Infrared spectroscopy of carbon monoxide adsorbed on Pt / L zeolite

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A series of 0.6 wt% Pt/MBaL zeolites, where M is Li, Na, K, Rb or Cs, were prepared and characterized by transmission electron microscopy, chemisorption, and infrared spectroscopy of adsorbed carbon monoxide. Greater than 90% of the exposed platinum in the samples is associated with small clusters, less than ≈ 7 Å across, inside the zeolite channels. The remaining fraction of exposed platinum is on 100–500 Å crystallites outside the channels. Adsorption of carbon monoxide on the platinum at 25°C produces a broad infrared band whose maximum shifts from 2065 to 2025 cm^{-1} as the alkali cations in the zeolite are changed from Li to Cs. This shift is indicative of electron transfer between the cations and the platinum clusters. Heating the Pt/L catalysts to 225°C produces new infrared bands at 2020–2015, 1975, and 1935–1920 cm^{-1}. The appearance of these low-frequency bands strongly suggests that the CO-covered platinum clusters change their structure during heating. We propose that the new structure is one in which the carbon monoxide molecules insert into spaces between the framework atoms of the L zeolite.

Keywords: Infrared spectroscopy; Pt / BaL zeolite catalysts; CO adsorption

1. Introduction

Bernard [1] discovered that platinum particles in L zeolite are very active and selective catalysts for the conversion of hexane into benzene. Since then a lot of research has been conducted to learn more about the chemical and physical properties of these catalysts [2–20]. Several studies [2,9,15,20] have revealed that platinum in L zeolite exhibits unusual adsorption sites for carbon monoxide. These sites are distinguished by a series of peaks appearing between 2050 and 1950 cm^{-1} in the infrared spectrum. It has been suggested that these bands are due to carbon monoxide adsorbed on platinum clusters which are "disturbed" by their close proximity to the zeolite lattice [2,3]. Through interactions with framework oxygen,

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possibly also involving protons, the electronic states of the platinum particles are changed, causing the infrared bands to shift to lower frequency [3,15].

We have recently reported on the changes in the infrared spectrum of adsorbed carbon monoxide on Pt/BaL following various treatments [20]. The series of infrared peaks between 2050 and 1950 cm^{-1} are not present after exposure to carbon monoxide at 25°C, but instead appear when the catalyst is heated to 225°C, and remain when it is cooled to room temperature. However, if the sample is exposed to several Torr of oxygen at 65°C, the peaks disappear in a few minutes. We have proposed that the bands between 2050 and 1950 cm^{-1} are due to carbon monoxide adsorbed on platinum in which the oxygen atoms of the molecules weakly bond to zeolite cations. Heating may be required to allow the Pt atoms and CO molecules to move into positions that facilitate bonding to the zeolite. On the other hand, oxygen adsorption on the Pt may rapidly destroy this arrangement.

In this paper, we provide additional data on carbon monoxide adsorption on Pt/BaL zeolites. Infrared spectra have been obtained for a series of 0.6 wt% Pt/BaL catalysts containing different alkali cations. The spectra are compared following carbon monoxide adsorption at 25°C and after heating to 225°C. In addition, the distribution of platinum particle sizes in the L zeolite samples has been identified by transmission electron microscopy.

2. Experimental

Barium was exchanged into 24 g of KL zeolite (Union Carbide) by stirring it in 1 ℓ of 0.3 M $Ba(NO_3)_2$ solution for 106 h at 25°C. The BaL sample was filtered, washed with 2 ℓ of deionized H_2O, dried in air for 48 h at 120°C, heated from 120 to 590°C over 2 h, and calcined in air for 16 h at 590°C. Different alkali elements were exchanged into the BaL by stirring 10 g of the zeolite in 1 ℓ of 0.3 M alkali-metal-nitrate solution for 72 h at 25°C. Each of these samples was filtered, washed with 1 ℓ H_2O, and dried for 96 h at 120°C. To each zeolite exchanged with barium and alkali metal, 0.6 wt% platinum was added by incipient wetness impregnation of $Pt(NH_3)_4Cl_2$. The catalyst samples were then heated in air from 25 to 250°C over 4 h, held for 1 h at 250°C, heated in air from 250 to 350°C over 6 h, and held for 3 h at 350°C. The calcined catalysts were stored in a desiccator until needed. The compositions of the Pt/BaL samples were determined by inductively coupled plasma emission spectroscopy (ICP) at Amoco Research Center, Naperville, IL. Transmission electron micrographs of the Pt/LiBaL catalyst were taken at NEC Research Institute, Princeton, NJ, using a Hitachi H9000NAR microscope at 300 kV.

