI catalysts and non-zeolitic supported-copper solids

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Received 12 February 1998; accepted 20 March 1998

The selective reduction of NO by C_3H_8 is performed on copper-based catalysts: Cu/Al_2O_3, Cu/SiO_2, $Cu/SiO_2–Al_2O_3$ solids, fresh and hydrothermally-treated Cu-MFI with various Si/Al ratios. For all the Cu-MFI solids and for the non-zeolitic supported-copper solids with low copper loadings, O_2 promotes the reduction of NO. The C_3H_8–NO reaction rate correlates with the number of accessible and isolated Cu^{n+} ions deduced from the infrared spectroscopy of adsorbed CO. When only one type of sites is detected, the FTIR spectroscopy of adsorbed CO allows an estimation of the copper dispersion.

Keywords: DeNOx, selective nitric oxide reduction, Cu-MFI catalysts, Cu/Al_2O_3, Cu/SiO_2, $Cu/SiO_2–Al_2O_3$, Cu on non-zeolitic supports, Si/Al ratio, copper active sites

1. Introduction

The reduction of nitrogen oxides into oxygen-rich mixtures is difficult to achieve because the major part of reducing gases reacts with oxygen instead of NO_x (non-selective reductants such as carbon monoxide, hydrogen, etc.). However, the selective catalytic reduction (SCR) of NO into N_2 by hydrocarbons (C_2H_4, C_3H_6, C_2H_6, C_4H_8, etc.) in lean conditions has been reported with various catalysts, such as zeolite-based solids, especially Cu-MFI and some Cu-free acid solids, H-MFI, alumina [1–3], etc. The presence of oxygen is essential for the NO reduction into nitrogen. The zeolite catalysts show a volcano-like activity dependence with the temperature and with the oxygen content [4].

The low thermal stability of Cu-MFI zeolites limits their use for the treatment of lean-burn engines emissions [2]. Nevertheless, they are good models for a better understanding since many questions remain open concerning the nature of the active species and the reaction pathways.

The state of copper in zeolite catalysts [5] and, more generally, in copper-based catalysts has been extensively characterized in the past and is reviewed by Centi and Perathoner [6]. Several species have been considered, in particular, well-dispersed and isolated copper ions interacting with the zeolite framework, via one or two oxygen-bridging bonds [7–11]. Large CuO particles on the external surface of zeolite crystallites differ significantly from multinuclear or isolated species inside the zeolite matrix. Isolated Cu^{n+} ions appear generally more active than copper oxides towards the NO reduction into N_2 [12–15]. For Cu-ZSM-5 solids with a low Si/Al ratio [14] and for Cu/Al_2O_3 solids [15], we have previously correlated the activity for the nitrogen formation with the number of isolated copper ions accessible to CO.

The purpose of the present work is to broaden the conclusions of these works to other solids, such as Cu-MFI with various Si/Al ratios, hydrothermally-aged Cu-MFI, Cu on other non-zeolitic supports (silica, silica–alumina) in connection with the FTIR spectroscopy of adsorbed CO.

2. Experimental

2.1. Catalysts

MFI zeolites with various Si/Al ratios (19, 22, 78, 130, 151, 319) were either commercially available solids or hydrothermally synthesized in an autoclave using sodium silicate, aluminium sulfate and tetrapropyl ammonium bromide as a template. The structures have been checked by infrared spectroscopy and XRD analysis.

For low Si/Al ratios (between 19 and 22), the copper ions were introduced using exchange (EXC), impregnation (IMP) and precipitation (PRE) procedures with copper nitrate, as already described [14,16]. By assuming that one Cu^{2+} ion replaces two protons or two Na^+ ions, a 1.2 wt% Cu loading corresponds to an exchange level of 44% for a Si/Al ratio equal to 19. For higher Si/Al ratios, copper ions were introduced by impregnation using copper nitrate. All the solids were calcined under an oxygen flow at 773 K. The solids are called Cu-MFI(Si/Al)-EXC (or IMP or PRE)-wt% Cu, with the value of the Si/Al ratio, the preparation procedure and the copper content. All the prepared Cu-MFI solids showed the XRD patterns of the parent zeolite, and copper oxides were not detected.

