FTIR study of low-temperature CO adsorption on Mn-ZSM-5 and MnY zeolites. Effect of the zeolite matrix on the formation of $Mn^{2+}(CO)_x$ geminal species

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Abstract

Adsorption of CO on Mn-ZSM-5 zeolite at 85 K results in formation of physically adsorbed CO, several kinds of H-bonded CO and $Mn^{2+}(CO)_x$ geminal species (2202 cm^{-1}). Decreasing the coverage during evacuation results in disappearance of the physically adsorbed CO and the H-bonded forms and in conversion of the dicarbonyls to linear Mn^{2+}–CO species (2214 cm^{-1}). The latter are quite stable at 85 K. Coadsorption ^{12}CO and ^{13}CO reveals that the CO molecules in the geminal polycarbonyls behave as independent oscillators. In contrast, CO adsorption at 85 K on MnNaY zeolite only leads to formation of linear Mn^{2+}–CO species (2210 cm^{-1}) and mono- and di-carbonyls associated with residual sodium cations. The results are interpreted as evidence that site-specified geminal carbonyls are formed with cations possessing an ionic radius bigger than a critical value. This value is different for different positions in various zeolites and is bigger for cations in S_{II} positions in Y zeolites than is the case of cations in a ZSM-5 matrix. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The possibility of bonding of more than one molecule to one surface site is of great importance for the heterogeneous catalysis because this facilitates the interaction between the adsorbed molecules. Therefore, it is of definite interest to know the factors determining the formation of geminal species. Simultaneous coordination of two or three molecules to one site is a well-known phenomenon. Typical examples are the di- and tri-carbonyls

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formed on supported Rh and Ru catalysts [1]. In these cases, however, the polycarbonyls are normally decomposed without passing through linear species. During the past years a new class of geminal species (the so-called *site-specified* geminal species [1]) was discovered [1–16]. All these species are formed on metal-exchanged zeolites or on related materials and are decomposed losing their ligands stepwise. A reason for the formation of site-specified geminal species is believed to be the low coordination of the charge-compensating metal cations. As a consequence, bonding of more than one molecule to one site occurs even when the adsorption is weak. Typical examples are adsorption of N_2 and CO on alkali- and alkaline-earth exchanged zeolites where the adsorbates are bound mainly by electrostatic forces. Coordination of two of these small molecules has been reported with Li^+ [2], Na^+ [3–6], K^+ [4], Rb^+ [4] and Cs^+ [4] in ZSM-5 [2,5], Y [3], EMT [4] or ETS-10 [6] matrices. Earlier studies on CaY revealed also formation of $Ca^{2+}(CO)_2$ [7] but more recently, it has been reported [8] that up to three CO molecules can be hold by one Ca^{2+} cation at low-temperature. These reports are in line with the observations of simultaneous coordination of up to three NH_3 molecules to one Ca^{2+} [9] or Sr^{2+} [10] cation from fully dehydrated CaX and SrX zeolites, respectively. The possibility of simultaneous coordination of more than one CO or N_2 molecule to one cationic site in Y zeolites has been recently confirmed by DF calculations [11]. A peculiarity of all these cases is the easy formation of mixed complexes. Therefore, site-specified geminal species are more important for heterogeneous catalysis because different reactant molecules can be coadsorbed on the coordination site.

We have found that, with alkali-metal exchanged EMT zeolites, geminal species are produced with the participation of Na^+, K^+, Rb^+ and Cs^+ ions, whereas only one CO or N_2 molecule can be coordinated to one exchanged Li^+ cation [4]. We have explained this phenomenon by the small ionic radius of Li^+ which allows the cation to penetrate in the plane of the oxygen atoms to which it is coordinated, thus hindering formation of geminal species. However, strong evidence of simultaneous coordination of two CO molecules to

one Li^+ cation from Li-ZSM-5 has been provided very recently [2]. All this suggests that the critical ionic radius, R_{C2}, above which simultaneous coordination of two molecules is possible, is different for the different zeolites, i.e., for the different positions of the cations and, most probably, for ZSM-5 is close to the cationic radius of Li^+.