The platinum dispersions of the fresh catalyst samples were determined by hydrogen titration of adsorbed oxygen in a volumetric chemisorption apparatus [21]. Each sample was heated in 200 cm^3/min H_2 from 25 to 500°C over 1 h, reduced for 1 h at 500°C, and cooled in 1×10^{-6} Torr vacuum from 500 to 25°C

(1 Torr = 133 N/m^2). Then the samples were exposed to 76 Torr O_2 for 1 h, evacuated to 1×10^{-6} Torr over 30 min, and exposed to several pressures of H_2 between 10 and 150 Torr. The amount of hydrogen adsorbed was determined by extrapolating the linear part of the adsorption isotherm back to zero pressure. On the 0.76% Pt/NaBaL catalyst and the NaBaL support, additional chemisorption measurements were made to determine the amounts of adsorbed hydrogen and carbon monoxide, and the amount of oxygen needed to titrate the adsorbed hydrogen.

Infrared spectra of adsorbed carbon monoxide were recorded as follows. A 13 mm diameter wafer of catalyst, weighing 0.14 g, was placed in an evacuable glass cell, heated in 200 cm^3/min H_2 from 25 to 300°C over 1 h, reduced 1 h at 300°C, evacuated to 1×10^{-6} Torr for 20 min at 300°C, and cooled to 25°C over 2 h. At 25°C, 1.9×10^{-7} moles of CO ($\approx$ 10% of a monolayer) were repeatedly dosed into the chamber, and the infrared spectrum was recorded after each dose. The intensity of the bands for adsorbed carbon monoxide increased until the saturation point was reached [22]. Next, infrared spectra were recorded after heating the samples to 125, 225, 305, 350 and 375°C, and cooling them back to 300, 225 and 35°C. Infrared spectra were recorded throughout these exposures to oxygen and carbon monoxide. The carbon monoxide dosing and heating experiments were also conducted on the BaL supports, and the infrared spectra of the supports subtracted from those of the catalysts. The data were collected on a Digilab FTS-40 spectrometer with a HgCdTe detector at 8 cm^{-1} resolution and coadding 256 scans.

The experiments described in the preceding paragraph were performed on the Pt/BaL catalysts before and after measuring their activities for heptane reforming. The procedure used to test the activity of the catalysts is described in another paper [23]. Briefly, the samples, in the form of 32 to 60 mesh-size pellets, were loaded into a fixed-bed microreactor. Then they were heated in 100 cm^3/min H_2 to 500°C over 1 h, reduced at this temperature for 2 h, cooled to 450°C, and exposed to the reaction mixture for 3 h. The conditions were 450°C, 0.16 atm heptane, 0.95 atm H_2, 6.7 atm He and a flow rate of 240 cm^3/min. After reaction, the samples were cooled in 100 cm^3/min H_2 to 30°C, purged in He for 5 min, and removed from the microreactor. The pellets were then ground into powder and pressed into a thin wafer. This wafer was inserted into the infrared cell, exposed to 200 cm^3/min H_2 at 25°C for 30 min, and dosed with carbon monoxide as described above.

To examine the effects of oxygen on the infrared spectrum of adsorbed carbon monoxide, one of the catalysts, 0.76% Pt/NaBaL, underwent an additional treatment. This sample was not exposed to heptane reforming prior to this experiment. After performing the standard cycle of carbon monoxide dosing, heating and cooling, the 0.76% Pt/NaBaL sample was exposed to $\approx$ 10 Torr of O_2 for 4 h and to $\approx$ 10 Torr of CO for 3 h, both at 65°C. A series of infrared spectra were collected throughout this treatment.

3. Results and discussion

3.1. CATION DISTRIBUTION

Shown in table 1 are the platinum loadings and the cation distributions in the catalyst samples. The cation to aluminium mole ratio equals 1.0 on all the samples except 0.54% Pt/CsBaL, where it is 0.96. This means that Pt/CsBaL may contain a few Brønsted acid sites, while the other samples are nonacidic. Infrared spectra of the OH stretching region confirm these results. Shown in fig. 1 are single-beam spectra of KBaL, 0.64% Pt/KBaL and 0.54% Pt/CsBaL. For KBaL and Pt/KBaL, one sharp peak is observed at 3740 cm^{-1} which is attributed to nonacidic, terminal silanol groups [15]. All the samples except Pt/CsBaL exhibit this spectrum. For Pt/CsBaL, a second peak is observed at 3675 cm^{-1} which may be assigned to acidic hydroxyl groups [15].

Comparison of the cation distributions in the zeolites (table 1) reveals that the amount of alkali increases and the amount of barium decreases with increasing size of the alkali atom. Similar results have been obtained by Newell and Rees [24]. Evidently, the larger alkali elements exchange more effectively with barium than the smaller ones. The KL zeolite initially has 8.55 K^+ and 0.55 Na^+ ions distributed between A, B, C and D sites in the lattice. The locations of these sites are: A, center of double six-membered rings; B, center of ε-cages; C, between ε-cages; and D, along main channel wall [25]. Newell and Rees [24] found that calcining a barium-exchanged sample near 600°C transfers 1.27 Ba^{2+} ions per unit cell into the A and B sites. Assuming that our calcination procedure yields this level of barium exchange, the distribution of cations in the C and D sites can be calculated. This calculation is shown in the last three columns of table 1. The values are given as the number of cations per unit cell, with the total charge summing to 4.77 M^+. The LiBaL and NaBaL supports have substantial amounts of Ba^{2+} and K^+ located together with the Li^+ and Na^+ in the C and D sites along the main channels. On the other hand, the RbBaL and CsBaL supports mainly have heavy alkali cations in these sites.