Cu/Al_2O_3 solids containing, after calcination at 773 K, 0.3, 1.7, 3.4 and 6.4 wt% Cu, were prepared by impregnating a non-porous alumina (aluminium oxyd-C from Degussa, BET area 100 $m^2\,g^{-1}$) with aqueous solutions of copper nitrate [14]. These solids are called Cu-Al-0.3, Cu-Al-1.7, Cu-Al-3.4, Cu-Al-6.4. From XRD patterns, the CuO phase was detected only in the solid containing 6.4 wt% copper. Cu/SiO_2 and Cu/SiO_2–Al_2O_3 (1.7 wt% Cu after calcination at 773 K) were also prepared by impregnating a silica from Degussa (Aerosil 200 $m^2\,g^{-1}$) and a silica–alumina (Ketjen 13% Al_2O_3, 410 $m^2\,g^{-1}$) with copper nitrate.

Thermal aging treatments were performed under a 10 vol% H_2O–air mixture at a total flow rate of 10 $l\,h^{-1}$ for 24 h at 923 K.

2.2. Catalytic activity measurements

The activity measurements were performed in a fixed-bed flow reactor using 100 mg of catalyst diluted with 400 mg of inactive low surface area α-Al_2O_3, as already described [14–16]. The typical mixture consisted of 2000 ppm NO, 2000 ppm C_3H_8, 0–10 vol% O_2, diluent He (total flow rate 10 $dm^3\,h^{-1}$). At a given temperature (generally 623 K), the effect of the O_2 content was studied. At a given O_2 content (generally 10 vol%), the reaction temperature was increased from 298 to 773 K (4 $K\,min^{-1}$) and then decreased.

CO_2, N_2O, O_2, N_2, CO, C_3H_8 were analyzed by gas chromatography. Furthermore, NO, N_2O, NO_2 and CO_2 were analyzed continuously on-line by means of IR and UV Rosemount analyzers. N_2O and CO formations were negligible. The main products were N_2, CO_2 and NO_2. NO_2 was formed at 298 K in the pipes of the apparatus in the presence of O_2, without catalyst. The catalytic activities were evaluated by the conversion of NO into N_2.

2.3. FTIR spectroscopy of adsorbed CO

The *in situ* treatments have been previously described [14,15]. After calcination at 773 K under O_2, the samples (thin disks of known weight) were degassed at 773 K for 1 h. The spectra were recorded as a function of time, in the presence of CO (around 50 Torr) at 298 K and upon evacuation at 298 K on a FTIR spectrometer (BRUKER IFS 48, resolution 2 cm^{-1}). The plot function was set to absorbance, and the background spectrum was subtracted. The optical densities of the νCO bands were normalized by taking into account the amount of introduced copper.

2.4. Volumetric measurements of CO adsorption

The measurements were performed in a classical volumetric apparatus. The calcined samples were outgassed at 773 K and then cooled to 298 K. The irreversible uptakes of carbon monoxide chemisorbed at room temperature were determined by the dual isotherm method. After the first CO isotherm and a short evacuation (30 min) at room temperature, a second isotherm was determined and extrapolations to zero pressure were made.

3. Results

3.1. Fresh and hydrothermally-treated Cu-MFI catalysts. Activity for nitrogen formation and copper ions accessible to CO (FTIR spectroscopy)

For Cu-MFI catalysts with a low Si/Al ratio (19 or 22), we have already shown [14] that the activity in NO reduction remarkably increases with the O_2 content in the 0.5–2 vol% range, then slightly decreases but is still high with 10 vol% O_2.

In fact, O_2 promotes the NO reduction into N_2 whatever the Si/Al ratio (figure 1) and the preparation procedure. For a given Si/Al ratio, the behaviour is similar whatever the copper content. For a given Cu content, the promotion of the activity by oxygen addition decreases when the Si/Al ratio increases. In all the cases, for a given O_2 amount, the activity exhibits a maximum with the temperature, maximum often close to 623 K.

After the aging treatment at 923 K with the 10 vol% H_2O–air mixture, the activity of the solid decreases (figure 2), the decrease being slightly lower for high Si/Al ratios.

