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Infrared Spectra of Adsorbed CO and Catalytic Conversion of Cyclohexane on Pt/Al_2O_3 and $Pt–Pb/Al_2O_3$ Catalysts

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Pt/Al_2O_3 and $Pt–Pb/Al_2O_3$ catalysts have been investigated by infrared (ir) spectroscopy of adsorbed carbon monoxide and selectivity for cyclohexane conversion. Addition of lead to Pt/Al_2O_3 catalysts decreases the frequency of the C–O stretching vibration from adsorbed CO and affects the dependence of the respective band intensities upon the CO surface coverage. In catalysis the addition of lead to Pt/Al_2O_3 strongly suppresses fragmentation and deactivation in the cyclohexane conversion. The spectroscopic results are consistent with an *s*-electron transfer from lead to platinum. This modification of platinum has catalytic consequences. Especially the hydrogenolysis of cyclohexane is inhibited. The ir and catalytic data are consistent with the conclusion that alumina-supported Pt–Pb catalysts exhibit both the ligand and ensemble effects.

INTRODUCTION

The properties of bifunctional Pt/Al_2O_3 catalysts in the conversion of hydrocarbons can be strongly modified by the addition of another metal (*1*, *2*). Often the total metal concentration is very low and the metal coverage of the alumina surface is low, too. One may question whether the two metals can be fixed close together on the alumina in order to prepare alloys or polymetallic clusters by simple impregnation. Changes of the catalytic activity by introducing a second metal can be due to modifications either of the acidic alumina or of the platinum. The ir spectroscopy of CO adsorbed on platinum provides a specific tool for the investigation of the metallic surface. In the present work the problem of the interaction between dispersed platinum and lead on alumina has been studied by applying ir spectroscopy and by examining catalyst activity in cyclohexane conversion.

EXPERIMENTAL

Catalysts were prepared by consecutive impregnation of alumina with appropriate aqueous solutions of H_2PtCl_6 and $Pb(NO_3)_2$. After drying and calcination the samples were reduced in hydrogen at 500°C. Both δ-Al_2O_3 (P 110 Cl—Degussa) and η-Al_2O_3 carriers were used in hydrogen adsorption and catalytic experiments, whereas only δ-Al_2O_3 was used for the ir measurements. Throughout this paper A, B, C, and D denote catalyst samples with δ-Al_2O_3 in contrast to A′, B′, C′, D′, and E′ which refer to η-Al_2O_3.

The vacuum apparatus, ir sample preparation, purifying procedures, and other experimental details are described elsewhere (*3–5*). The ir spectra were recorded on a Carl Zeiss UR-10 double-beam spectrometer applying reference beam screening to obtain suitable baselines.

Hydrogen uptakes were determined at

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0°C in a flow system using the pulse technique and Ar as carrier gas.

Cyclohexane conversion was studied in an integral reactor with a hydrogen flow of 3 liters/h saturated with cyclohexane (partial pressure of 250 Torr). Each time the reactor was loaded with 0.3 g of catalyst (0.3–0.8 mm in diameter) diluted with 0.7 g α-Al_2O_3. Reaction products were analyzed by gas–liquid chromatography.

RESULTS

1. Hydrogen Adsorption

The data are listed in Table 1. The increase in platinum concentration from 0.5 to 5.0 wt% results in a decrease in the dispersion. Addition of lead generally decreases the H/Pt ratio and this fall is drastic for 5 wt% Pb on δ-Al_2O_3. However, a slight increase for 2 wt% Pb on δ-Al_2O_3 is also observed.

2. Carbon Monoxide Adsorption

The ir spectra of carbon monoxide adsorbed on the monometallic Pt/Al_2O_3 samples A and B and on the bimetallic Pt–Pb/Al_2O_3 sample D are shown in Fig. 1. There exists a certain difference between platinum catalysts with low and high Pt concentration. Two overlapping bands are observed for sample A, while the band is broad and shifted to higher frequencies for sample B.

