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FORMATION OF CHINI TYPE Pt-CO COMPLEXES IN BASIC ZEOLITES

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Colored samples are obtained upon CO reaction at room temperature with Pt^{2+} ions incorporated in basic zeolites such as PtNaY and PtCsNaX. Their characterization, carried out by UV-visible and infrared spectroscopy, show strong analogies with Chini complexes. This suggests that complexes $[Pt_3(CO_3(\mu_2CO)_3]_n^{2-}$ of the Chini type may be formed and stabilized in the supercages of basic zeolites.

1. Introduction

The adsorption of CO on metal Pt particles has been much studied in order to characterize support-metal interactions and geometric surface effects [1–6]. For zeolites, the basic forms give new infrared bands not observed in acidic materials [2,6]. Those bands are assigned to CO interacting with some specific Pt atoms disturbed by very close framework oxygen atoms [2,6]. Little has been done on the study of CO interacting with Pt ions before any reduction. Several not well defined infrared bands were observed in PtKL [2] and the formation of colored materials was noticed for PtNaY [7] i.e. for basic zeolites. With palladium, the formation of $Pd_{13}(CO)_x$ clusters in NaY is reported [8]. The present work describes the formation of Pt-CO clusters in basic zeolites revealed by means of infrared and UV-visible spectroscopies. The chemical nature of the zeolite is changed from acidic to basic by neutralization of the protons by Na^+ or Cs^+ ions and by increasing the Al content.

2. Experimental

MATERIALS

Three samples of Y zeolite with a Si/Al ratio of 2.4 are used. They are NaY from Union Carbide, NH_4Y obtained by ammonium exchange of NaY and HY formed upon calcination of NH_4Y at 573 K in conditions which avoid ultrastabilization. The materials were exchanged with a $Pt(NH_3)_4Cl_2$ solution at pH 5.5 as in [6] in order to lead the zeolite with about 4 wt% Pt. The unit cell formulas of the samples are $Pt_{3.2}Na_{43}(NH_4)_{6.6}Y$ (PtNaY), $Pt_{3.1}(NH_4)_{44.4}Na_{5.5}Y$ ($PtNH_4Y$) and $Pt_3H_{44}Na_6Y$ (PtHY). A $Pt_{3.6}Cs_{44}Na_{29}(NH_4)_{5.8}X$ (PtCsNaX) zeolite with a Si/Al ratio of 1.2 is less extensively studied.

CO ADSORPTION

Wafers (20 mg, 18 mm diameter) are placed in an infrared cell. Evacuation is carried out at 353 K for 16 hrs for PtNaY, for 20 hrs for PtHY and at 373 K for 24 hrs for $PtNH_4Y$. CO is introduced in the cell at the evacuation temperature (120 Torr for PtNaY, 100 Torr for $PtNH_4Y$ and PtHY). It is allowed to interact with the zeolite for several hours. Infrared spectra are recorded at this stage and after further heating in the pressure of CO. The spectrophotometer is a Perkin Elmer 580 B equipped with a data station.

UV-visible spectra are obtained for the PtNaY sample treated in the same conditions as for infrared studies.

3. Results

Figure 1A depicts the infrared spectra in the range 1700–2300 cm^{-1} for CO adsorbed on PtNaY after subtraction of the CO gas. The wafer, evacuated at 353 K for 15 hrs, gives spectrum 1-a. Bands of water and of the amminated complex in a range not represented here at 1640 and 1380 cm^{-1} respectively are still present. After adsorption of CO for 15 hrs at the same temperature (spectrum b), small bands of adsorbed CO are formed at 1805 and 2027 cm^{-1}. Those bands do not characterize metallic platinum. Simultaneously a bright red-purple color develops. Increasing the contact time with a pressure of 120 Torr CO for 15 hrs at 373 K, the previous bands of the adsorbed phase grow and a shoulder appears near 1850 cm^{-1} (spectrum c). After 48 hrs contact with CO at 373 K (spectrum d) bands at 2026 and 1800 cm^{-1} become very strong. The ratio of their absorbance is close to one. Simultaneously the red-purple color becomes darker. In all the experiments conducted in the presence of CO, bands are formed at 2349, 1715 and 1365 cm^{-1}. They characterize CO_2 adsorbed on faujasites containing alkaline cations [9,10]. CO_2 might be formed from CO acting as a reducing agent. After recording spectrum d, a further treatment at 473 K for 2 hrs in the presence of CO changes the color from red-purple to grey while the broad bands 1800–2025 cm^{-1} disappear and new broad bands overlap at 2055 and 2063 cm^{-1}. These wavenumbers agree with what is obtained for highly dispersed CO on metallic platinum in NaY [6].

