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IR SPECTROSCOPIC STUDY OF Pt/KL ZEOLITES USING ADSORPTION OF CO AS A MOLECULAR PROBE

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FTIR spectra of CO adsorbed on Pt/KL catalysts show that the relative band intensities and the total dispersion markedly depend on the catalyst preparation method (ion exchange, incipient wetness impregnation or co-impregnation with KCl). The CO stretching frequency of the dominant band for linear CO is shifted to higher wavenumbers, parallel with the proton concentration in the reduced catalyst, which is derived independently from the intensity of the IR bands of the OH groups. The results are in accordance with the model that electron-deficient platinum particles are platinum-proton adducts.

Keywords: FTIR Spectroscopy, Pt/KL zeolite catalysts, CO adsorption as probe molecule

1. Introduction

The ability of Pt/KL catalysts to convert linear C_{6+} alkanes into aromatics has motivated considerable research on these catalysts. In unpublished work we observed that their performance in catalyzing hexane dehydrocyclization at atmospheric pressure and their TPR profiles strongly depend on the method of catalyst preparation [1]. This finding has motivated the present FTIR study, comparing Pt/KL samples of different preparation histories using CO as a probe molecule. Previous FTIR work on Pt/KL has been reported by Bezoukhanova et al. [2] who used samples containing 5 wt% Pt, which is much higher than the typical Pt loading of Pt/KL hexane dehydrocyclization catalysts. In the present work, samples with 0.5 wt% of Pt have been studied.

Bezoukhanova et al. [2] observed a marked dependence of the CO stretching frequency for linear Pt-CO upon the nature of the alkali cation. They interpret this findings in terms of the electric charge of the Pt particle. Pt is often "electron-deficient" inside zeolites [3], as evidenced by a shift of the CO stretch-

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ing frequency to higher wavenumbers. Alkali ions in the L zeolite apparently lower the net positive charge on the Pt particles.

Larsen and Haller [4] characterized the Pt particles inside ~ 1 wt% Pt/KL, modified by alkaline earth elements, and studied the catalytic performance of these catalysts. Their results support the conclusion of [2] that the nature of the cation is an important factor affecting the electronic state of platinum.

2. Experimental

The samples were prepared by one of three methods: (1) ion exchange of $Pt(NH_3)_4Cl_2$, further called Pt/KL-IE; (2) incipient wetness impregnation of KL with $Pt(NH_3)_4Cl_2$, further called Pt/KL-IW or (3) co-impregnation of the zeolite with $Pt(NH_3)4Cl_2$ and KCl, as proposed by Poeppelmeier et al. [5], further called Pt/KL-IW + KCl. More details of the preparation will be described in a forthcoming paper [6]. All samples contained 0.5 wt% of Pt after drying. Calcination and reduction of the samples were performed inside the IR cell. Thin, self-supported wafers with a diameter of 8 mm and a mass per cross sectional area of ~ 7–13 mg/cm^2 were pressed and placed into the sample holder.

Before the spectroscopic measurements, the samples were heated in oxygen at a flow rate of 120 ml/min, ramping the temperature at 0.5 K/min from 300 K to 770 K, then holding at 770 K for 2 h. After calcination the system was purged with He at 770 K for an additional 20 min period and cooled to 300 K in He. The reduction temperature was ramped from 300 K to 620 K at a rate of 8 K/min and kept at 620 K in flowing H_2 for 20 min. The samples were then purged at 620 K with He for 20 min and cooled in flowing He to 300 K, whereafter the background spectra of the reduced samples were measured. A CO/He mixture with a volume ratio of 5:30 and a total flow rate of 70–80 ml/min was passed through the cell for 10 min, followed by purging with He for 10–20 min in order to remove gaseous CO.

The cell for the IR measurements has been described in [7]. The spectra were measured at 300 K using a Nicolet 60SX Fourier-Transform spectrometer with a resolution of 1 cm^{-1}.

3. Results and discussion

Fig. 1 shows the IR-spectra of the samples Pt/KL-IE, Pt/KL-IW and Pt/KL-IW + KCl measured in the region of the stretching vibrations of OH groups. The most intense band at 3740 cm^{-1} should be ascribed to terminal silanols located at the external surface of zeolite microcrystallites. The low intensity bands at 3690 cm^{-1} and 3650–3630 cm^{-1} are assigned to nonacidic OH groups, usually present in cationic forms of zeolites [7], and bridging acidic OH groups, respectively. For