Hydrogen adsorption on samples A, A′, B, and B′ (Table 1) indicates higher platinum dispersion of samples A and A′ with only 0.5 wt% Pt. Therefore the frequency fall of the band from adsorbed carbon monoxide could be due to an increase in the degree of dispersion. Such a dependence of the infrared band position on the platinum particle size has recently been found by Solomennikov *et al.* (*6*). The presence of particles of various sizes, containing surface atoms with different coordination numbers, was regarded as an explanation of this phenomenon. Taking into consideration the above-mentioned dependence, the spectra in Fig. 1 indicate that: (i) sample A exhibits a bimodal platinum particle size distribution (*7*), (ii) the amplitude of particle size distribution is wide with sample B resulting in the appearance of a broad band with a flat maximum extending from 2060 to 2090 cm^{-1} (Fig. 1b).

TABLE 1

Hydrogen Adsorption

Sample	Metals (wt%)		H/Pt atomic ratio	
	Pt	Pb	δ-Al_2O_3	η-Al_2O_3
A, A′	0.5	—	1.33	1.25
B, B′	5.0	—	0.26	0.84
C, C′	5.0	2.0	0.30	0.59
D, D′	5.0	5.0	0.02	0.31
E′	0.5	0.5	—	1.07

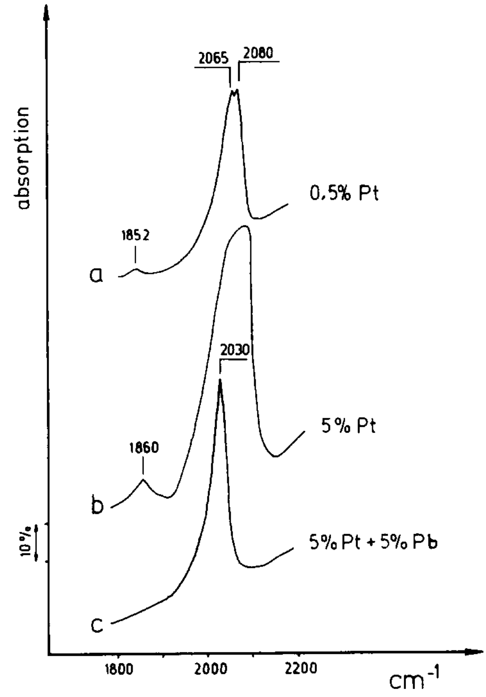

FIG. 1. Infrared spectra of CO adsorbed on supported platinum at 35°C: (a) sample A ($P_{CO} = 3 \times 10^{-2}$ Torr); (b) sample B (P_{CO} = 10 Torr); (c) sample D (P_{CO} = 10 Torr).

Addition of lead to a Pt/Al_2O_3 catalyst produces significant changes of the ir spectra observed after carbon monoxide adsorption (Fig. 1 and Table 2): (i) a 60-cm^{-1} frequency shift from 2090 to 2030 cm^{-1}, (ii) decrease in amplitude of the particle size distribution, (iii) disappearance of the low-frequency band (1850–1860 cm^{-1}). A similar frequency shift of the CO band has recently been observed with silica-supported Pt–Pb samples (*8*).

Parallel experiments clearly showed that no carbon monoxide chemisorption occurred on both δ-Al_2O_3 and Pb/δ-Al_2O_3 under the conditions applied in this study.

Absorption peaks arising from carbon monoxide adsorbed on Pt/Al_2O_3 and Pt–Pb/Al_2O_3 were shifted not only by added lead but also by variation of the CO coverage. Several phenomena are considered which may cause frequency shifts with variation of the surface coverage, e.g., dipole–dipole coupling (*9*) and island formation (*10*). The values of the CO band frequency at full coverage and certain residual coverages are given in Table 2. The residual coverage is defined as the adsorbed amount of CO remaining on the surface after desorption at a particular temperature. Desorption temperatures were chosen in such a way as to obtain still detectable and uniformly intense bands for all the ir samples (Table 2). With decreasing CO coverage on the Pt/Al_2O_3 samples the frequency falls by 32 cm^{-1}, whereas the shift is smaller for the Pt–Pb/Al_2O_3 samples C and D and depends on the lead concentration (Table 2).