Table 1
Composition of the Pt/BaL catalysts

Alkali (M^+)	Platinum (wt%)	Cation/Al mole ratio	Distribution of cations[a] (mol% of total)			Cations in C and D sites (No. per unit cell)		
			M^+	$2Ba^{2+}$	K^+	M^+	Ba^{2+}	K^+
Li	0.66	1.01	7.8	37.9	54.3	0.71	0.46	3.14
Na	0.76	1.00	15.5	35.7	48.8	1.41	0.36	2.64
K	0.64	1.01		30.1	69.9		0.10	4.56
Rb	0.57	1.00	45.9	29.9	24.2	4.19	0.09	0.40
Cs	0.54	0.96	37.2	28.4	34.5	3.26	0.00	1.15

[a] Barium counts double because of the 2+ charge.

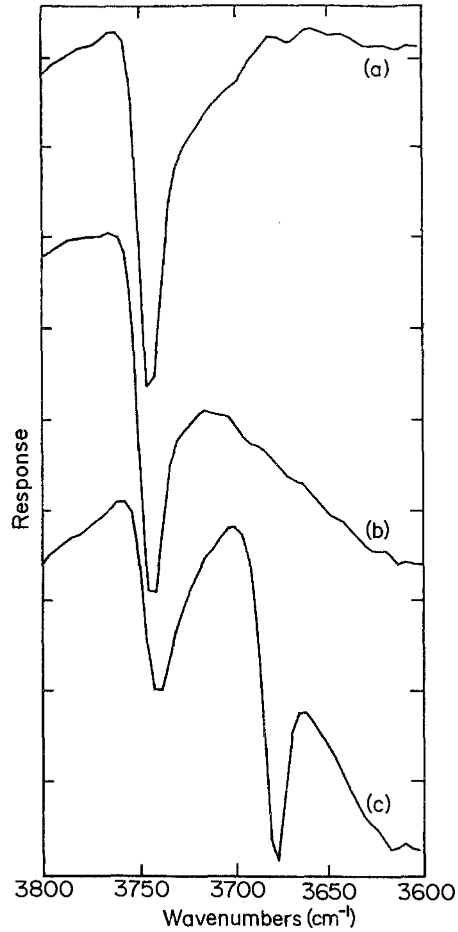

Fig. 1. Response of the infrared beam through (a) KBaL support, (b) 0.64% Pt/KBaL, and (c) 0.54% Pt/CsBaL at 25°C.

3.2. PLATINUM PARTICLE SIZES

Shown in fig. 2 is a micrograph of the 0.66% Pt/LiBaL sample. Most of the zeolite particles in the picture exhibit a splotchy, mottled gray contrast (point A). This mottled appearance is due to electron beam damage, which destroys the crystal structure, and causes the small platinum clusters in the pores to break up and diffuse into the alumino-silicate matrix [26]. Energy dispersive X-ray analysis (EDX) confirms that platinum is distributed throughout the zeolites. In a few areas, the zeolite lattice is still visible (point B). These regions also contain platinum, although no metal particles are evident. If platinum particles 7–12 Å in diameter were in the pores, they should be visible because the larger clusters scatter more strongly. Their absence suggests that the platinum inside the zeolite exists as small clusters less than ≈ 7 Å across. Also evident in the upper portion of the picture is a large metal particle approximately 300 Å across (point C). Other micro-