The infrared spectra of CO adsorbed on copper ions have been widely described ([14,17–24] and references therein). As already shown [14,16], the Cu-MFI solids with a low Si/Al ratio (19 or 22) are characterized, in the presence of CO, by a νCO band at 2152 cm^{-1} which was shifted to 2160 cm^{-1} after evacuation at 298 K. It was assigned

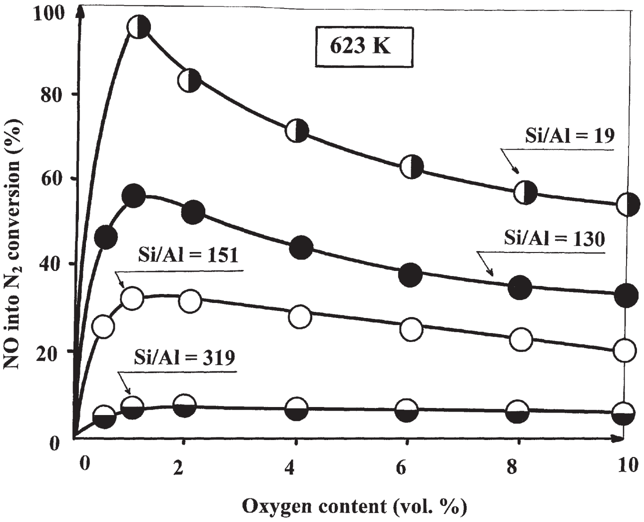

Figure 1. Conversion of NO into nitrogen as a function of the O_2 content for various Cu-MFI catalysts (Si/Al = 19, 130, 151, 319) containing 4 wt% Cu and prepared by impregnation. Reaction temperature 623 K.

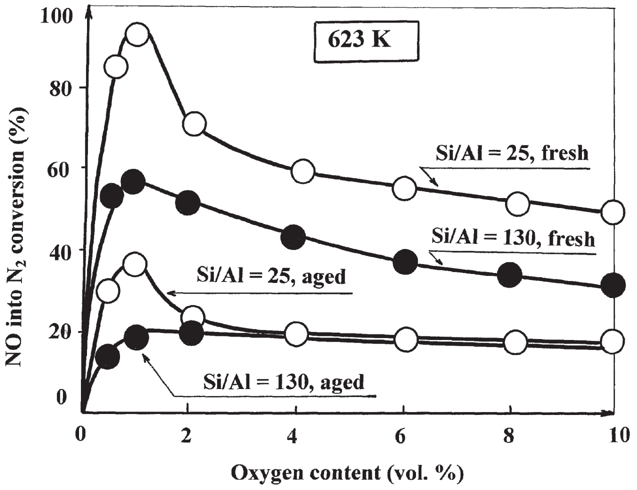

Figure 2. Conversion of NO into N_2 at 623 K as a function of the O_2 content for fresh and aged solids (treatment at 923 K with a 10 vol% H_2O–air mixture). Solids prepared by impregnation and containing 4 wt% Cu. Si/Al = 25 and 130.

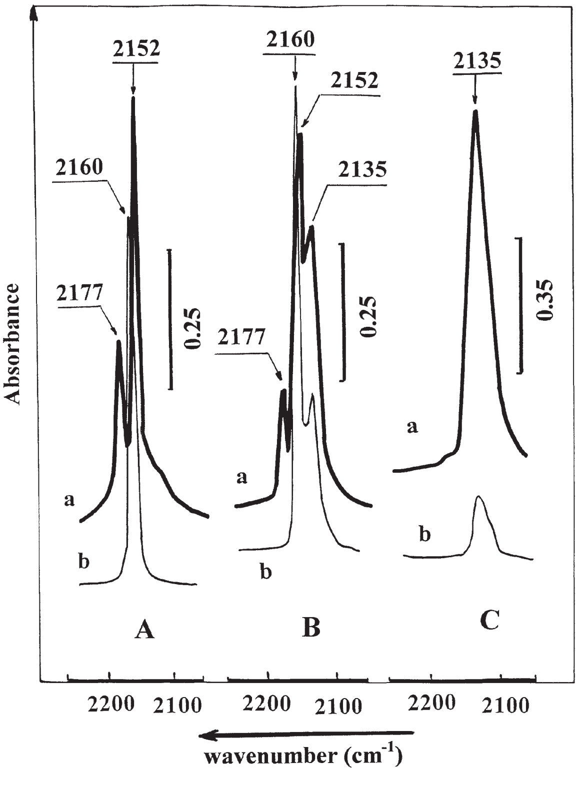

Figure 3. FTIR spectra of CO adsorbed at 298 K on Cu-MFI catalysts with various Si/Al ratios. (A) Cu-MFI(19)-EXC-1.2 or Cu-MFI(19)-IMP-1.2; (B) Cu-MFI(130)-IMP-4.0; (C) Cu-MFI(319)-IMP-3.5. (a) After 1 h of contact with 50 Torr CO at 298 K; (b) after evacuation at 298 K during 1 h.

