In situ Diffuse Reflectance Infrared Investigations of Coadsorption and Intrazeolite Reactions of Hexacarbonyl Molybdenum(0) and Organic Ligands

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Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) investigations indicate that under thermal activation, the coadsorption, by vapour-phase loading, of $Mo(CO)_6$ and C_6H_6 or C_6H_5N in the $Na_{85}X$ faujasite-type zeolite leads to the grafted $Mo(CO)_3$ moiety, whereas $(\eta^6\text{-}C_6H_6)$ $Mo(CO)_3$ and $(C_5H_5N)_x$ $Mo(CO)_{6-x}$ (x = 1,2,3) are obtained in $Na_{55}Y$; no reaction is observed in the dealuminated Y* zeolite before the desorption.

The structural and chemical features of zeolites, *i.e.* their crystalline, open-pore structures with well-defined adsorption sites and ion-exchange capability can dictate a specific intrazeolite chemistry. Current research on carbonyl entrapped in faujasite-type zeolites with large pores is aimed at improved understanding of the mechanism(s) by which the intracavity metal carbonyl chemistry takes place.[1-5]

Among the methods used for the identification of molecular species in macroporous solids—including EXAFS, MAS–NMR spectroscopy—infrared transmission spectroscopy is the most widely employed.[1,2,4] However, the diffuse reflectance technique using crude powdered samples is well suited to the study of solid–gas exchange process and *in situ* chemistry.[6,7] Some new perspectives have come from the use of this technique in intrazeolite organometallic chemistry.[8]

Here we describe a new approach to the study of the evolution of coadsorption and subsequent reaction of $Mo(CO)_6$ and organic ligands. The coadsorption of $Mo(CO)_6$ and arene or pyridine was realized by vapour-phase loading in the framework of faujasite-type zeolites. DRIFTS studies were undertaken as functions of the Si/Al ratio of the zeolite, loading levels of $Mo(CO)_6$ and ligands, size of ligands and temperature.

The zeolites used were $Na_{85}X$ (Si/Al = 1.26), $Na_{55}Y$ (Si/Al = 2.5) and Y* (Si/Al = 60) faujasite-type. The X, Y and Y* dehydrated zeolites are characterized by a cage system in which the α-cage or super-cages (1.3 nm) connected by windows (0.8 nm) can only be penetrated by $Mo(CO)_6$ (0.8 nm) and small molecules such as C_6H_6 and C_5H_5N (0.59 nm).

The key part of the *in situ* DRIFTS apparatus is a version of the Harrick Scientific equipment, which was modified by the attachment of vacuum lines to the sample compartment of the spectrometer. The loading levels were estimated from the intensities of several IR bands using known samples as references. The $Mo(CO)_6$ was sublimed into a fully dehydrated zeolite samples held at 280 K. DRIFTS spectra were taken during the course of the sublimation. The spectra of all samples exhibited at first only a broad structureless band in the region of the ν(CO) fundamentals. In the case of aluminated zeolites $Na_{55}Y$[1,8-10] and $Na_{85}X$,[9] at low coverage (1 $Mo(CO)_6$ per 100 α-cages) six resolved bands emerged after equilibration for 24 h. Only one band corresponding to ν6 (E_{1u} of O_h) was observed for the aluminium-free zeolite Y*. Subsequently, benzene was coadsorbed *via* sublimation onto $Na_{85}X$, $Na_{55}Y$ and Y* zeolite samples loaded with $Mo(CO)_6$ at low coverage and the DRIFTS spectra indicate that at 280 K, no reaction occurs. However, after subtraction of the spectrum of benzene the remaining spectrum does not correspond exactly to the spectrum of $Mo(CO)_6$ adsorbed alone in the zeolites. The most significant differences were observed for $Na_{55}Y$. This effect can be interpreted by the presence in the same super-cage of both C_6H_6 and $Mo(CO)_6$ and competitive interaction with the cations of the internal surface. The coadsorption of C_6H_6 onto $Mo(CO)_6$-loaded zeolite at high coverage occurs to a very small extent because of the pore blocking by $Mo(CO)_6$. The zeolites loaded at high level are, therefore, not suitable for the *in situ* DRIFTS study. The adsorption of C_6H_6 into $Na_{55}Y$[11,12] and $Na_{85}X$ has been extensively described previously by the IR transmission spectroscopy. In addition, the adsorption sites and molecular dynamics of C_6H_6 in $Na_{55}Y$ are well documented.[13]

The DRIFT spectra, recorded during the thermal treatment of the 0.1 $Mo(CO)_6$, 16 C_6H_6–$Na_{85}X$ loaded zeolite, were assigned by comparison with DRIFT spectra recorded during