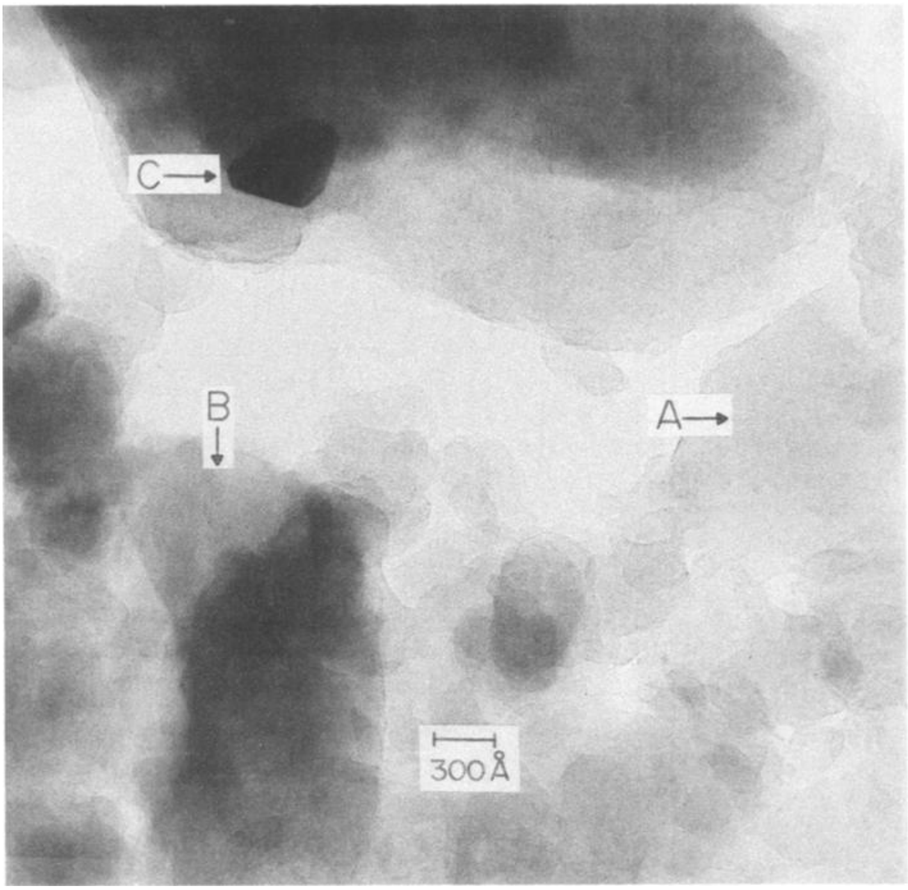

Fig. 2. Transmission electron micrograph of 0.66% Pt/LiBaL.

graphs show similar features: mottled images of zeolites with no particles visible, but which contain platinum according to EDX; and one or two platinum crystallites in the size range of 100–500 Å. These results indicate that the catalysts have a bimodal distribution of platinum, consisting of large crystallites outside the zeolites and small clusters ($\lesssim 7$ Å) inside the zeolites.

The platinum dispersions of the 0.6 wt% Pt/BaL samples are shown in table 2. These values were determined by hydrogen titration of adsorbed oxygen. To check the consistency of these results against other chemisorption methods, hydrogen and carbon monoxide adsorption isotherms were recorded of the 0.76% Pt/NaBaL catalyst. In addition, H_2 titration, H_2 adsorption and CO adsorption isotherms were recorded of the NaBaL support. The isotherms of the support yielded straight lines with positive slopes. These lines intersected the origin at zero uptake for H_2 titration and adsorption, but at a negative uptake for CO adsorption. The platinum dispersions measured by hydrogen titration, hydrogen adsorption, and carbon

Table 2
Distribution of platinum in the Pt/BaL catalysts

Alkali	Pt dispersion (%)	Percentage of Pt in:		Exposed Pt in clusters (%)
		crystallites (*m*)	clusters (*n*)	
Li	77	26	74	96
Na	50	56	44	88
K	62	42	58	94
Rb	72	31	69	96
Cs	72	31	69	96

monoxide adsorption on 0.76% Pt/NaBaL are $50 \pm 3, 54 \pm 1$ and $51 \pm 0.5\%$, assuming the reaction stoichiometries are $3H/PtO_s$, H/Pt_s and CO/Pt_s [21]. The latter value for CO is obtained in the case where the support adsorption isotherm is subtracted from the catalyst adsorption isotherm. These results show good consistency among the different chemisorption techniques. Therefore, hydrogen titration of adsorbed oxygen is a suitable method for estimating the platinum dispersion.

In the literature, CO/H adsorption ratios below 1 are often reported for Pt/L catalysts [7,10,13,16]. The CO/H ratio obtained for 0.76% Pt/NaBaL is 0.94. However, if no correction is made for the support adsorption isotherm, this ratio falls to 0.81. Larsen and Haller [10] have measured a CO/H ratio of 0.7 for a series of Pt/BaL catalysts with different dispersions. They did not make a correction for carbon monoxide adsorption on the support. Their ratio is in reasonably good agreement with the value measured in this study.

Due to the bimodal distribution of the platinum in the zeolite, the dispersions shown in table 2 cannot be used to estimate metal particle sizes. Rather they may be used to estimate the fraction of platinum associated with the clusters inside the pores and with the crystallites outside the pores: Assuming the dispersion of the clusters and the crystallites is 1.0 and 0.1 [27], respectively, the fraction of platinum present as crystallites, *m*, is given by

$$m = (1 - D_{\mathrm{Pt}})/0.9, \tag{1}$$

where D_{Pt} is the dispersion. The fraction of platinum present as clusters, *n*, is given by

$$n = 1 - m. \tag{2}$$

Finally, the fraction of the exposed platinum that is contained in the clusters is calculated by dividing *n* by D_{Pt}. These calculations are summarized in table 2. They indicate that a relatively large fraction of the platinum is outside the zeolite, ranging from 26% for 0.66% Pt/LiBaL to 56% for 0.76% Pt/NaBaL. However, in spite of this, 88–96% of the exposed platinum in the catalysts is associated with the clusters inside the pores. It is this latter platinum that determines the chemisorption behavior.

3.3. CARBON MONOXIDE ADSORPTION SITES

Shown in fig. 3 are infrared spectra for a saturation coverage of carbon monoxide on 0.76% Pt/NaBaL at 25 and 225°C, and after cooling to 25°C. Two broad absorptions appear in all three spectra. The first band, extending from 2100 to 1900 cm^{-1}, is due to carbon monoxide adsorbed on platinum [28]. Whereas the second band, extending from 1900 to 1700 cm^{-1}, is due either to some form of bridge-bonded CO on Pt, or to a carbonate species adsorbed on the support [29]. This latter feature is not observed when the zeolite support is exposed to carbon monoxide.