to CO adsorbed onto isolated Cu^+ ions arising from the reduction of isolated Cu^{2+} ions (figure 3(A)) [14,17,25–29]. Dicarbonyl $Cu^+(CO)_2$ species are detected by a band at 2177 cm^{-1} (ν_s mode) which disappears upon evacuation at 298 K. The ν_{as} mode lies at 2151 cm^{-1} and it is not detectable because of its overlapping with the 2152 cm^{-1} band of the Cu^+CO species.

Table 1
Optical densities of the 2152–2160 cm^{-1} band (normalized per gram Cu) after 1 h under 50 Torr CO at 298 K (2152 cm^{-1}) and after 1 h evacuation at 298 K (2160 cm^{-1}).

Solids	CO, 298 K, 1 h	Vacuo, 298 K, 1 h
Fresh Cu-MFI(19)-EXC-1.2[a]	3972	3268
Fresh Cu-MFI(19)-IMP-2.6	2335	1862
Fresh Cu-MFI(19)-PRE-3.8	1765	1583
Fresh Cu-MFI(78)-IMP-4.1	727	602
Fresh Cu-MFI(130)-IMP-4.0	1160	855
Fresh Cu-MFI(151)-IMP-4.2	800	666
Fresh Cu-MFI(319)-IMP-3.5	0	0
Aged Cu-MFI(19)-EXC-1.2	1241	934
Aged Cu-MFI(130)-IMP-4.0	829	342

[a] Same values for the Cu-MFI(19)-IMP-1.2 solid. Aging treatment was performed at 923 K.

A $ZO^-(CuOH)^+$ species is probably formed during the exchange process, $Cu^{2+}(OH)^-$ being linked to only one Al atom [11,22] (ZO^- represents the zeolite framework). From simultaneous FTIR and UV-visible studies, we have confirmed [17] that the cuprous ions are generated by reduction under vacuum or under CO (or H_2), and that CO adsorbed on Cu^{2+} or on Cu^0 is not detected by infrared spectroscopy. These copper centers reducible by thermal treatment under vacuum are bonded to extra-lattice oxygen probably introduced as OH [11].

When the Si/Al ratio increases, a new νCO band is observed at 2135 cm^{-1} (figure 3(B)). A part of CO is adsorbed on Cu^+ ions surrounded by CuO species (non-isolated Cu^+ ions) because of the partial reduction of bulk CuO as in the case of the Cu/Al_2O_3 solids with high copper loadings [15]. We have also observed such a band by contacting unsupported CuO with CO at 298 K. When the Si/Al ratio increases, the number of isolated Cu^+ ions accessible to CO decreases, and the number of non-isolated Cu^+ ions accessible to CO increases. When the Si/Al ratio reaches 319, non-isolated Cu^+ ions are the only species detected, the band at 2152–2160 cm^{-1} being no more observed (figure 3(C)). Table 1 gives the optical densities (normalized per gram of copper) of the 2152–2160 cm^{-1} band for some fresh and 923 K-aged solids.

Aging, at 923 K, of the Cu-MFI(19)-EXC-1.2 solid leads to a decrease in the number of isolated Cu^+ ions accessible to CO (table 1) but not to the appearance of a band at 2135 cm^{-1}. Some copper ions become inaccessible to CO, but an agglomeration is not detected after the aging at 923 K. However, such an agglomeration is observed (2135 cm^{-1} band due to Cu^+ arising from the reduction of bulk CuO) after aging at 1073 or 1173 K. Let us also note that the ratio of the intensities of the bands at 2135 cm^{-1} (CO on non-isolated Cu^+ ions) and 2152–2160 cm^{-1} (CO on isolated Cu^+ ions) increases from 0.6 to around 0.8 after aging of the Cu-MFI(130)-IMP-4.0 solid.