In further experiments concerned with adsorption–desorption sequences, the integrated intensities (I_r) of the ir bands from carbon monoxide adsorbed on samples A, C, and D were plotted vs the number of adsorbed CO molecules per gram of Pt (Fig. 2).

Desorption curves were obtained as follows. It was assumed that full CO coverage was achieved at a residual pressure of 5×10^{-2} Torr, since above this value the integrated intensity of the CO band was not significantly changed. Thus after achieving a full coverage by addition of CO at pressures higher than 5×10^{-2} Torr, the sample was evacuated at elevated temperatures. Further, the desorbed amount was determined by subsequent stepwise readsorption of carbon monoxide until a pressure of 5×10^{-2} Torr was reached.

Plotting the integrated intensities (I_r) against the number of CO molecules adsorbed per gram of platinum, an interesting discrepancy between the platinum sample (curves a, a′) and Pt–Pb samples (curves b, b′ and c, c′) is observed (Fig. 2). The slopes of the curves are quite different. Furthermore, the hystereses within the adsorption and desorption sequences (Fig. 2) with the

TABLE 2

Infrared Band Frequencies from CO Adsorbed on δ-Alumina-Supported Pt and Pt–Pb

Sample	Metals (wt%)		ν_{CO}^1 (cm^{-1}) (P_{CO} = 10 Torr)	ν_{CO}^2 (cm^{-1}) (at certain residual coverage)[a]	$\Delta\nu_{CO}^{1b}$ (cm^{-1})	$\Delta\nu_{CO}^{2c}$ (cm^{-1})
	Pt	Pb				
A	0.5	—	2078	2046 (315°C)	32	40
B	5.0	—	2090	2058 (275°C)	32	38
C	5.0	2.0	2040	2025 (175°C)	15	4
D	5.0	5.0	2030	2020 (80°C)	10	No shift

[a] Desorption temperature at which certain residual coverage was reached is given in parentheses ($P_{CO}^{residual} < 10^{-4}$ Torr). The spectra were taken at 35°C.

[b] $\Delta\nu_{CO}^1 = \nu_{CO}^1 - \nu_{CO}^2$.

[c] $\Delta\nu_{CO}^2$—frequency shift due to ethylene coadsorption on partially covered catalyst samples with CO ($\theta_{CO} \approx 0.3$; $P_{C_2H_4}$ = 5 Torr). At this coverage the CO band is not split.

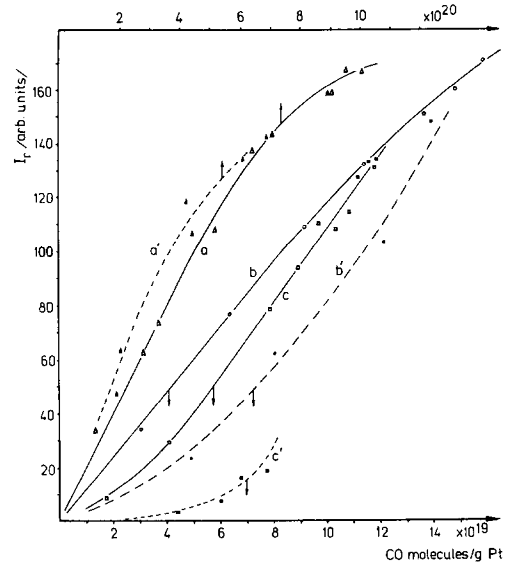

FIG. 2. Integrated intensities of the ir CO band versus number of adsorbed CO molecules per gram of platinum. Adsorption (a, b, and c) and desorption (a', b', and c') curves of A, C, and D, respectively.

Pt–Pb samples (curves b, b' and c, c') are opposite to that of the Pt sample (curves a, a').