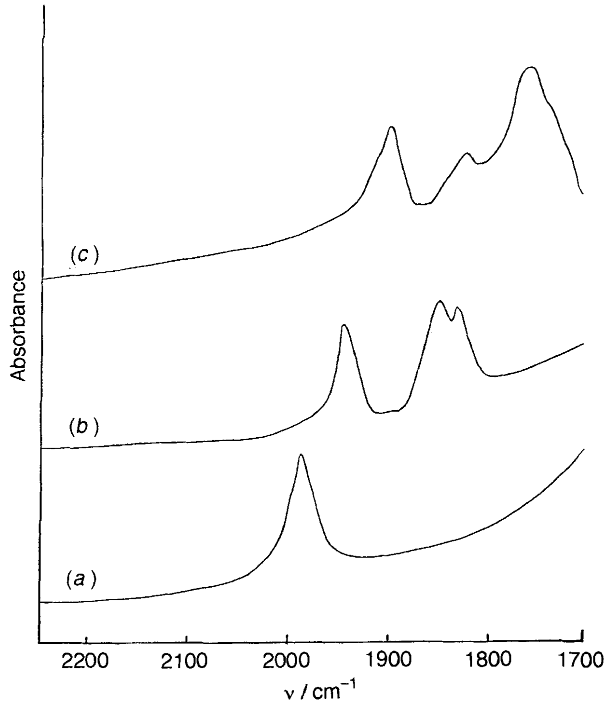

Fig. 1 DRIFT spectra after subtraction of the C_6H_6 residual spectra of (*a*) 0.1 $Mo(CO)_6$, 10 C_6H_6–Y* system at 420 K; (*b*) 0.1 $Mo(CO)_6$, 16 C_6H_6–$Na_{55}Y$ at 350 K, (*c*) 0.1 $Mo(CO)_6$, 10 C_6H_6–$Na_{85}X$ at 420 K

the thermolysis of 0.1 $Mo(CO)_6$, $Na_{85}X$ zeolite. Heating of the latter above 350 K causes a complete change of the set of ν(CO) bands (Fig. 1). The two bands observed at 1990 and 1770 cm^{-1} were assigned to the vibrational ν(CO) modes of the intrazeolite subcarbonyl species corresponding to the $Mo(CO)_3$ moiety.[14] This grafted species $Mo(CO)_3$ $(O_z)_3$(O_z = oxygen atom of the zeolite framework) appeared to be stable up to 573 K.

However, during the thermal treatment of the 0.1 $Mo(CO)_6$, 16 C_6H_6–$Na_{55}Y$, a completely different behaviour was observed. Under the same experimental conditions, as described above for the NaX zeolite, heating above 423 K again causes a change in the ν(CO) set of bands. The three bands observed at 1948, 1857 and 1832 cm^{-1} (Fig. 1), do not correspond to the intrazeolite $Mo(CO)_3$ subcarbonyl species.[3,4,8,14,15] However, they are in good agreement with the spectra reported previously for the intrazeolite (η^6-C_6H_6) $Cr(CO)_3$–$Na_{55}Y$ species.[4] The three ν(CO) bands derived from the A_1 and E modes of the free molecule indicate that the local symmetry is low. In contrast to benzene, large arene molecules such as 1,3,5-triethylbenzene are effectively size-excluded from the porous volume and the IR spectrum of the grafted $Mo(CO)_3$ moiety is detected in the DRIFT spectra under thermal treatment of 0.1 $Mo(CO)_6$–$Na_{55}Y$ zeolite.

During the thermal treatment of the 0.1 $Mo(CO)_6$, 10 C_6H_6–Y* loaded zeolite no change was observed in the DRIFT spectra before the desorption of both benzene and $Mo(CO)_6$. The one-band spectrum of $Mo(CO)_6$ entrapped in Y* zeolite was run in the ν(CO) region and no intracavity reaction occurred between $Mo(CO)_6$ and C_6H_6 in the 280–573 K temperature range.

Next, pyridine was substituted for benzene. After the loading of the $Na_{55}Y$ with $Mo(CO)_6$ at low coverage, C_5H_5N was adsorbed. At 280 K, no drastic effect was detected in the DRIFT spectrum in the ν(CO) region, except at high coverage with C_5H_5N. In that case the ν(CO) set of bands of $Mo(CO)_6$ gradually decreases and disappears before the saturation by C_5H_5N. Under thermal treatment above 432 K of the 0.1 $Mo(CO)_6$, 8 C_5H_5N–$Na_{55}Y$ loaded zeolite, the six-line spectrum of the entrapped $Mo(CO)_6$ was gradually replaced by a three-line spectrum, in which the 1902, 1760 and 1736 cm^{-1} bands are in good agreement with the $(C_5H_5N)_3$ $Mo(CO)_3$ species in a low local symmetry. It would be noted that the free molecule exhibits two bands at 1908 (A_1) and 1777 cm^{-1} (E).