For a given copper amount, activities and infrared spectra are identical whatever the preparation procedure (Cu-MFI(19)-EXC-1.2 and Cu-MFI(19)-IMP-1.2 solids).

Table 2
Rate of NO reduction into N_2 ($\mathrm{mol\,s^{-1}\,g^{-1}(Cu)} \times 10^{-6}$) as a function of the oxygen content and of the copper amount, with the Cu/Al_2O_3, Cu/SiO_2, $Cu/SiO_2–Al_2O_3$ solids.[a]

Solid			Cu–Al	Cu–Al	Cu–Al	Cu–Al	Cu–Si	Cu–Si–Al
Cu (wt%)			0.3	1.7	3.2	6.4	1.7	1.7
NO into N_2	O_2 (%)	0	15	12	26	12	1.2	1.5
		1	90	22	13	7	10	18
		2	90	20	10	5	11	12
		4	62	18	3	2.5	9	5
		10	48	18	0	0	0	0
O.D./g(Cu)			1024	351	–	–	136	215

[a] Reaction temperature 773 K. The optical densities normalized per gram of copper are also given (after 10 min vacuo at 298 K).

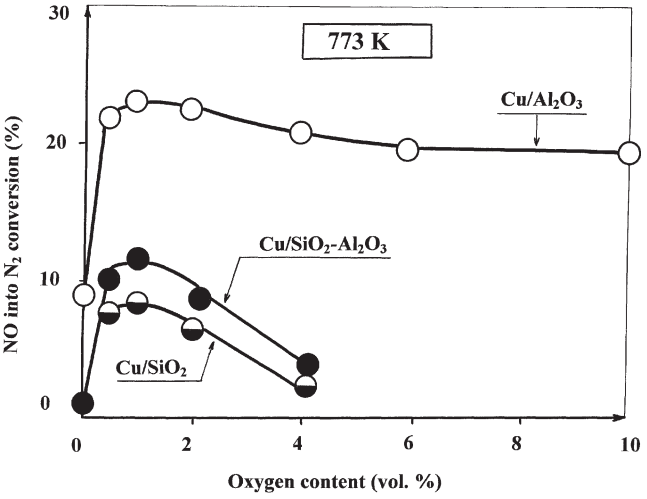

Figure 4. Conversion of NO into N_2 as a function of the O_2 content for copper on non-zeolitic supports (alumina, silica, silica–alumina) with a loading of ca. 1.7 wt% Cu. Reaction performed at 773 K.

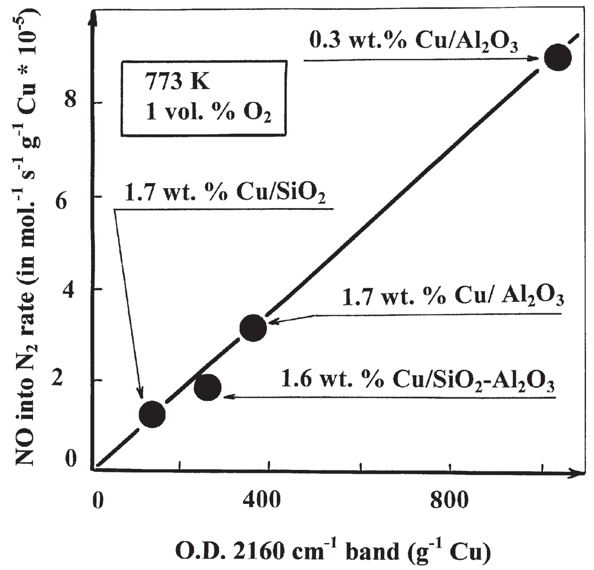

Figure 5. NO reduction into N_2 expressed in moles of NO converted per second and per gram Cu as a function of the optical density of the 2160 cm^{-1} band (normalized per gram Cu and after evacuation at 298 K for 10 min) for Cu on non-zeolitic supports. Reaction performed at 773 K in the presence of 1 vol% O_2.

3.2. Copper on non-zeolitic supports (Al_2O_3, SiO_2, $SiO_2–Al_2O_3$). Activity for nitrogen formation and copper ions accessible to CO (FTIR spectroscopy)

We have already shown, in the case of the Cu/Al_2O_3 solids [15], that, for the highest Cu-loaded samples (3.2 and 6.4 wt% Cu), the activity decreases as soon as oxygen is introduced. By contrast, for low copper loadings (Cu-Al-0.3 and Cu-Al-1.7 solids), the NO reduction into N_2 is enhanced by the oxygen addition (table 2), as in the case of the Cu-MFI catalysts.