Although the most systematic studies have been performed on zeolites with exchanged cations from groups IA and IIA of the periodic system, site-specified geminal carbonyls have also been observed for zeolites exchanged with cations to which CO is bonded by σ- or by σ- and π-bonds. The most typical examples are the formation of $Ag^+(CO)_2$ species with Ag-ZSM-5 [12]; $Cu^{2+}(CO)_2$ and $Cu^+(CO)_3$ species with Cu-ZSM-5 [13–15]; and $Ni^{2+}(CO)_2$ and $Ni^+(CO)_3$ species with Ni-ZSM-5 [16]. The latter two cases indicate, once again, that the process is favoured by a big cationic radius: decreasing oxidation state of the cation is accompanied by an increase of its ionic radius so that even three molecules can be coordinated simultaneously to one cation provided its radius is sufficiently large.

Analysing these observations, one can expect that all cations larger than Li^+ in a ZSM-5 matrix can coordinate two small molecules, whereas the critical ionic radius for simultaneous coordination of three molecules, R_{C3}, should be between 0.72 and 0.96 Å (the radii of Cu^{2+} and Cu^+, respectively) [17]. However, it appears that with Y and EMT zeolites (having identical structures of the cationic positions) R_{C2} is between 0.74 and 0.96 Å (the radii of Li^+ and Cu^+, respectively). Note that the Cu^+ cations possess a sufficiently large ionic radius to form even tricarbonyls in CuY [18].

It should be pointed out that the above picture is somewhat simplified, because the process also depends on the electrophilicity of the cation. Thus, Na^+ and Ca^{2+} possess similar ionic radii (0.97 and 0.99 Å, respectively) but only dicarbonyls have been reported with Na-EMT, whereas tricarbonyls can be formed with CaY [8]. To eliminate this factor, one has to study a system where CO adsorption is relatively strong, i.e., the carbonyls should be detectable at ambient temperature.

To obtain more information about the possibility of formation of site-specified geminal spe-

cies, we studied CO adsorption on Mn-ZSM-5 and MnY samples. Needless to say, that Mn-ZSM-5 is a sample of significant interest because of its promising properties in the selective catalytic reduction of nitrogen oxides [19].

IR bands due to Mn^{n+}–CO surface complexes have been recorded at 2213–2172 cm^{-1} [20–28] and at 2144–2114 cm^{-1} [21,22,29]. These vibrations are generally assigned to Mn^{2+}–CO species [20,23,24] but some authors [21,25,29] have reported that they characterise Mn^{3+}–CO carbonyls. The surface complexes are easily decomposed after evacuation and are in some cases detected at low temperatures only, which indicates formation of an electrostatic and a σ-bond only between manganese ions and CO. Carbonyls stable towards evacuation (band at 2213 cm^{-1}) have been detected with Mn-ZSM-5 [27]. CO adsorption on MnY zeolites leads to the appearance of a Mn^{2+}–CO band at 2208–2200 cm^{-1} [20,24]. At low temperatures Soltanov et al. [24] have detected one more band at 2187 cm^{-1} which has also been attributed to Mn^{2+}–CO species.

2. Experimental

The Mn-ZSM-5 sample (19 wt% Mn) was prepared by dispersing NH$_4$-ZSM-5 (SiO$_2$/Al$_2$O$_3$ = 30, Zeolyst International) in 0.01 M NH$_4$NO$_3$ solution at a pH = 6.5. Then, a solution of Mn(CH$_3$COO)$_2$ was added dropwise while the suspension was stirred. After 48 h the mixture was alkalized by ammonia (1:1) until pH = 12.0. The solid was filtered, washed well with deionized water, dried and calcined at 673 K.

The MnNaY sample (12 wt% Mn) was prepared by conventional ion-exchange with 0.1 M solutions of MnCl$_2$. The starting NaY material was a commercial Grace Davison product (SP No. 6 – 5257.0101). After preparation, the sample was filtered, washed, dried and calcined at 673 K.

Carbon monoxide (99.997) was supplied by Linde. Labelled carbon monoxide (^{13}CO) was provided by Aldrich Chemical, and had an isotopic purity of 99.0 at.%. It contained about 10% of ^{13}C^{18}O.

The IR spectra were recorded on a Bruker IFS-66 spectrometer with a spectral resolution of 2

cm^{-1}. Self-supporting pellets were prepared from the samples and treated directly in the IR cell. The latter was designed for low-temperature experiments and connected to a vacuum-adsorption apparatus with a base pressure below 10^{-3} Pa. Prior to the adsorption measurements, the samples were activated by 1 h calcination at 773 K and 1 h evacuation at the same temperature.