At room temperature (spectrum a), the infrared band for carbon monoxide adsorbed on platinum consists of a main peak at 2075 cm^{-1} and shoulders at 2115 and 1955 cm^{-1}. The peak at 2075 cm^{-1} is characteristic of carbon monoxide adsorbed on supported platinum catalysts, such as Pt/SiO_2 or Pt/Al_2O_3 [28–32]. This feature is due to adsorption on the platinum clusters inside the zeolite pores because these clusters make up most of the exposed platinum in the sample. Evidently, the clusters are not interacting strongly with the L zeolite framework, since the position of this peak is no different than that observed for conventional catalysts.

The shoulder at 2115 cm^{-1} may be assigned to one of two adsorption sites. The first possibility is the exposed platinum on the large particles outside the pores, since the peak frequency is the same as that observed at saturation coverages of CO

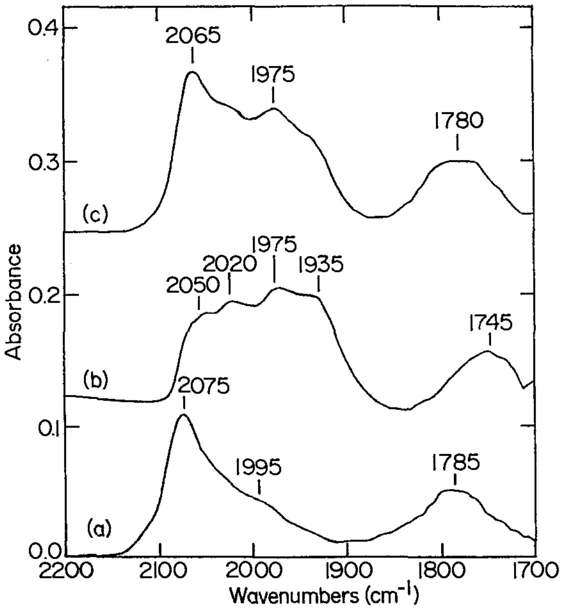

Fig. 3. Infrared spectra of carbon monoxide adsorbed on 0.76% Pt/NaBaL at (a) 25°C, (b) 225°C, and (c) after cooling to 25°C.

on Pt(111) [28]. The second possibility is platinum atoms on the small clusters adjacent to oxygen atoms of the zeolite lattice. This assignment is based on the study by Primet [30], which showed that carbon monoxide coadsorbed with oxygen exhibits an infrared band at this frequency. Additional results presented below suggest that the latter assignment is most likely correct. The other shoulder in the spectrum at 1995 cm^{-1} is assigned to carbon monoxide adsorbed on platinum clusters which are strongly interacting with the zeolite wall. Since the dominant band in the infrared spectrum is the peak at 2075 cm^{-1}, and this peak is typical of CO adsorbed on Pt/SiO_2 and Pt/Al_2O_3, it is concluded that following carbon monoxide adsorption at 25°C, most of the platinum clusters in the pores are not interacting with the zeolite framework.

When the 0.76% Pt/NaBaL catalyst is heated to 225°C (spectrum b, fig. 3), the peak at 2075 cm^{-1} decreases in intensity and shifts to 2050 cm^{-1}, the shoulder at 2115 cm^{-1} disappears, and new peaks appear at 2020, 1975, and 1935 cm^{-1}. Upon cooling to 25°C (spectrum c, fig. 3), the peak at 2050 cm^{-1} increases in intensity and shifts to 2065 cm^{-1}, the shoulder at 2115 cm^{-1} rises just above the baseline, and the peaks at lower frequencies decrease slightly in intensity. The appearance of the overlapping bands at 2020, 1975, and 1935 cm^{-1} indicates that heating the sample generates new adsorption sites for carbon monoxide on the platinum clusters in L zeolite. The new sites influence those that were originally present, as evidenced by the shift in the high-frequency peak from 2075 to 2065 cm^{-1} and the drop in intensity of the shoulder at 2115 cm^{-1}. We conclude that the new adsorption sites are formed by restructuring the CO-covered platinum clusters in such a way that they strongly interact with the zeolite walls.

The total integrated intensity of the infrared spectrum of adsorbed carbon monoxide increases upon heating and cooling the sample. The areas under the broad band between 2100 and 1900 cm^{-1} are 9.0, 13.9 and 15.1 cm^{-1} in spectra a, b, and c of fig. 3, respectively. The gain in absorption intensity on heating from 25 to 225°C is accompanied by a drop in the carbon monoxide uptake from 0.51 to 0.23 CO/(total Pt). This means that the molecular absorption coefficients of the Pt–CO species present at 225°C are greater than those of the Pt–CO species present at 25°C. A rough estimate of the difference in the molecular absorption coefficients is obtained by dividing the ratio of the integrated peak areas by the ratio of the CO uptakes at 225 versus 25°C: $(13.9/9.0)/(0.23/0.51) = 3.4$. The increase in molecular absorptivity is due to an increase in the dipole moment of the carbon monoxide molecule, which in turn is due either to lengthening the C–O bond or to increasing the $C^{\delta+}-O^{\delta-}$ charge separation [29]. These changes in the state of the carbon monoxide molecule can arise through increased back donation of electrons from the Pt into the π^* orbital of CO. In addition, they may occur through direct interaction of the carbon monoxide molecule with the zeolite lattice.