The thermolysis of the loaded zeolite does not lead to the intrazeolite $Mo(CO)_3$ moiety as was observed[4,8,14,15] with the 0.1 $Mo(CO)_6$–$Na_{55}Y$ zeolite with the two CO bands at 1908 and 1770 cm^{-1}. The $Mo(CO)_6$-C_5H_5N intrazeolite reactions were found to be reversible under CO at low pressure, it is possible to restore entrapped $Mo(CO)_6$ through the transient $(C_5H_5N)_2$ $Mo(CO)_4$ and $(C_5H_5N)Mo(CO)_5$ species. The characteristic ν(CO) bands of the latter intrazeolite species are found to be in the same wavenumber range as reported previoulsy for the free molecules, except for some modifications induced by the zeolite framework.

As expected, the experimental results clearly demonstrate the size-exclusion of molecules larger than the 12-ring entrance window of the α-cage. In addition, at high coverage the 'pore blocking' phenomena hinders the migration of those molecules small enough to gain free access to the α-cage. With analogous size and shape constraints imposed by the pore of the faujasite-type zeolites studied, the behaviour of the porous support depends dramatically on the Si/Al ratio of the zeolite. The porous supports can act as a solvent, a reagent or a catalyst.

In the dealuminated Y* zeolite (Si/Al *ca.* 60), the behaviour of the coadsorbed C_6H_6 and $Mo(CO)_6$ towards reactivity appears comparable to the properties previously reported in homogeneous solution. In the $Na_{85}X$ zeolite (Si/Al = 1.26) it was demonstrated previously[12,14] that the base strength of the lattice oxygen increases with the Al content, suggesting an increase in the negative charge on the oxygen atom. The oxygen atoms of the internal surface of the α-cage act as a strong reagent towards the entrapped $Mo(CO)_6$ despite the presence of C_6H_6. In contrast, the intracavity electrostatic field and the base strength of the $Na_{55}Y$ zeolite framework (Si/Al = 2.5) act as catalysts to the intracavity reaction between $Mo(CO)_6$ and arene or pyridine. The intrazeolite chemistry of the entrapped $Mo(CO)_6$ is unexpected and unprecedented. It suggests a supramolecular assembly of $Mo(CO)_6$, organic ligands and extra framework ions in the porous system.

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References

1 M. C. Connaway and B. E. Hanson, *Inorg. Chem.*, 1986, **25**, 1445.
2 R. L. Schneider, R. F. Howe and K. L. Watters, *Inorg. Chem.*, 1984, **23**, 4600.
3 G. A. Ozin, S. Özkar, H. O. Pastore, A. J. Pöe and E. J. S. Vichi, *J. Chem. Soc., Chem. Commun.*, 1991, 141.
4 S. Ozkar, G. A. Ozin, K. Moller and T. Bein, *J. Phys. Chem.*, 1989, **93**, 4205.
5 A. Borvornwattananont, K. Moller and T. Bein, *J. Phys. Chem.*, 1989, **93**, 4205.
6 J. J. Venter and M. A. Vannice, *J. Phys. Chem.*, 1989, **93**, 4158.
7 M. Rigole, C. Depecker, G. Wrobel, P. Legrand, M. Gelton and J. P. Bonnelle, *J. Phys. Chem.*, 1990, **94**, 6743.
8 C. Bremard, E. Dennelin, C. Depecker and P. Legrand, *Structure and Reactivity of Surfaces*, 1989, 219.
9 H. Des Grousilliers, C. Bremard, C. Depecker and P. Legrand, *Proceedings of the International Workshop on FTIR Spectroscopy*, ed. E. F. Vansant, Antwerpen Belgium 1990, pp. 84–91.
10 A. Zecchina, S. Borgia, E. E. Platero and C. O. Arean, *J. Catal.*, 1990, **125**, 568.
11 A. de Malmann and D. Barthomeuf, *J. Phys. Chem.*, 1989, **93**, 5636.
12 A. de Malmann and D. Barthomeuf, *Zeolites*, 1988, **8**, 292.
13 A. N. Fitch, H. Jobic and A. Renouprez, *J. Phys. Chem.*, 1986, **90**, 1331.
14 Y. Okamoto, T. Imanaka, K. Asakaru and Y. Iwasawa, *J. Phys. Chem.*, 1991, **95**, 3700.
15 Y. You-Sin and R. F. Howe, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 2887.