Reversible occlusion of CO in Cs-impregnated X and Y zeolites

E. Garrone,*[a] N. Russo,[a,b] P. Marturano,[a] B. Onida,[b] F. Di Renzo[c] and M. Laspéras[c]

[a] Dipartimento di Chimica Inorganica, Fisica e dei Materiali,Università di Torino, Via P. Giuria 7, 10125, Torino, Italy. E-mail: garrone@ch,unito.it
[b] Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129, Torino, Italy
[c] Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, ENSCM, 8 rue Ecole Normale, 34296 Montpellier France

Cs_2O in the supercages of Cs-impregnated X and Y zeolites attacks the siliceous portions of the lattice (siloxane bridges), with formation of $(Si–O^-Cs^+)_2$ groups which allow the occlusion (reversible at high temperature) of CO in the sodalite units, as indicated by the formation of an IR band at 2150 cm^{-1}.

Basic zeolites (bearing alkali metal counterions) arouse much interest these days, because they may possibly replace in catalysis harsh chemicals like sodium hydroxide. Besides cationic exchange of the original Na$^+$ for Cs$^+$, to increase basicity, samples are further impregnated[1] with Cs acetate, which, on thermal treatment, converts to Cs_2O. The nature of such an oxide in the zeolite matrix depends on the activation conditions and is currently under discussion.[2]

In the course of a systematic study of basic centres in Cs-exchanged and Cs-impregnated X and Y zeolites,[3] we made the intriguing observation that a weak band at 2150 cm^{-1} is formed in the IR background spectrum, recorded at room temperature, of impregnated (but not simply exchanged) samples in the activation step (lower curve in Fig. 1). This activation step consists of thermal treatment (during which decomposition of the acetate takes place) and subsequent oxidation under oxygen at 823 K as described by Laspéras et al.[3]

Two Cs impregnated samples, with different Cs contents (8 and 24 atoms per unit cell) were considered, with both Y and X zeolites. IR spectra were recorded on a Perkin-Elmer 1760-X spectrophotometer equipped with a MCT cryodetector, at a resolution of 2 cm^{-1}.

The intensity of the IR band at 2150 cm^{-1} was larger for Y than for X zeolites, and it varied with the Cs_2O content. Outgassing at about 820 K depletes the band. Its peak position is strongly indicative of CO interacting with Na$^+$ cations, which

are left behind in the exchange process. Thermal decomposition of the acetate is likely to yield CO: such an assignment cannot, however, be made lightly, because CO adsorption on alkali-exchanged zeolites only takes place at temperatures around 77 K[4,5] under substantial CO pressure.

Heating of the impregnated samples in a CO atmosphere at temperatures around 770 K followed by cooling in the same atmosphere leads to an enormous increase in the intensity of the 2150 cm^{-1} band (upper curve in Fig. 1), so that even the ^{13}C satellite band can be observed, though the natural abundance of ^{13}C is only 1%. This confirms beyond doubt that the band is due to CO held in the solid. The nature of the species giving rise to the peak appearing at 2137 cm^{-1} is not discussed here. If heating in CO is followed by evacuation at the same temperature before cooling, a decrease of the original band is observed: CO contact at room temperature has no effect. Prolonged heating of the samples holding CO at 823 K in vacuum depletes the band.

A plausible assignment of the band under discussion is the stretching mode of CO molecules interacting with Na$^+$ cations: these latter, however, are not those normally exposed at the supercages, but are instead the Na$^+$ cations inside the sodalite cages, usually not accessible to molecules, though the mineral sodalite is known to occlude large rare-gas atoms like Kr.[6]

We favour Na$^+$ over Cs$^+$ as the centre of interaction for the following reasons: (i) the ν(CO) frequency is closer to the values reported in the literature for the former cation; (ii) if reference is made to the standard geometry of the sodalite cage. There is not enough room for Cs$^+$ cations and CO molecules to coexist in the cage.

We have checked, by means of computer graphics, that a CO molecule may be occluded in the sodalite cages of an X zeolite, of composition close to the one studied by us, for which structural data are available.[7] One CO molecule may be hosted in the cavity: little room is left, however, so that the molecule is actually trapped in the sodalite cage. Indeed, the ratio between the frequencies of ^{12}CO and ^{13}CO (see Fig. 1) indicates that the motion is particularly anharmonic. The peculiarity of such an interaction occurring at room temperature also accounts for the lower frequency observed for related CO in comparison with that observed for CO interacting at 77 K with Na$^+$ cations in supercages (2154 cm^{-1}).

Thermal treatments in CO, even at high temperatures, of the simply exchanged samples do not cause the appearance of the 2150 cm^{-1} band. This is therefore strictly related to the presence of Cs_2O. On the other hand, the intensity of the 2150 cm^{-1} band is much higher with Y than with X zeolite, i.e. the occlusion of CO is greater, the larger the Si content of the sample. Chemical attack of the lattice by Cs_2O is indicated by the loss of crystallinity we observed in the XRD patterns for thermal treatment above 670 K. A plausible mechanism is then the reaction of siloxane bridges with caesium oxide: Si–O–Si + $Cs_2O \rightarrow (Si–O^-Cs^+)_2$, to yield a microcluster of Cs silicate, according to rather elementary chemistry. The cleavage of the
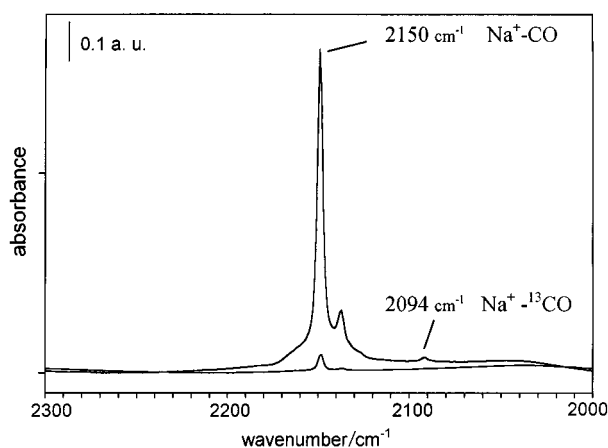
Fig. 1 Infrared spectra of Cs impregnated X zeolite (24 Cs per unit cell). Lower curve: after activation at 823 K; upper curve: after heating in CO atmosphere at 770 K for 1 hour and cooling in the same atmosphere.

siloxane bridge widens the window giving access to the sodalite cage, which is partially obstructed by the Si–O⁻Cs⁺ groups. At high temperatures, thermal movement of these groups may give CO molecules access to sodalite cavities, which is then prevented at low temperatures.

Whereas occlusion phenomena are known in some fields of chemistry (clathrates, matrix isolation), to our knowledge, the phenomenon reported here is the first case of reversible occlusion in the solid state: it may probably be extended to other suitably sized molecules like nitrogen and oxygen, and to other zeolitic systems.

Notes and References

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