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$Cu^+(H_2)$ and $Na^+(H_2)$ adducts in exchanged ZSM-5 zeolites

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Cu(I) ions in Cu-ZSM-5 form $Cu^+(H_2)$ complexes, stable at room temperature and sub-atmospheric H_2 pressure, which do not have any homogeneous analogue except for matrix-isolated $[Cu(\eta^2\text{-}H_2)Cl]$. Comparison with the unstable $Na^+(H_2)$ adducts formed in the parent Na-ZSM-5 zeolite allow the conclusion that the Cu(I)/H_2 bond is governed by σ–π overlap forces.

Extraframework Cu(I) counterions in Cu(I)-ZSM-5 are sited in a structurally well defined environment, highly coordinatively unsaturated and easily accessible to molecules moving inside the zeolite channels.[1] This confers them with very peculiar chemical properties which include specific catalytic activity in $deNO_x$ reactions[2] and the ability to form uncommon complexes like the homopletic $[Cu(CO)_3]^+$ tri-carbonyl[3] and the $Cu^+(N_2)$ dinitrogen adducts.[4] Some of us have recently shown[5] that intrazeolitic Cu(I) can also be active in binding molecular hydrogen, a rather surprising finding when considering that the sole Cu(I)/dihydrogen complex presently known is the $[Cu(\eta^2\text{–}H_2)Cl]$ adduct isolated by co-condensation of CuCl and H_2 in an Ar matrix.[6]

In this communication, FTIR spectroscopic evidences are given of the formation of $Cu^+(H_2)$ complexes, stable at 293 K and sub-atmospheric H_2 pressure, in Cu-ZSM-5. The fate of these species in a H_2 atmosphere over the whole 300–20 K temperature range is also investigated and their spectroscopic features compared with those of similar $Na^+(H_2)$ species formed at 20 K in Na-ZSM-5. The interest of a microporous system able to reversibly adsorb H_2 at room temperature is self-evident, because it satisfies one of the pre-requisites for hydrogen storage.

Cu(I)-ZSM-5 was prepared by reaction of H-ZSM-5 (Si/Al = 90) with gaseous CuCl,[7] a procedure leading to the 1 : 1 substitution of the zeolite acidic protons exclusively with isolated Cu^+ ions (*i.e.* to a very well defined system from the point of view of the copper ions' local environment).[1a] Fig. 1(a) shows the spectra obtained upon dosage of hydrogen at 300 K and by progressive lowering of the temperature down to 15 K; Fig. 1(b) illustrates the effect of reducing the H_2 equilibrium pressure at 15 K. It is seen that the H_2/Cu(I)-ZSM-5 interaction at 300 K gives rise to absorptions at 3222 (very weak), *ca.* 3130 (very weak and broad) and 3079 (weak) cm^{-1}. This triplet disappears upon outgassing at 300 K and reappears by readmission of H_2, meaning that we are dealing with species reversible at RT. Upon lowering the temperature from 300 to 80 K in a H_2 atmosphere all the above bands gain intensity (with narrowing). The further decrease of the temperature from 80 to 15 K causes the gradual upward shift (while broadening) of the 3079 cm^{-1} component (which results in finally being located at *ca.* 3108 cm^{-1}); this effect is conceivalably associated with H_2 condensation inside the internal zeolitic spaces and pore filling by a liquid-like phase.† Lowering the H_2 pressure at 15 K readily restores the initial triplet [which at this temperature is not sensitive even to prolonged outgassing: Fig. 1(b)]. The peaks are slightly more intense and narrow with respect to those observed at RT.

The 3222, 3130 and 3079 cm^{-1} triplet is not observed on the parent Na-ZSM-5 zeolite (*vide infra*) (as well as in experiments we performed on Silicalite, a zeolite having the same MFI structure of ZSM-5 but with an entirely siliceous framework) and its attribution to an Cu(I)/H_2 interaction is therefore straightforward.