3. Carbon Monoxide and Ethylene Coadsorption on Pt/Al_2O_3 and Pt–Pb/Al_2O_3 Catalysts

It is well known that band frequencies due to carbon monoxide adsorbed on supported platinum are affected by coadsorption of some vapors and gases provided free surface area is available (*11–13*). Experiments performed in the present study demonstrated a 40-cm^{-1} frequency fall after addition of ethylene to Pt/Al_2O_3 (sample A) partly covered with carbon monoxide ($\theta_{CO} = 0.3$). No shift was observed after ethylene addition to sample D under the same experimental conditions (Table 2). The direction of the frequency shift is an indicator for the nature of interaction between adsorbates and the metallic surface. Since a downward shift is observed, ethylene appears to be an electron donor, i.e., metal *d* electrons are enabled to enter the antibonding molecular orbitals of CO (*12, 13*).

4. Cyclohexane Conversion

The catalytic effect of lead addition was investigated in the cyclohexane conversion on two types of carrier: δ-Al_2O_3, commonly used in ir experiments, and η-Al_2O_3, often applied in reforming catalysts. The results are shown in Table 3 and Fig. 3. The reaction was examined at increasing temperature. The bimetallic catalysts proved to be very stable, whereas the monometallic ones suffered severe deactivation and decreasing selectivity in aromatization with time and temperature. The beginning of deactivation yielded methane as the only by-product. With increasing time other fragmentation products (C_2–C_5) were formed and the relative content of methane was decreased. This was due to self-poisoning of the hydrogenolytic splitting. Then further products without C–C bond rupture were formed by dehydrogenation (cyclohexane and cyclohexadiene) and by isomerization (methylcyclopentane and methylcyclopentene). The main advantage of the bimetallic catalysts over the monometallic ones is both the inhibition of fragmentation and resistance to deactivation.

DISCUSSION

The strong variation of the ir spectra from CO adsorbed on Pt–Pb/Al_2O_3 catalysts gives clear evidence that a considerable part of the lead atom content is fixed in the direct neighborhood of the platinum atoms.

The observed fall in the CO band frequency due to the addition of lead can be explained by two models: (i) a "physical" effect causing a decrease in the platinum particle size or an increase in Pt dispersion, and (ii) a chemical effect resulting in an electronic interaction between platinum and lead.

The ir data cannot be discussed in terms of the former model only. Recently Solomennikov *et al.* (*6*) found a decreasing CO band frequency with increasing platinum

TABLE 3

Cyclohexane Conversion

Catalyst carrier	T (°C)	t (min)	Conversion (%)		Benzene (%)		Methane (%)		C_2–C_5 (%)		Other C_6 (%) (see below)	
			Pt	Pt–Pb	Pt	Pt–Pb	Pt	Pt–Pb	Pt	Pt–Pb	Pt	Pt–Pb
η-Al$_2$O$_3$	500	15	100	100	97.3	100	2.7	0	0	0	0	0
(samples B′	530	50	100	100	96.0	100	4.0	0	0	0	0	0
and D′)	530	190	32.6	100	20.3	100	0.65	0	1.75	0	9.9	0
	545	250	26.6	97.1	14.8	96.8	0.8	0.3	1.5	0	9.5^a	0
δ-Al$_2$O$_3$	500	15	99.8	100	99.4	100	0.4	0	0	0	0	0
(samples B	530	50	99.8	99.0	99.0	99.0	0.7	0	0	0	0	0
and C)	530	125	98.6	99.6	96.9	99.6	0.3	0	0.2	0	0.7	0
	545	190	93.1	98.9	89.2	98.1	0.4	0	0.2	0	1.8	0.8
	545	245	49.8	99.3	41.8	97.8	0.2	0	0.2	0	7.6^b	1.2^c

Other C_6:	Methylcyclopentane	Methylcyclopentene	Methylpentanes	Cyclohexene	C_6 dienes
a	1.3	4.4	—	1.6	2.2
b	0.5	4.8	0.8	0.9	0.6
c	0.4	0.6	0.2	—	—

Note. t = time on stream.