For low copper amounts (for instance, 1.7 wt%), the oxygen promotion occurs whatever the support (alumina, silica, silica–alumina), but Cu/Al_2O_3 is more active than Cu/SiO_2 and $Cu/SiO_2–Al_2O_3$ (figure 4, table 2).

In the case of the alumina support, the nature of the copper species has already been investigated by the infrared spectroscopy of adsorbed CO, high copper loadings favoring the formation of bulk oxides and low copper loadings favoring the formation of isolated Cu species [15]. Whatever the support, the solids present the νCO bands assigned to CO onto isolated Cu^+ ions (2152–2160 cm^{-1}) and to CO onto non-isolated Cu^+ ions (2130–2135 cm^{-1}). Furthermore, the optical density of the 2152 cm^{-1} band varies according to the sequence $Cu/Al_2O_3 > Cu/SiO_2–Al_2O_3 > Cu/SiO_2$, i.e., in the same order as the catalytic activity (table 2).

Let us note that copper dispersed on alumina is, however, not as active as Cu-MFI. For instance, at 623 K and with 1 vol% O_2, the activity is equal to 77×10^{-9} and to 1200×10^{-9} mol NO converted into N_2 per second and per gram Cu, for the Cu-Al-1.7 and Cu-MFI(19)-EXC-1.2 solids, respectively.

3.3. Correlations between the rate of NO reduction into N_2, the number of isolated copper ions (FTIR) and the amount of CO (volumetry)

It seems clear that the more active sites for the NO reduction into N_2, i.e., for the C_3H_8–NO reaction, are isolated Cu^{n+} ions. A $Cu^{2+}(OH)^-$ species linked to the zeolite framework (ZO^-) is likely [5,6,11,20].

For zeolitic and non-zeolitic solids, the activity for the NO reduction into N_2, at a given temperature (namely at

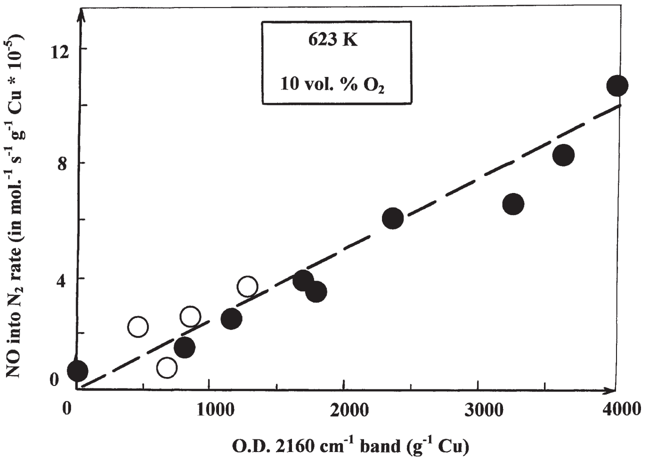

Figure 6. NO reduction into N_2 expressed in moles of NO converted per second and per gram Cu as a function of the optical density of the 2152 cm^{-1} band (normalized per gram Cu and after 1 h under CO at 298 K) for the Cu-MFI solids. Reaction performed at 623 K in the presence of 10 vol% O_2. (●) Fresh solids; (○) aged solids.