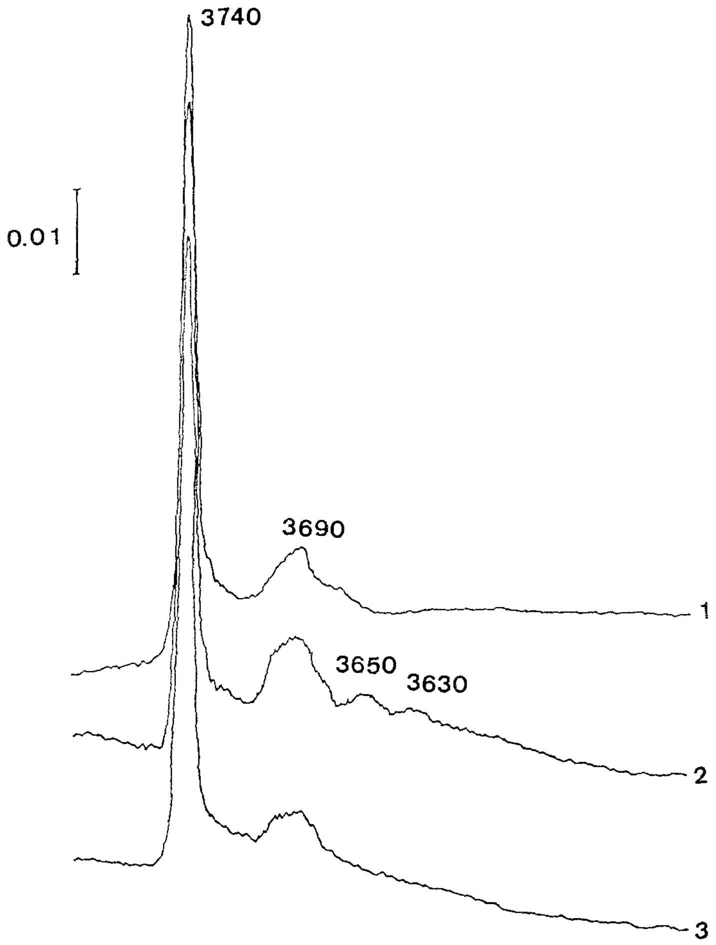

Fig. 1. IR-spectra of OH-groups in Pt/KL-IW (1), Pt/KL-IE (2) and Pt/KL-IW + KCl (3).

all samples the concentration of acidic hydroxyls is very low; it decreases from Pt/KL-IE to Pt/KL-IW to Pt/KL-IW + KCl.

Fig. 2 shows the IR spectra of CO adsorbed at 300 K on Pt/KL samples prepared by the various methods. For all samples the spectra contain mainly the bands attributed to linear Pt carbonyls (ν_{CO} = 207–1950 cm^{-1}). These results are in good agreement with literature data; the linear CO complex is usually found predominant for Pt [2]. The intensities of the IR-bands, attributed to the bridging Pt carbonyls are very low, e.g. the weak band at 1919 cm^{-1} and the broad, probably unresolved bands at 1870–1760 cm^{-1}.

The total intensities of all CO bands provide information about the metal dispersion. Integration over all bands attributed to Pt carbonyls (2067–1760 cm^{-1}) shows that the Pt dispersion in Pt/KL-IW is significantly higher than the dispersion of Pt/KL-IE, while Pt/KL-IW + KCl has an intermediate dispersion,

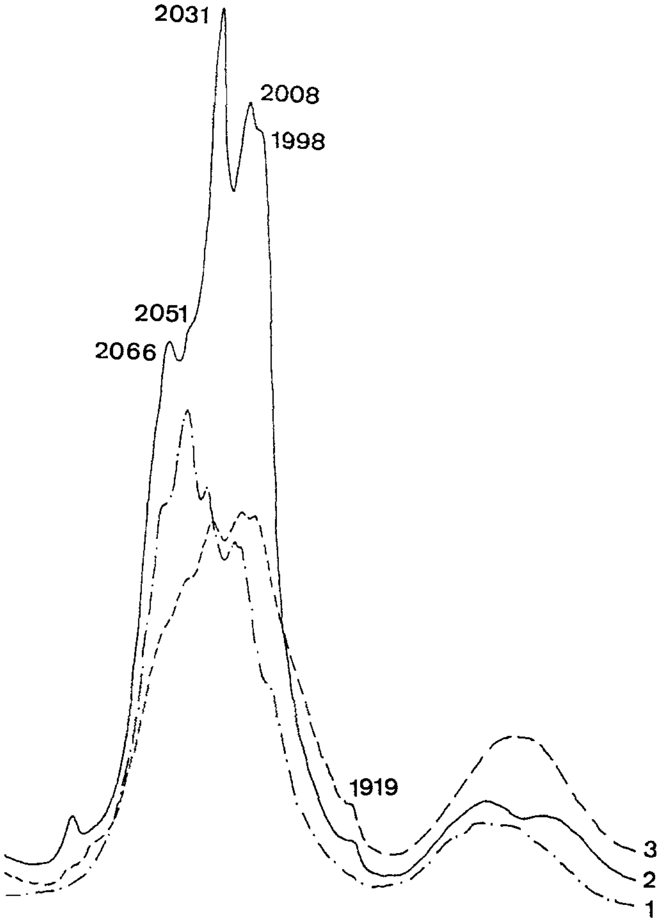

Fig. 2. IR-spectra of CO adsorbed on Pt/KL-IE (1), Pt/KL-IW (2) and Pt/KL-IW+KCl (3).

similar to Pt/KL-IE. These data are in good agreement with independent results of our volumetric CO chemisorption measurements [6].