For a more detailed assignment, it is noteworthy that $[Cu(\eta^2\text{-}H_2)Cl]$, where H_2 is thought to be bonded to Cu^+ in a side-on fashion (in C_{2v} symmetry), is characterized by a very weak IR absorption at 3222 cm^{-1} [ν(HH) mode of the H_2 ligand].[6] The band at the same frequency in Fig. 1 hence represents evidence that CuCl/H_2 adducts with the same (or very similar) composition and structure of the matrix-isolated species are also present inside the CuZSM-5 channels. These are plausibly formed on residual cuprous chloride still remaining entrapped in the zeolite voids after the exchange procedure. As we had no evidence of the 3222 cm^{-1} band when performing similar experiments on bulky or silica-supported CuCl (where clustering is not prevented), it is also concluded that residual intrazeolitic CuCl must be in a molecularly dispersed form. The bands at 3130 and 3079 cm^{-1} are assigned to similar $Cu^+(H_2)$ adducts formed on the ions counterbalancing the ZSM-5 framework negative charge. The presence of a doublet can be accounted for by recalling that in the ZSM-5 MFI structure Cu^+ can occupy slightly different locations[1a,4,8] and indeed the existence of two sites differing for the number of equivalent framework oxygen ligands entering the Cu(I) first coordination sphere, schematically O_2Cu^+ and O_3Cu^+, has been proposed.[1a] The larger downward shift (*ca.* 1030 and 1080 cm^{-1} with respect to gaseous H_2) of the ν(HH) of the $[Cu(H_2)Z]$ complexes (where Z stands for zeolitic framework) as compared with that of the matrix-isolated and intrazeolitic $[Cu(H_2)Cl]$ adducts (*ca.* 940 cm^{-1}) deserves some comment. It is widespread opinion that a large shift (of the order of 1000 cm^{-1}) of the ν(HH) frequency in Cu(I)–dihydrogen molecular complexes in side-on configuration is the symptom of a strong interaction involving weak electrostatic (charge-induced dipole and charge quadrupole) and strong chemical (donation from the H_2 σ orbital and back-donation from the 3dπ Cu^+ orbitals) contributions.[5,6,9] The σ donation in the 4s orbital and back-donation from the dπ orbitals of Cu(I) are

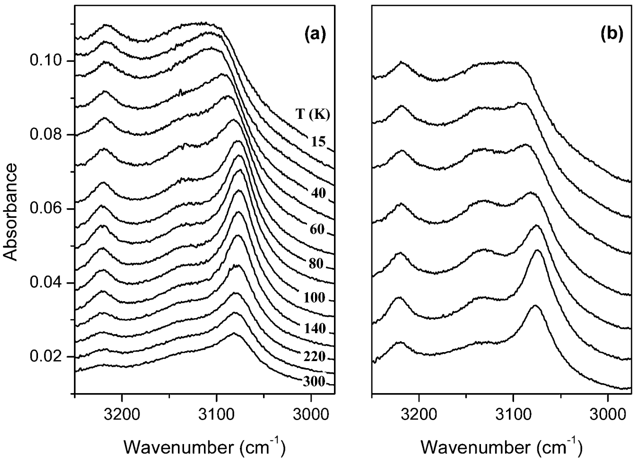

Fig. 1 IR spectra of H_2 adsorbed on Cu(I)-ZSM-5 (previously outgassed for 1 h at 773 K) as a function of: (a) the temperature (varied in the 300–15 K interval) at nearly constant gas phase equilibrium pressure (3 kPa); and (b) the gas phase equilibrium pressure (upper curve: 3 kPa; lower curve: $< 1 \times 10^{-4}$ kPa) at constant temperature (15 K).

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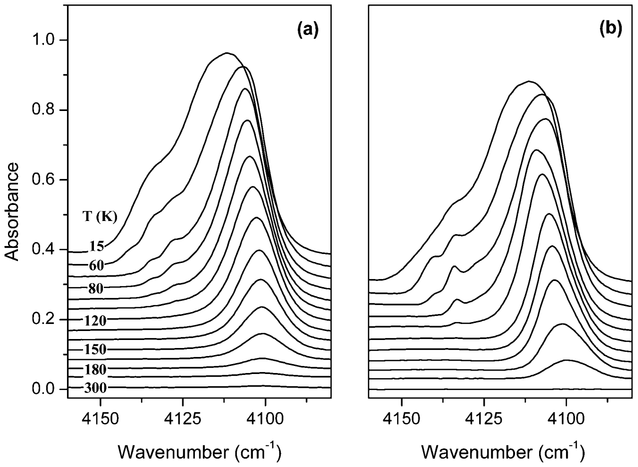

Fig. 2 IR spectra of H_2 adsorbed on Na-ZSM-5 as a function of (a) the temperature and (b) the H_2 equilibrium pressure. The experimental conditions are the same as for Fig. 1.