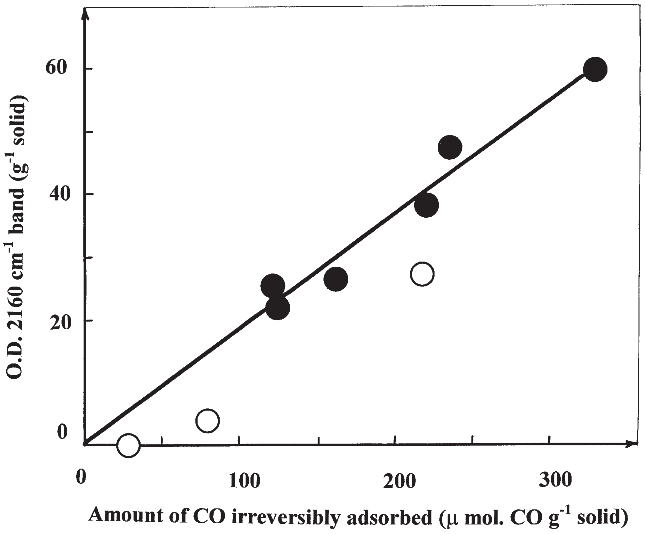

Figure 7. Optical density of the 2160 cm^{-1} band (after evacuation of CO at 298 K for 1 h), normalized per gram of solid, as a function of the amount of irreversibly adsorbed CO at 298 K (per gram of solid) determined by volumetry. (●) Cu-MFI solids with a unique νCO band at 2160 cm^{-1} (low Si/Al ratios); (○) Cu-MFI solids with two νCO bands (2160 + 2135 cm^{-1}) (high Si/Al ratios).

623 and 773 K) and expressed per gram of copper, varies linearly (or almost linearly) with the optical density of the 2160 cm^{-1} band assigned to CO adsorbed onto isolated Cu^+ ions (figures 5 and 6).

Let us note that, with the Cu-MFI(319)-IMP-3.5 solid, the NO reduction into N_2 is not equal to zero, in spite of the absence of the 2152 cm^{-1} band (figures 1, 3(C) and 6). This indicates that a small activity can be obtained with bulk CuO or Cu_2O oxides.

Figure 7 shows that, for the Cu-MFI solids characterized by a unique νCO band due to CO onto isolated Cu^+ ions (2160 cm^{-1} after evacuation at 298 K), i.e., for Cu-MFI solids with a low Si/Al ratio, the optical density of the 2160 cm^{-1} band (normalized per gram of solid) increases linearly with the amount of irreversibly adsorbed CO at 298 K determined by volumetry. It is concluded that, for these solids, all the sites accessible to CO are isolated Cu^{n+} ions, and that the infrared spectroscopy gives an estimation of the copper dispersion. When the solids possess also non-isolated Cu^{n+} ions accessible to CO (high Si/Al ratios), this linearity is, of course, no more observed (figure 7).

4. Concluding remarks

With all the Cu-MFI solids, oxygen is necessary for the reduction of NO by propane. Maxima with the temperature and with the oxygen content are always observed.

The NO into N_2 reduction rate correlates with the number of accessible isolated species (or small copper oxide aggregates), as already stated [13–15,30–33]. $(CuOH)^+$ species or oligomers are likely, Cu being linked to an extra-framework O (or OH) ligand since reducible under vacuum [6,10,11]. The present paper demonstrates that this correlation occurs whatever the Si/Al ratio, the copper content, the type of support and the aging state (fresh or hydrothermally-aged solids).

Whatever the exchange degree, the isolated ions evidenced by their νCO IR band (Cu^+CO species) are the only species detected when the Si/Al ratio remains moderate. Even with an exchange degree reaching 140% (Si/Al = 19, 3.8 wt% Cu), no bulk oxides have been detected by CO adsorption. For high Si/Al ratios, non-isolated Cu^{n+} ions (belonging to bulk CuO and Cu_2O oxides) accessible to CO are also detected. Aging at 923 K leads to an decrease in the number of isolated ions without agglomeration. Such an agglomeration occurs after aging at 1073 K.

When only one type of site is detected, i.e., isolated copper ions, the optical density of the νCO band leads to an estimation of the number of surface copper ions accessible to CO and gives access to the copper dispersion.

This correlation between the NO reduction into N_2 and the number of isolated copper ions is also observed when copper is deposited on non-zeolitic supports, alumina, silica and silica–alumina, O_2 promoting the NO reduction only in the case of low copper loadings.

However, Cu on MFI (reactions generally performed at 623 K) remains more active than Cu on non-zeolitic supports (reactions generally performed at 773 K), showing the additional influence of the zeolitic framework. From literature data giving the activation energy for the NO reduction (between 63 and 125 $kJ\,mol^{-1}$) [34,35], we have estimated that, for a same value of the optical density of the νCO band of the isolated Cu^+ ions, a Cu-MFI solid is 3–33 times more active than a Cu/Al_2O_3 solid. The zeolite morphology may affect the coordination of the cation, the relative diffusivities of the reactants and/or the activation of the hydrocarbon molecule.

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