3. Results and discussion

3.1. Characterization of the samples

The IR spectrum of the activated Mn-HZSM-5 sample contains three sharp bands with maxima at 3745, 3662 and 3610 cm^{-1} in the OH stretching region. The band at 3745 cm^{-1} is assigned to silanol groups, whereas that at 3610 cm^{-1} characterizes the acidic bridging hydroxyls of the zeolite [30]. The band at 3662 cm^{-1} is most probably due to Al–OH species [31]. The band at 3610 cm^{-1} exhibits a lower intensity as compared to the initial H-ZSM-5 sample. The results show that, irrespective of the high concentration of manganese, the ion exchange is not complete.

Three very weak bands at 3744, 3670 and 3622 cm^{-1} are present in the spectrum of the activated MnNaY sample. The bands at 3744 and 3670 cm^{-1} can be assigned to Si–OH and Al–OH groups, respectively, while the band at 3622 cm^{-1} is attributed to Al^{3+}–OH or Mn^{2+}–OH species.

3.2. Adsorption of CO on Mn-ZSM-5

Introduction of CO (10 Pa) to the Mn-ZSM-5 sample at 85 K results in appearance, in the IR spectrum, of bands with maxima at 2202, 2193, 2173 and 2139 cm^{-1} and several shoulders located at 2214, 2166 and 2155 cm^{-1} (Fig. 1, spectrum a). Decrease in the equilibrium pressure leads to a fast disappearance of the band at 2139 cm^{-1}. The bands at 2155 and 2166 cm^{-1} also decrease with the coverage (Fig 1, spectra b–d) whereas the band at 2173 cm^{-1} is more stable (Fig 1, spectra b–f). These three bands are assigned to different forms of H-bonded CO. Indeed, the changes in these bands are accompanied by synchronous
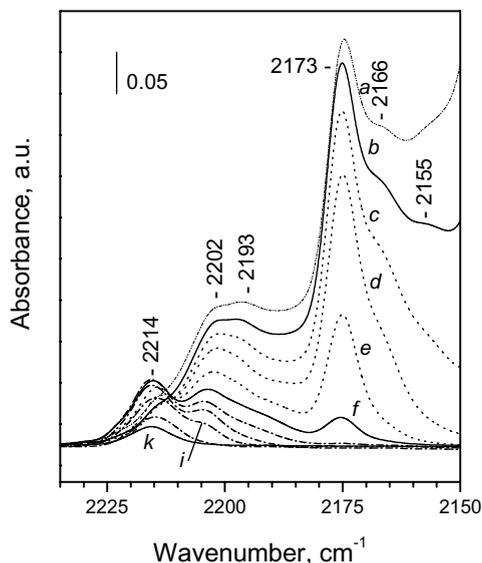
Fig. 1. FTIR spectra of CO (10 Pa equilibrium pressure) adsorbed at 85 K on Mn-ZSM-5 (a), changes of the spectra under dynamic vacuum at 85 K (b–h) and at increasing temperatures up to 115 K (i–k).

shifts of the hydroxyl bands to lower frequencies. Since these bands are beyond the aim of the present study, they will be not discussed in more detail.

In the region above 2180 cm^{-1}, evacuation at 85 K and increasing temperatures results in a fast decrease in intensity of the band at 2193 cm^{-1} and a slower disappearance of the 2202 cm^{-1} band. At the same time a band at 2214 cm^{-1} with a shoulder at 2222 cm^{-1} develops, rises in intensity and shifts to 2216 cm^{-1} (Fig. 1, spectra h–k). Then this band starts to decrease (Fig. 1, spectrum g) while the band 2202 cm^{-1} disappears completely. The results show that at high coverages and at 85 K two or more CO molecules are adsorbed simultaneously on one Mn^{2+} site (see below). These geminal polycarbonyls easily lose one (or more) of their CO ligands during evacuation at 85 K thus being converted into Mn^{2+}–CO linear species. Analysis of the literature data [20,23,24,27,28] indicates that the oxidation state of manganese in the carbonyl complexes is indeed 2+.