synergistic and lead to the formation of three centre Cu(I)/H_2 covalent bonds where back-donation weakens the H–H bond to a very large extent. This is reflected in the relatively large interaction energy (60–80 kJ mol^{-1}).[5,6] The covalent character of the Cu(I)–H bonds in the side-on $Cu^+(H_2)$ species also accounts for the low intensity of the ν(HH) mode because the H–H stretching is not accompanied by strong dipole oscillations along the covalent Cu(I)–H and H–H bonds. Based on the considerations concerning the shift, we can conclude that overlap forces are stronger in the H_2 complexes formed on intrazeolitic Cu^+ counterions than in entrapped or matrix-isolated [$Cu(H_2)Cl$]. Concerning the detailed assignment of the 3130 and 3079 cm^{-1} absorptions, we think that their respective attribution to $(O_3Cu^+)H_2$ and $(O_2Cu^+)H_2$ adducts is straightforward. In this way in fact the Cu(I) sites in lowest coordination are associated with the largest shift of the adsorbed hydrogen, as expected. The upward shift (and broadening) of the bands due to the $(O_3Cu^+)H_2$ and $(O_2Cu^+)H_2$ species in the temperature range 80–15 K, *i.e.* in conditions where the zeolite channels are filled by a liquid-like phase, is due to solvatation and transformation of the pristine $Cu^+(H_2)$ into $Cu^+(H_2)_n$ polynuclear adducts. This is accompanied by weakening of the Cu^+–(H_2) interaction and, consequently, by a shift of the ν(H–H) band toward that of gas phase H_2.[9] Outgassing the sample at 15 K [Fig. 1(b)] leads to a nearly reversibly image. It is, however, noticeable the higher intensity of the ν(HH) bands after outgassing at 15 K as compared with the first spectra of Fig. 1(a): this is a consequence of the stability of the $Cu^+(H_2)$ molecular complexes at this temperature, in agreement with the estimated interaction energy.

The hypothesis of the presence of an extensive covalent metal–hydrogen interaction in intrazeolitic $Cu^+(H_2)$ is confirmed by the spectra of the Na-ZSM-5/H_2 system, where the Na^+ centres (sited in identical or very similar positions of Cu^+ and having the same charge to ionic radius ratio) are expected to show negligible ability to interact covalently with H_2. The utility of such a comparison for elucidating the relative role of electrostatic and covalent forces in influencing the frequency and intensity of adsorbed hydrogen has been well established in the case of matrix-isolated dihydrogen/alkali and dihydrogen/transition metal cation adducts.[9,10] The spectral sequences obtained on Na-ZSM-5 (fully analogues to those of Cu-ZSM-5 in Fig. 1) are illustrated in Fig. 2. The following can be commented upon. (i) $Na^+(H)_2$ adducts, responsible for the ν(HH) absorption at 4100 cm^{-1}, are formed only below 180 K. The shift of the H–H mode is -60 cm^{-1}, in good agreement with the 70–75 cm^{-1} value calculated for naked $Na^+(H_2)$ adducts (see Bushnell *et al.*[10] and refs. cited therein); the small difference is due to the fact that the positive polarizing field of intrazeolitic Na^+ is partially counterbalanced by that of the negatively charged framework. The shift is on the contrary definitely smaller (more than one order of magnitude) than that of the analogous Cu(I) adducts. This undoubtedly confirms an overwhelming contribution of the σ-donation/dπ back-donation contribution (absent in the Na^+/H_2 interaction) to the ν(HH) shift in $Cu^+(H_2)$. (ii) The band due to the $Na^+(H_2)$ species reach a maximum at *ca.* 70 K. The much higher integrated intensity of the associated band with respect to $Cu^+(H_2)$ is noteworthy. While it is agreed that the low intensity of the H–H stretch in the $Cu^+(H_2)$ adduct is a consequence of the covalent character of the metal–H bond, nothing can be found in the literature about the activation of the ν(H–H) mode by interaction with alkali cations.[10,11] Our experimental results certainly demonstrate that this activation is remarkable and leads to an IR band of unexpected intensity. On a qualitative ground we can state that the highly polar bond between the alkali cation and the hydrogen molecule induces a distinct dipole oscillation during the H–H vibration. (iii) When the temperature approaches 15 K the 4100 cm^{-1} band is upward shifted by a few wavenumbers and tails on the high frequency side (where weak bands appear at 4140, 4132 and 4127 cm^{-1}). These changes, not discussed in detail for brevity, are due to the H_2 interaction with residual (external) silanol groups and filling of the channels by a liquid-like phase (*vide supra*) which transforms the $Na^+(H_2)$ adducts into $Na^+(H_2)_n$. (iv) The Na^+/H_2 adducts are all reversible at 15 K [Fig. 2(b)].

We finally outline that spectral sequences like that in Fig. 2(a) allow the estimation of the adsorption enthalpy[12] of the $Na^+(H_2)$ adducts, which is 11 kJ mol^{-1}, in good agreement with the computed values (8–12 kJ mol^{-1}).[10]

Notes added in proofs: we became aware during the proof corrections stage that strong Cu(I)/H_2 complexes were also observed on Cu(II)-ZSM-5 zeolites prepared by wet exchange.[13]

Notes and references

† In the 80–15 K interval H_2 condenses even on the outer surface of the zeolite microcrystals, as evidenced by the erosion of the 3750 cm^{-1} ν(OH) band due to external ≡SiOH groups and the appearance of a broader absorption at 3743 cm^{-1} due to ≡$SiOH(H_2)_n$ surface adducts (results not shown for brevity).

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