dispersion for various Pt/Al$_2$O$_3$ catalysts. In their experiments the carbon monoxide adsorption onto a sample with the highest dispersion (D = 94%) gave rise to a band at 2060 cm^{-1} ($P_{CO} = 1 \times 10^{-4}$ Torr). In our experiments the increase in Pt dispersion (Table 1, cf. samples A and B) is accompanied by a 12-cm^{-1} downward shift of the CO band frequency (Table 2). However, the admission of lead to platinum produces an additional strong displacement of the band down to 2030 cm^{-1} (Table 2) and affects the hysteresis between the adsorption and desorption curves (Fig. 2). Our experiments with Pt/Al$_2$O$_3$ catalysts of various dispersion showed no variation of slope and hysteresis of these curves. All the results are consistent with the conclusion that the chemical effect of lead on platinum, as envisaged by the latter model, is clearly pronounced.

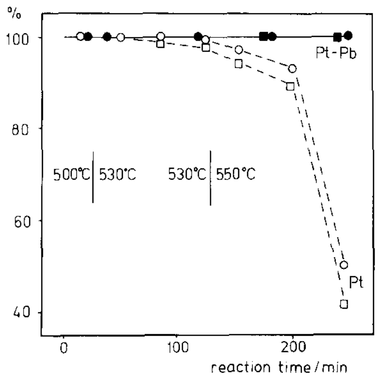

FIG. 3. Conversion of cyclohexane with increasing reaction time and temperature. Total conversion (○, ●) and benzene formation (□, ■) over samples B and C, respectively.

The former model conflicts also with the hydrogen adsorption and catalytic data. The H/Pt ratio with sample D is very low (Table 1); however, the frequency of the CO band with this sample is the lowest (Table 2). Apparently, this cannot be explained as an effect of Pt dispersion on the ν_{CO} shift since the highest band frequency with monometallic catalysts is detected for the sample of the lowest dispersion (Tables

1 and 2, cf. samples A and B; Ref. (*6*)). With sample C the H/Pt ratio is only slightly increased in comparison with sample B (Table 1), although a strong downward shift of the CO band is also observed (Table 2). Again, the variation of platinum dispersion with supported Pt–Pb catalysts is insufficient to interpret correctly the experimental data. The catalytic effect characteristic of bimetallic catalysts as found with sample C, namely, decreased deactivation and fragmentation, is also observed with sample D′ (Table 3), and with various bimetallic catalysts containing 0.5 wt% Pt on η-Al_2O_3 (*14*). However, the H/Pt ratio with these catalysts is decreased in contrast to the case with catalyst C. In general, all these results suggest an electronic influence on platinum in accordance with the conclusions drawn from the ir experiments.

Details of the electronic interaction between Pt and Pb can be derived from coadsorption experiments. Coadsorption of ethylene and CO on platinum produces a low-frequency shift of the CO band indicating electron donation from ethylene to platinum (*12, 13*). The interaction of lead with platinum gives a frequency fall, too, and therefore lead should act as a donor. Provided platinum has already accepted electrons from lead, further electron transfer from adsorbed ethylene to the platinum atoms should be inhibited and the influence on the CO band frequency is expected to be negligible. In fact, the experiment proves that ethylene coadsorption on supported Pt and Pt–Pb catalysts gives rise to a significant downward shift of the CO band only with the monometallic samples (Table 2). Besides that, it is reasonable to suggest that the increase in electron density of the platinum atoms ought to weaken the bond between ethylene and the surface metal atoms as a result of the reduced electron transfer. Weak and completely reversible ethylene adsorption on Pt–Sn alloys has been observed by programmed desorption experiments (*15*). A recent ir study of Pt–Sn/Al_2O_3 catalysts (*16*) has revealed an influence of coadsorbed ethylene on the CO band frequency similar to that already described with the Pt–Pb catalysts.

The model of electron-donating lead is supported by results from the Pt–Sn system. A corresponding *s*-electron transfer from tin to platinum has been suggested from Mössbauer experiments with Pt–Sn alloys (*17*) and Pt–Sn/Al_2O_3 catalysts (*1*). It may be expected that the *s*-charge transfer from lead to platinum would be accompanied by a compensatory increase in the *d*-charge transfer ability of platinum. Therefore a larger fraction of *d*-electron density is transferred to the π^*-antibonding orbitals of CO in accordance with the experimentally observed frequency fall of the CO band (Fig. 1, Table 2).