Room temperature CO adsorption (70 kPa equilibrium pressure) also produces the bands at

2214, 2202 and 2169 cm^{-1} (the maxima are slightly shifted due to temperature change). The bands at 2202 and 2169 cm^{-1} drop in intensity with decreasing pressure, whereas the band at 2214 cm^{-1} and its shoulder at 2222 cm^{-1} are still present in the spectrum even after prolonged evacuation.

3.3. Coadsorption ^{12}CO and ^{13}CO on Mn-ZSM-5

It is known that, when CO adsorption is weak, the CO molecules in geminal species behave as independent oscillators. On the contrary, when the adsorption is strong, the CO modes of the dicarbonyls are split into symmetric and antisymmetric stretching vibrations. Although CO adsorption on Mn^{2+} ions from Mn-ZSM-5 appears to be relatively weak, it is stronger than CO adsorption on alkali- and alkaline-earth cations in zeolites and one could expect splitting of the CO modes in the dicarbonyls. Looking for additional information of this, we studied the coadsorption of ^{12}CO and ^{13}CO (ca. 25 mol% ^{12}CO).

Adsorption of a ^{12}CO and ^{13}CO isotopic mixture (200 Pa equilibrium pressure, followed by a short evacuation) on Mn-ZSM-5 at 85 K results in the appearance of a series of bands in the 2220–2050 cm^{-1} spectral region. Their maxima are at 2202, 2175, 2165, 2152, 2139, 2127, 2092 and 2075 cm^{-1} (Fig. 2, spectrum a). A shoulder at 2214 cm^{-1} is also visible. Decrease in coverage leads to essentially the same changes of the surface species as those observed with the ^{12}CO adsorption experiments (Fig. 2, spectra b–o). Taking into account the results obtained after adsorption of CO, and the ^{12}CO–^{13}CO isotopic shift factor (0.97777) we assign the above bands as follows: 2214 cm^{-1}, to Mn^{2+}–^{12}CO; 2202 cm^{-1}, to the $v(^{12}$C–O) stretches of Mn^{2+}(CO)$_x$ species; 2175 cm^{-1}, to OH–^{12}CO; 2165 cm^{-1}, to Mn^{2+}–^{13}CO with participation of some OH–CO vibrations; 2152 cm^{-1}, to the $v(^{13}$C–O) modes of Mn^{2+}(CO)$_x$ species; 2139 cm^{-1}, to physically adsorbed ^{12}CO; 2127 cm^{-1}, to OH–^{13}CO; and 2092 cm^{-1}, to physically adsorbed ^{13}CO. The band at 2075 cm^{-1} arises from H-bonded ^{13}C^{18}O.

These results suggest that no measurable splitting of the CO modes occurs with Mn^{2+}(CO)$_x$ species.
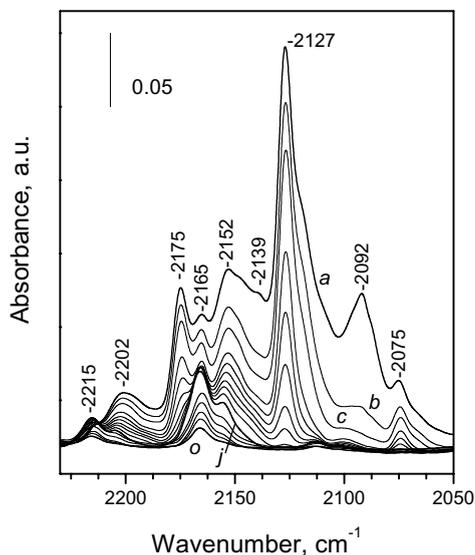
Fig. 2. FTIR spectra of a ^{12}CO–^{13}CO isotopic mixture (ca. 25 mol% ^{12}CO) adsorbed at 85 K on Mn-ZSM-5. Initial equilibrium pressure of 200 Pa and evolution of the spectra under dynamic vacuum at 85 K (a–o).

Fig. 3. FTIR spectra of CO (20 Pa equilibrium pressure) adsorbed at 85 K on MnNaY (a), changes of the spectra under dynamic vacuum at 85 K (b–g) and at increasing temperatures up to 243 K (h–m).