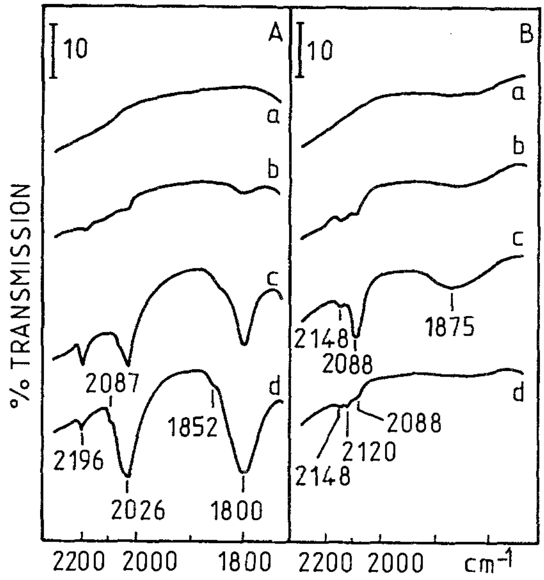

Fig. 1. Infrared spectra of PtNaY(A) and PtHY(B). (A) a: PtNaY evacuated (15 hrs, 353 K); b: after heating at 353 K for 15 hrs with P_{CO} = 120 Torr; c and d: after heating at 373 K for 15 and 48 hrs. (B) a: PtHY evacuated (20 hrs, 353 K); b and c: after heating at 373 K for 15 and 48 hrs, P_{CO} = 100 Torr; after evacuation at 298 K and further heating at 353 K for 15 hrs with P_{O_2} = 100 Torr.

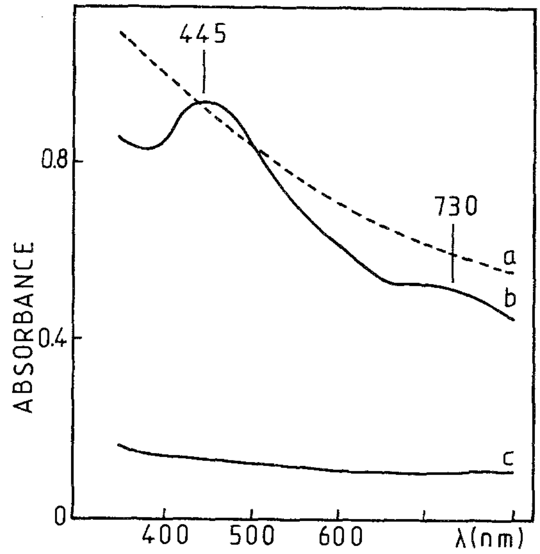

Fig. 2. UV visible spectra of PtNaY, a: before any heating and contact with CO; b: after evacuation at 353 K and heating for 15 hrs at 373 K with P_{CO} = 100 Torr; c: after H_2 reduction at 573 K followed by CO adsorption for 15 hrs at 573 K (P_{CO} = 100 Torr).

Neither color nor CO infrared bands in this wavenumber range are observed in PtNaY if the amminated complex is decomposed by oxygen treatment before CO adsorption or if the zeolite does not contain platinum.

The UV visible spectra of PtNaY pretreated in the same conditions as previously give the spectra of fig. 2. After CO adsorption for 15 hrs at 373 K spectrum b shows bands at 445 and 730 nm which are not observed in spectrum a for the non heated starting sample without CO or in spectrum c related to PtNaY after metal reduction in hydrogen and CO adsorption.