The catalytic experiments reveal a very strong effect of added lead. Fragmentation, other side reactions, and deactivation are suppressed. When the monometallic catalysts become non-selective, methane in addition to benzene is formed, while the bimetallic catalysts remain selective and stable (Table 3). They inhibit hydrogenolysis and deactivation.

Hydrogenolysis is increased with decreasing particle size (*18*). However, lead decreases hydrogenolysis. This gives a further argument that lead addition does not decrease the platinum particle size.

The electronic interaction between platinum and lead should increase the electronegativity of platinum and therefore should give a ligand effect in catalysis (*19*). The modified platinum atoms are less active in C–C bond splitting of the adsorbed cyclohexane molecule: hydrogenolysis is decreased. This conclusion is in accordance with the concept of Ptak and Boudart (*20*). They found a correlation of decreasing hydrogenolysis with increasing electronegativity of some transition metals. Furthermore one has to consider not only that the platinum itself is modified but that a neighboring Pt atom is replaced by Pb. This gives a dilution effect. The absence of the band at 1860 cm^{-1} with the Pt–

Pb/Al_2O_3 catalyst (Fig. 1c), assigned to multiple-bonded CO molecules, also indicates that Pt atoms are diluted by Pb atoms. A strong suppression of the number of multiple-coordinated species has been observed by Soma-Noto and Sachtler (*21*) in an ir study of CO adsorption on Pd–Ag/SiO_2. This effect was explained by the dilution of Pd by Ag in the surface layer. A similar dilution of an active metal by an inactive one is known with the Ni–Cu system. Added Cu strongly suppresses hydrogenolysis in the dehydrogenation of cyclohexane according to an ensemble effect (*22*). Therefore the inhibition of the hydrogenolytic splitting in the Pt–Pb system is caused both by the ensemble effect and the ligand effect. This conclusion is in complete agreement with the ir data. For the Pd–Ag system it has been found that the ligand effect is of minor importance since the frequency of the linear band from adsorbed CO is not changed (*21*). Our experimental results clearly show that the Pt–Pb system exhibits both the ligand and ensemble effects: the low-frequency shift of the linear CO band is accompanied by the disappearance of the band at 1860 cm^{-1} (Fig. 1, Table 2).

It may be questionable whether a ligand effect is necessary at all to explain the catalytic influence of lead. However, the dehydrogenation of cyclohexane on Pt proceeds at about 320°C without C–C bond rupture, whereas under these conditions all $Pt-Pb/\eta-Al_2O_3$ catalysts are strongly poisoned. The inhibition of this facile reaction is only explicable by a ligand effect (*14*).

The inhibition of deactivation on the bimetallic catalysts may be due to inhibition of hydrogenolysis. This reaction is usually accompanied by deactivation. Another possibility is that the adsorption of poisoning residues on bimetallic catalysts is decreased. Such a mechanism is proposed for Pd–Sn catalysts (*23*).

Finally, some influence of the carrier has to be considered. The monometallic Pt catalyst on $\delta-Al_2O_3$ is more resistant to deactivation than that supported on $\eta-Al_2O_3$ (Table 3). Different Pb/Pt ratios are necessary for active and stable bimetallic catalysts. This ratio is 2 wt% Pb/5 wt% Pt on $\delta-Al_2O_3$, but 5 wt% Pb/5 wt% Pt on $\eta-Al_2O_3$. Active bimetallic catalysts with only 0.5 wt% Pt on $\eta-Al_2O_3$ have also been reported for Pb/Pt ratios between 1 and 2, whereas larger amounts of lead are poisonous (*14*). The cyclohexane conversion over the 5 wt% Pb–5 wt% $Pt/\delta-Al_2O_3$ catalyst is very low, about 10%, and the hydrogen adsorption is extremely low. The influence of Pb on Pt is stronger when $\delta-Al_2O_3$ is applied in comparison with the case of $\eta-Al_2O_3$.

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