A band at ~ 2075–2090 cm^{-1} usually found for CO adsorption on supported Pt and ascribed to CO on large Pt particles, typically located at the external surface of a zeolite [2], is absent in the spectra of our Pt/KL zeolites. This result is not surprising in view of the low Pt loading and it indicates that all observable Pt is inside the zeolite channels.

The spectra of the samples prepared by different procedures all exhibit the same maxima of the IR-bands: 2066, 2051, 2031, 2008, 1998 and 1919 cm^{-1}. However, the relative intensities of these bands differ significantly for the three samples. Apparently there is a definite set of Pt states in Pt/KL, independent of the preparation method, but the population of these states varies largely.

Indeed, for the ion-exchanged sample, Pt/KL-IE, the bands at 2066 and 2051 cm^{-1} predominate, whereas the low-frequency bands are considerably weaker. In contrast, for the sample prepared by incipient wetness impregnation, Pt/KL-IW, the band at 2031 cm^{-1} is the dominant feature of the spectrum, with the bands between 2008 and 1998 cm^{-1} also being fairly strong. For the zeolite prepared by co-impregnation with KCl, Pt/KL-IW + KCl, the bands between 2008 and 1998 cm^{-1} predominate with the high frequency bands being much weaker. The intensity of bridging carbonyl bands is quite significant.

The shift in the dominant peaks of linear CO from 2066 and 2051 cm^{-1} for PT/KL-IE, to 2031 cm^{-1} for Pt/KL-IW, to 2008–1998 cm^{-1} for Pt/KL-IW + KCl apparently reflects a regular decrease in "electron-deficiency" of the adsorbing Pt particles. This result can be interpreted in terms of our model on the origin of electron-deficiency [9]. In a number of papers it was shown for zeolite supported palladium that the criteria for electron deficiency, including the blue-shift of the stretching vibration of adsorbed CO and the change in binding energy measured by XPS, all correlate positively with the proton concentration inside the zeolite cages carrying the Pd particles [10–13]. It was, therefore, proposed that "electron-deficient" metal particles are in fact metal-proton adducts e.g. $(Pd_nH)^+$. The positive charge of such an adduct will not be localized on the hydrogen atom but distributed over all $n+1$ atoms of the adduct. To form the adduct it is possible, but not necessary that proton-oxygen bonds are broken. If the proton is bridging between cage wall oxygens and metal, it will help to anchor the metal particle.

This model was confirmed in the case of Pd/NaY by CO adsorption: As CO molecules are adsorbed, the proton is displaced from the surface of the Pd particle and bonded to a cage wall oxygen, giving rise to an increase in the intensity of the IR band of the OH group. This increase in the OH band intensity due to CO adsorption by Pd has been found to be reversible: upon desorption of CO from the metal, the OH band intensity decreases. This evidence proves in a rather convincing manner that proton and CO compete for the same metal sites; it is, therefore, a strong support for the metal-proton adduct model for electron-deficiency of zeolite supported palladium.

The above order of decreasing blue-shift of the CO stretching frequency corresponds precisely to the decreasing proton concentration in the samples as found by the IR spectra of the OH bands. This sequence is also to be expected on the basis of the preparation conditions.

In the ion exchanged samples the zeolite matrix is negatively charged, compensating the positive charge of the ion exchanged Pt^{2+} ions. During reduction with H_2:

$$Pt^{2+} + H_2 \Rightarrow Pt^0 + 2H^+ \qquad (1)$$

two protons are formed. In the sample prepared by incipient wetness impregnation most anions are Cl^- ions. During reduction with H_2:

$$Pt^{2+} + H_2 + 2Cl^- \Rightarrow Pt^0 + 2HCl\uparrow \qquad (2)$$

reaction (2) will be in competition with (1); therefore, less protons will remain in the zeolite. The rationale of co-impregnating $Pt(NH_3)_4Cl_2$ with an excess of KCl (see ref. [5]) is, that an excess of Cl^- ions shifts the equilibrium:

$$H^+_{zeol} + Cl^+_{zeol} = HCl\uparrow \qquad (3)$$

to the right, so that the concentration of residual protons in the zeolite becomes virtually zero. It is therefore clear why the order of decreasing proton concentration in the reduced catalysts is: *Pt/KI-IE* > *Pt/KI-IW* > *Pt/KL-IW* + *KCl* as actually found by FTIR.

This sequence is precisely the order in which the position of the dominant IR band of the linear CO on Pt has been found to shift to lower wavenumbers. The present data are, to our knowledge, the first indications, that the metal-proton adduct model, originally proposed for zeolite supported palladium, might also be valid for zeolite supported platinum.

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