3.4. Adsorption of CO on MnY at 85 K

Adsorption of CO (20 Pa equilibrium pressure) on MnNaY at 85 K results in the appearance of one very intense band at 2167 cm^{-1} and two bands at 2210 and 2120 cm^{-1} (Fig. 3, spectrum a). In agreement with data from the literature [3,4], the band at 2167 cm^{-1} is assigned to Na$^+$(CO)$_2$ species. The band at 2120 cm^{-1} has a more complex origin: it arises from the overlap of bands due to Na$^+$(^{13}CO)$_2$ (from natural ^{13}C abundance) and O-bonded CO [2,4]. The band at 2210 cm^{-1} is not observed with Mn-free samples and is thus attributed to manganese carbonyls.

Short evacuation results in disappearance of the 2167 cm^{-1} band and appearance of a new band at 2176 cm^{-1} characterising Na$^+$–CO monocarbonyls [3,4] (Fig. 3, spectrum b). The latter band is formed during the decomposition of the Na$^+$(CO)$_2$ species. The ^{13}CO satellite of the 2176 cm^{-1} band is now clearly visible at 2128 cm^{-1}, whereas the 2118 cm^{-1} band corresponds to Na$^+$–OC complexes. At the same time the band at 2210 cm^{-1} negligibly increases in intensity (see the inset in Fig. 3) and difference

spectra show disappearance of a weak component at 2193 cm^{-1} and a very weak one at 2217 cm^{-1}.

Further evacuation (Fig. 3, spectra b–g) leads to a gradual decrease in intensity and disappearance of all carbonyl bands associated with sodium cations. The band at 2210 cm^{-1} is stable toward evacuation at 85 K, but decreases in intensity and disappears on evacuation at increasing temperatures (Fig. 3, spectra h–m). These results indicate that the band at 2210 cm^{-1} is to be assigned to Mn^{2+}–CO linear species which are not converted into dicarbonyls even at 85 K and high pressures. Only negligible conversion to Mn^{2+}(CO)$_2$ species probably occurs at CO pressures > 20 Pa. Comparison with the results obtained with Mn-ZSM-5 shows that the carbonyls on MnY are less stable, which is consistent with their lower stretching frequency.

3.5. Coordination of more than one molecules to one Mn^{2+} cation

It is known that the cationic radii are not constant values, but also depend on the coordination number of the cation [17]. However, for a given

zeolite position, i.e., the same coordination, the real radii will be proportional to the radii reported in the literature. Cations in Y zeolites are located in S_I, S_{II} and $S_{II'}$ positions, but, especially at low temperatures, cations in S_{II} positions only are accessible for adsorption. Although not all details are well-known for all systems, it is believed that these cations are coordinated to three oxygen atoms from the six-ring windows [32]. A detailed XRD study of Mn^{2+} ions in faujasite and their CO sorption complexes has been recently published [33]. It has been reported that the Mn^{2+} cations occupy S_I (where are inaccessible for adsorption) and S_{II} sites (with trigonal planar coordination). Hence, small cations as Mn^{2+} (ionic radius of 0.80 Å [17]) can penetrate the six-rings, which should hinder formation of geminal species for steric reasons. Indeed, after CO adsorption linear monocarbonyls are formed. A small departure of the Mn^{2+} towards tetrahedral coordination has also been observed. Thus, according to our results and the results reported in [33], R_{C2} for faujasite type zeolites (S_{II} positions) appears to be larger than 0.80 Å (the ionic radius of Mn^{2+}).

ZSM-5 is a pentasil zeolite. According to recent theoretical studies [34], Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} cations in ZSM-5 are preferentially located in flat five-rings. By analogy, one can expect the same location for Mn^{2+} cations. It has been also shown that cations in over exchanged samples (as our Mn-ZSM-5 specimen) can be located in rings not containing aluminum [35]. Since the dimension of the five-rings in ZSM-5 is smaller than the dimension of the six-rings in faujasite, cations would penetrate in five-rings with more difficulty. That is why the R_{C2} for ZSM-5 is smaller than for Y zeolites and Mn^{2+} cations in Mn-ZSM-5 are able to coordinate two or more CO molecules simultaneously.

4. Conclusions

- Mn^{2+} cations in Mn-ZSM-5 zeolites can coordinate more than one CO molecules stepwise at low-temperature. In contrast, Mn^{2+} cations in MnY zeolites are able to coordinate one CO molecule only even at a low-temperature.

- The ability of cations in a zeolite matrix to coordinate two or more CO molecules depends on the ionic radius of the cation and on the nature of the zeolite site.

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