Shown in fig. 4 are a series of infrared spectra recorded during exposure of 0.76% Pt/NaBaL to ≈ 10 Torr of oxygen at 65°C followed by ≈ 10 Torr of carbon monoxide at 65°C. This experiment was conducted immediately after CO adsorp-

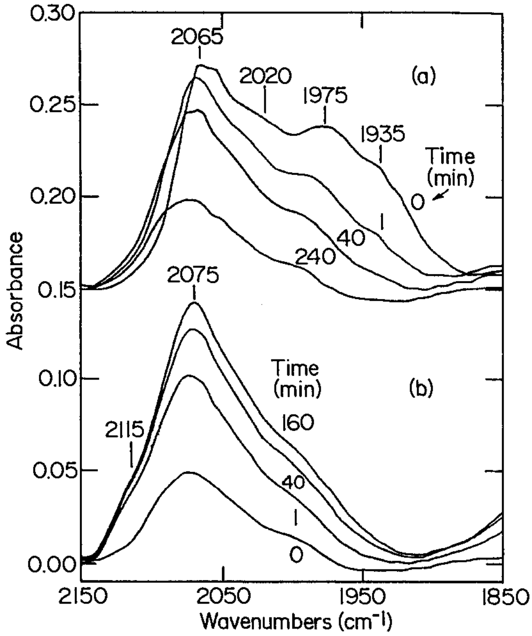

Fig. 4. Infrared spectra of carbon monoxide adsorbed on 0.76% Pt/NaBaL during exposure to (a) ≈10 Torr of O_2 at 65°C and (b) ≈10 Torr of CO at 65°C.

tion, heating and cooling. Upon introducing the oxygen, the peaks at 2020, 1975 and 1935 cm^{-1} decline rapidly, and are nearly gone after 1 min of exposure. By contrast, the peak at 2065 cm^{-1} declines slowly, dropping to one third its original intensity in 240 min. This intensity decrease is accompanied by a 10 cm^{-1} shift to higher frequency. These results reveal that oxidation at 65°C destroys the strong interaction between the CO-covered platinum clusters and the zeolite walls.

Upon subsequent exposure to carbon monoxide, the peak at 2075 cm^{-1} and the shoulder at 2115 cm^{-1} grow in intensity, while the peaks at low frequency do not reappear. The carbon monoxide displaces nearly all the adsorbed oxygen in 160 min. The integrated intensity of the infrared band is 13.3 cm^{-1} after 160 min, rising to 14.1 cm^{-1} after 19 h of exposure to carbon monoxide. The spectrum obtained after this last CO exposure exhibits the same shape as the spectrum obtained after the first CO exposure (fig. 3, spectrum a), except that the area under the band has increased by 57%. This suggests that some redispersion of the platinum may occur when the sample is exposed to carbon monoxide, heated to 225°C, then oxidized at 65°C. Following these treatments, the sample was again heated to 225°C and cooled to 25°C. The infrared spectra obtained at 225 and 25°C are identical to those obtained the first time the sample was heated and cooled. This demonstrates that the restructuring of the platinum clusters is a reversible process. The strong interaction of the CO-covered Pt cluster with the zeolite can be repeatedly created by heating to 225°C and destroyed by oxidation at 65°C.

Infrared spectra of carbon monoxide adsorbed on the 0.6 wt% Pt/BaL catalysts at 25°C are shown in fig. 5. These data were obtained after the samples had been tested for heptane reforming, as described in the experimental section. Infrared spectra taken before treating the catalysts for heptane reforming are exactly the same as these, except that they are shifted $\approx$ 10 cm^{-1} to higher frequency (compare the spectra for Pt/NaBaL in figs. 3 and 5). Examination of the infrared spectra in the figure reveals that each catalyst exhibits a broad band near 2050 cm^{-1} due to CO adsorbed on the Pt clusters. The position of this band shifts from 2065 to 2020 cm^{-1} as the alkali element in the zeolite is changed from Li to Cs. This shift may be ascribed to an electronic interaction between the platinum clusters and the supports [33]. The heavier alkali elements negatively polarize the platinum clusters. The increased charge on the platinum leads to more back donation of electrons into the CO π^* orbital and a downward shift in frequency. An analogous effect is observed for carbon monoxide adsorbed on platinum in acidic Y zeolites, where the infrared bands shift up in frequency with increasing acidity of the support [33].