Infrared spectra obtained with PtHY before any reduction are reported in fig. 1B. The adsorption of CO and heating at 373 K give spectra b and c after 15 and 48 hrs respectively. Simultaneously the sample becomes grey. Both spectra show bands at 1875, 2088 and 2148 cm^{-1}. No band characteristic of CO_2 was observed suggesting no reduction with CO. The sample $PtNH_4Y$ has a very light pink color after CO adsorption and heating at 373 K for 30 hrs. Its infrared spectra are very similar to those of PtHY reported in fig. 1B. No bands are formed in the range 1800 or 2025 cm^{-1}. By contrast the non protonic PtCsNaX zeolite gives a bright red-orange color after evacuation at 373 K and further heating with CO at 353 K. Depending on experimental conditions a red-purple or a yellow-green color is observed. As NaY, CsNaX zeolite, i.e. without platinum, does not show a color or specific infrared bands upon CO adsorption.

4. Discussion

In PtHY the two bands at 1875 and 2088 cm^{-1} may be assigned to CO adsorbed on metal platinum particles. They characterize the bridging and linear CO in the case of high CO coverage [6]. This assignment is confirmed by spectrum d (fig. 1B) showing that the metal platinum in the sample of spectrum c can be oxidized giving a band at 2120 cm^{-1} characteristics of CO in the species $Pt\langle^{O}_{CO}$ [11]. The presence of metal particles in the sample is also confirmed by electron microscopy of the wafers. The metal could be formed by self-reduction with ammonia evolved from the decomposition of $Pt(NH_3)_4Cl_2$. A higher temperature (573 K) is required for such a reaction to occur in PtNaY [12]. The 2148 cm^{-1} band arises from CO adsorbed on some partly reduced $Pt^{\delta+}$ form of platinum [13].

In PtNaY no metallic platinium could be detected by electron microscopy in the colored materials after CO adsorption. The infrared bands observed at 2026 and 1800 cm^{-1} simultaneously with the bright red-purple color and the UV-visible bands of fig. 2 suggest to consider which type of complex could be formed. In solution two types of Pt complexes are formed whether the medium is acidic or basic. In formic acid solution $Cs[PtCO]Cl_3$ is known. It gives CO bands reported in table 1 [14]. The values are different from the ones observed in PtNaY. By contrast Chini complexes which general formula is $[Pt_3(CO)_3(\mu_2\ CO_3]_n^{2-}$ require

Table 1

Complex	IR wavenumbers	Color	Ref.
$Cs[PtCO]Cl_3$	2120(s), 2101(w), 2047(s), 2000 (vvw)		[14]
$[Pt_3(CO)_3(\mu_2CO)_3]_n^{2-}$			
$n = 2$	1990(vs), 1818(m), 1795(s)	orange-red	[15]
$n = 3$	2030(vs), 1855(sh), 1842(s), 1835(sh), 1810(w)	red-violet	[15]
$n = 4$	2045(vs), 2025(sh), 1880(w), 1860(s), 1840(sh), 1828(w)	blue-green	[15]
$n = 5$	2055(vs), 1890(w), 1870(s), 1840(w), 1825(w)	yellow-green	[15]
$[Pt_6(CO)_{12}]^{2-}$ [a]	1970(s), 1790(s)		[18]
$[Pt_9(CO)_{18}]^{2-}$	2005(s), 1810(s)		[18]
$[Pt_{12}(CO)_{24}]^{2-}$	2025(s), 1830(s)		[18]
$[Pt_{15}(CO)_{30}]^{2-}$	2040(s), 1850(s)		[18]
Pt/NaY	2025(s), 1852(sh), 1800(s)	red-purple	present work

[a] Clusters supported on γ-Al_2O_3. The negative charge is compensated by $[N(C_2H_5)_4]^+$.