Shown in fig. 6 are the infrared spectra of the 0.6 wt% Pt/BaL catalysts recorded after heating to 225°C. All the spectra contain four overlapping peaks centered at 2065, 2015, 1975, and 1920 cm^{-1}. The positions of these peaks are not sensitive to changing the alkali elements in the L zeolite. As was observed for 0.76% Pt/NaBaL, the integrated intensities of the bands at 225°C are about 1.5 times higher than the integrated intensities of the bands at 25°C. Upon cooling from

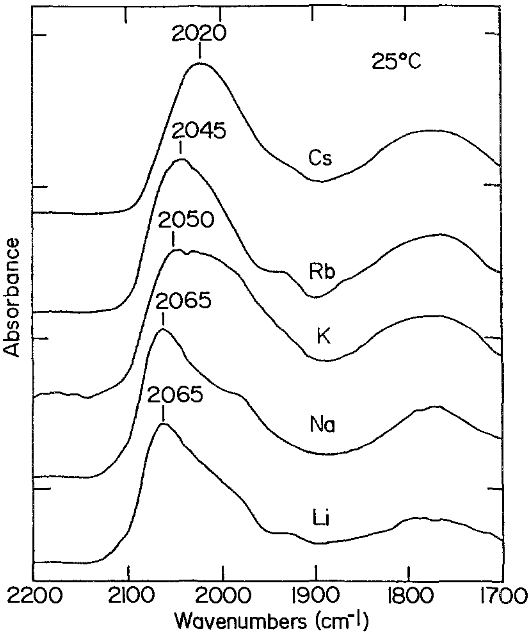

Fig. 5. Infrared spectra of carbon monoxide adsorbed on the 0.6 wt% Pt/BaL catalysts at 25°C.

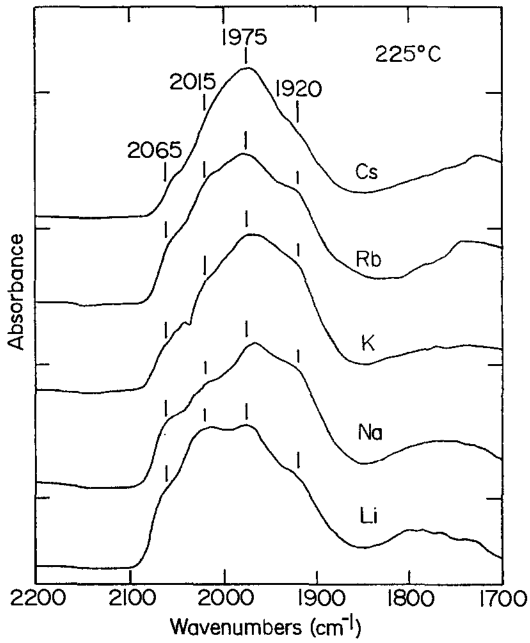

Fig. 6. Infrared spectra of carbon monoxide adsorbed on the 0.6 wt% Pt/BaL catalysts at 225°C.

225 to 25°C, the infrared spectra of all the samples change the same way as that shown in fig. 3: the peaks between 2000 and 1900 cm^{-1} decrease slightly in intensity, while the peak near 2065 cm^{-1} grows back in. These results indicate that the CO-covered platinum clusters in all the BaL zeolites restructure during heating to 225°C. Since the frequencies of the bands are the same for every sample, electronic interactions between the platinum clusters and the zeolite are not significant after restructuring.

The infrared bands between 2050 and 1900 cm^{-1} for adsorbed carbon monoxide on Pt/L catalysts have been observed by other researchers [2,9,15]. Barthomeuf [2] exposed a series of 5 wt% Pt/L catalysts, exchanged with Li, K and Rb, to between 10 and 60 Torr of carbon monoxide at room temperature. She found that over a period of time, a broad band near 2000 cm^{-1} appeared and grew to be a relatively intense feature in the infrared spectrum. Larsen and Haller [9] characterized the sites for carbon monoxide adsorption on 0.9 wt% Pt/L catalysts exchanged with Mg, Ca and Ba. In agreement with the present work, they found that the low-frequency bands appear upon heating the catalysts to 225°C. The positions of these bands depend on the cations in the zeolite: for Pt/MgL and Pt/CaL, the peaks are at 2050 and 1990 cm^{-1}, while for Pt/BaL, the peaks are at 2040, 1980 and 1935 cm^{-1}. Sachtler and co-workers [15] exposed several Pt/KL catalysts to 108 Torr of carbon monoxide at 25°C and observed a series of sharp, overlapping peaks at 2066, 2051, 2031, 2008, 1998 and 1919 cm^{-1}. The relative intensities of these peaks depend on whether the platinum is deposited by ion exchange or by incipient wetness impregnation. The results reported in these different studies indicate that the adsorption sites on the platinum clusters are affected by the method of depositing the metal and the distribution of cations in the L zeolite.