basic media to be formed [15,17]. They can be supported on silica or γ alumina [18]. The CO wavenumbers in THF solution and the color of the cluster dianions listed in table 1 depend on n. The bands close to 2000 cm^{-1} are assigned to linear CO while the bands between 1800–1900 cm^{-1} correspond to bridging CO [16]. The relative absorbance of those two strong bands is close to 1 which may be related to the same number of the terminal and bridging CO in the complex. This is in contrast to CO adsorbed on metal platinum where bridging CO bands are very small compared to linear CO ones [6]. The range of CO wavenumbers of Chini complexes is comparable to that of CO adsorbed on Pt-naY also given in table 1. Platinum on HY or NH_4Y does not give such bands and no bright color. Their acidic character may prevent the formation of complexes. The zeolites studied here may be ranked with regards to their framework oxygen basicity in the order HY < NH_4Y < NaY < CsX [19], HY being typical of acidic zeolite. Only the actually basic ones, NaY and CsX are able to generate colored platinum complexes.

If one considers the need for basicity, the wavenumbers range of infrared bands, the similar absorbance of the two strong bands and the colors observed, the results suggest that clusters of the Chini type may be formed from $Pt(NH_3)_4Cl_2$ in basic zeolites upon CO adsorption. This analogy suggests that the 2026 cm^{-1} band in fig. 1A would correspond to linear CO while the 1800 cm^{-1} band would be bridging CO.

The Chini clusters supported on silica or alumina are stable up to 393–453 K at low Pt level (0.05–0.5 wt% Pt) or 473–623 K at higher Pt content (1.8–2%)

[18]. The present Pt-CO species in the zeolite NaY containing 4 wt% Pt are decomposed after evacuation at 473 K, i.e. in the same temperature range.

The question arises of the number of Pt atoms in the clusters which could be estimated from CO wavenumbers and of their location in the zeolite cavities. The comparison of the wavenumbers of strong and very strong bands in the Chini complexes in solution [15] or supported on γ-Al_2O_3 [18] shows in table 1 a shift to low values by 15 to 30 cm^{-1} when the clusters are supported. This may originate from an interaction with the alumina surface. In the case of platinum on NaY where an interaction also occurs the wavenumbers have to be different from those in solution. Due to the different geometry of an alumina surface and of the supercage of the zeolite one may not expect necessarily the same shift from the complexes in solution for the two solids and for linear and bridging CO. The value of 2026 cm^{-1} and 1800 cm^{-1} for the infrared bands in PtNaY together with the red purple color are in line with $n = 3$, i.e. 9 Pt atoms in the Chini complex $[Pt_3(CO)_3(\mu_2\ CO)_3]_n^{2-}$. In contrast to the γ-alumina case where the clusters sit on an almost flat surface, in the cages of zeolites it is embedded in cavities whose size is close to its dimension. The supercage of the faujasite structure, common to NaY and CsNaX, is 1–1.2 nm in diameter. It is connected to four other supercages by windows made of twelve-ring oxygen belonging to AlO_4 and SiO_4 tetrahedra. The diameter of those openings is 0.74 nm [20]. An approximate size of the Chini clusters can be evaluated from the atomic distances determined in ref. [15]. For $n = 3$ the elliptical section is 0.8 × 0.875 nm and the length of the pseudocylinder is 0.61 nm. Such a cluster fits the supercage. After decomposition upon heating at 473 K the platinum would agglomerate and form metal Pt particles. In PtCsNaX giving different colors of the Pt complex one may envision that the complex could eventually extend in two adjacent supercages through the 12-R aperture between two cavities being able to reach a number $n = 5$ in the complex formula. Studies are still in progress for a better characterization of this complex. It is stabilized in the zeolite by interaction with the framework oxygen which are the basic sites. Its size, close to that of the supercage prevents an easy extraction. Furthermore out of "its solvent"–the zeolite–it may be destroyed or come back to the form stabilized in solution, loosing its characteristics observed in the zeolite.

In conclusions the results obtained justify to consider that colored Pt-CO complexes are formed in the supercage of basic zeolites like PtNaY or PtCsNaX upon CO reaction with $Pt(NH_3)_4Cl_2$ ions entrapped in the zeolites cavities. Their structure would be similar to the Pt Chini complexes known to exist in basic media. In PtNaY the complex would involve three Pt triangles.

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