Infrared bands between 2050 and 1900 cm^{-1} for adsorbed carbon monoxide have never been observed for platinum supported on acidic, H^+-forms of zeolites [3,33]. However, they have been observed for platinum supported on NaY and NaX zeolites. De Mallmann and Barthomeuf [3] exposed the latter catalysts to several Torr of carbon monoxide at 300°C for 15 h, then evacuated the cell at 175°C and recorded the infrared spectrum. Absorption bands were observed at 2049 and 1993 cm^{-1} for Pt/NaY and at 2033 and 1968 cm^{-1} for Pt/NaX. By comparison to Pt/BaL, the low-frequency bands on these samples were less intense and did not contain multiple peaks or shoulders. Evidently, the specific adsorption sites generated on the platinum clusters depend upon the zeolite crystal structure.

Barthomeuf [12] originally suggested that the low-frequency bands are due to CO adsorbed on "very small Pt clusters embedded in the framework", but later she [3] concluded that they are due to CO adsorbed on Pt atoms "interacting strongly with adjacent and negatively charged framework oxygen atoms". This interaction is supposed to transfer electrons to the platinum atoms. The platinum atoms in turn back donate more electron density into the CO π^* orbital, and shift the infrared bands to lower frequency. However, this theory is not consistent with the results presented in this and other papers. First of all, electrons transferred to the platinum clusters will not be localized at specific atoms, but will distribute over the entire cluster. The effect of electron transfer on the infrared spectrum would be to shift the peaks to lower frequencies without changing the number or shape of these peaks. This is precisely the trend observed for the high-frequency bands (fig. 5), but not for the low-frequency bands (fig. 6). Furthermore, a smooth trend of decreasing frequencies should be observed starting with Pt on acidic HY and ending with Pt on basic BaL. One finds to the contrary that the low-frequency bands are only obtained for platinum on NaY, NaX, KL or BaL, and the number and distribution of these bands is different on every zeolite. Finally, the theory of electron transfer does not explain why the platinum clusters change their structure during heating or during exposure to high CO pressures. In the catalysis literature, there is no precedent for electron transfer being an activated process, or for its causing metal particles to restructure.

We propose that the low-frequency infrared bands are due to a direct interaction between the adsorbed carbon monoxide molecules and the zeolite lattice. It is envisioned that the carbon monoxide molecules insert into the lattice between the framework Si, Al and O atoms. The CO-covered platinum cluster may be thought of as a spiked ball and the zeolite as a wire-mesh tube in which the spikes on the ball poke through the holes in the wire mesh. This interaction could be stabilized by an ion–dipole interaction between the oxygen atom on the CO molecule and the cations in the zeolite, as suggested in our previous paper [20]. There are several locations in the zeolite lattice where the carbon monoxide molecules could penetrate, such as the square faces of the ε-cages, the faces of the double six-membered rings, or the spaces between neighboring double six-membered rings. Each overlapping peak in the broad band between 2050 and 1900 cm^{-1} may be assigned to a carbon monoxide molecule inserting into one of these locations.

Our proposed assignment is consistent with the changes observed in the infrared spectrum of adsorbed carbon monoxide with heating and cooling the Pt/BaL catalysts. At room temperature, the carbon monoxide adsorbs on the platinum clusters without interacting with the zeolite walls, and infrared bands typical of highly dispersed platinum catalysts are recorded. Upon heating the sample or applying a high CO pressure, the platinum clusters restructure to allow the carbon monoxide molecules to insert between the framework atoms of the L zeolite lattice. This process transforms the infrared spectrum into a series of overlapping bands between 2050 and 1900 cm^{-1}. The low-frequency bands disappear rapidly upon exposure to oxygen at 65°C, because the coadsorbed oxygen destroys the platinum structure required for the zeolite interaction. While our explanation of the low-frequency bands may be viewed by some as highly speculative, it nevertheless has the advantage of agreeing with all the experimental data.

Throughout the preceding discussion, we have claimed that the platinum inside the L zeolite is in the form of small clusters. The term "clusters" is chosen because the platinum in the pores does not form particles visible in the electron micrographs, indicating that they are less than ≈ 7 Å in diameter. However, these platinum clusters should not be confused with molecular, platinum–carbonyl clusters of the Chini type [34–36]. The latter are ionic complexes with a −2 charge that must be stabilized by counterions such as NH_4^+. These complexes exhibit strong absorbances in the ultraviolet and visible region of the spectrum. By contrast, the Pt/L catalysts do not contain any NH_4^+ after oxidation at 350°C and reduction at 500°C. After CO adsorption and heating, the platinum clusters do not exhibit ultraviolet or visible absorption bands, nor are their infrared spectra similar to that of the Chini complexes.

4. Conclusions

At room temperature, carbon monoxide adsorbs on the platinum clusters in the L zeolite without interacting strongly with the framework. The infrared spectrum consists of a broad band near 2050 cm^{-1} typical of CO on highly dispersed Pt. This band shifts to lower frequency with increasing alkali cation size, indicating that the cations affect the electronic state of the metal. Heating the Pt/L catalysts causes the CO-covered Pt clusters to restructure. A series of new bands appear at 2020–2015, 1975, and 1935–1920 cm^{-1}. We propose that these bands are due to carbon monoxide molecules inserting into the spaces between the zeolite framework atoms.

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