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An X-Ray Absorption Edge Study of Zeolite-Supported Platinum

P. H. LEWIS

From the Texaco Research Center, Beacon, New York 12508

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Platinum in a large pore zeolite (Linde SK-200: 0.5% Pt/Ca Y zeolite) was characterized by X-ray absorption edge spectroscopy, acid solubility studies, X-ray diffraction line-broadening, and hydrogen adsorption measurements. The absorption edge data show that all the platinum was reduced to a zero-valent state, and that on the average this platinum is smaller in size than that found in conventional reforming catalysts. Sixty percent of the reduced platinum is small enough in size to dissolve in acid; X-ray diffraction shows the remaining 40% is present as 60 Å metal crystals. These data in conjunction with hydrogen adsorption data showing an uptake of 0.5 hydrogen atom per platinum atom lead to an estimate of 10 Å for the size of the acid-soluble platinum, small enough to fit inside the zeolite cages.

The exposure of zero-valent platinum to hydrogen leaves the platinum with a negative charge. The exposure of zeolite-supported platinum to hydrogen at 300°C and 1 atm pressure for 1-2 hr produces a larger change in the platinum X-ray absorption edge spectrum than does a similar exposure at 100°C. This has been interpreted to mean that a stronger platinum–hydrogen bond is formed at 300°C. For every platinum atom in the sample 0.5 hydrogen atom is adsorbed after a 1-hr exposure at either 100° or 300°C and 1 atm pressure. This hydrogen affects the X-ray absorption edge spectrum. Therefore, it is this hydrogen that is bonded to platinum and serves as a measure of its size. An additional 1.2 hydrogen atoms can be adsorbed per sample platinum atom at 300°C under 1 atm pressure by waiting 20 or more hours. This additional hydrogen does not affect the platinum absorption edge spectrum and is therefore interpreted to be not adsorbed by the catalyst platinum.

INTRODUCTION

Zeolites are now in widespread use as catalysts. These catalysts are quite often prepared to contain small amounts of platinum. Interest in the state of this metal was greatly whetted by published reports (*1*) that, when reduced, the platinum remains dispersed as discrete atoms within the zeolite crystals. The evidence for this rests on the high hydrogen adsorption capacity of the catalyst. It was reported, also, that when the platinum was exposed to hydrogen at 300° a stronger bond was formed than when exposed at 100°.

It seemed desirable to examine the chemical and physical state of zeolite-supported platinum using other techniques. It had been shown that X-ray absorption edge spectroscopy can be used to determine the chemical state of platinum in catalysts (*2*) and to obtain a qualitative indication of its state of dispersion. Now X-ray absorption spectroscopy will be used to follow the changes in the chemical state of the platinum as the catalyst is reduced in hydrogen, degassed, and then reexposed to hydrogen at two temperatures. The method as yet cannot be used to determine the size of the platinum in the zeolite because a reliable calibration has not yet been achieved. It will be possible nevertheless to use the method in a qualitative way to compare the platinum dispersion in the zeolite catalyst with that found for platinum in conventional reforming catalysts. Estimations of platinum size were also obtained by combining X-ray diffraction, acid solubility, and volumetric gas adsorption measurements.

THE X-RAY ABSORPTION EDGE TECHNIQUE

Platinum Absorption Spectrum

The absorption spectrum of platinum (*3*) is shown in Fig. 1, where the absorption coefficient, *u*, is plotted versus X-ray wavelength. The general increase in absorption with X-ray wavelength is interrupted by discontinuities called absorption edges. The absorption coefficient is influenced by the chemical and physical state of the platinum only at absorption edges (*3,4*). The L_3 absorption edge was chosen to study the Pt/zeolite catalyst because it occurs at a convenient wavelength and because the change in *u* is greater at this edge.

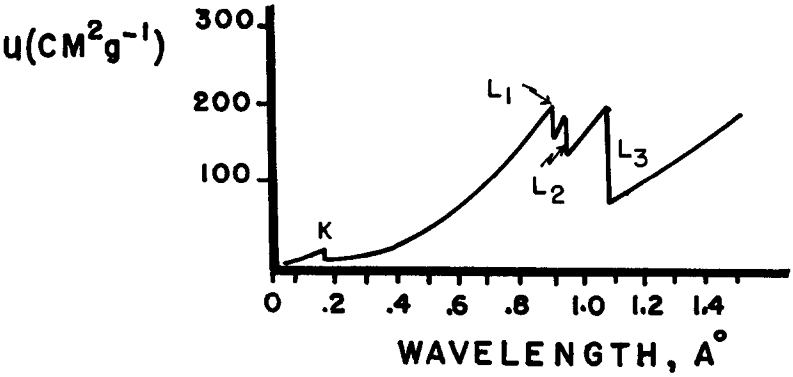

FIG. 1. The absorption spectrum of platinum.

L_3 *Platinum Absorption Edge Spectrum*

Figure 2 shows the L_3 absorption edge spectrum obtained by Beeman and Friedman (*5*) for a sheet of pure platinum metal. The edge is divided into two parts. The longer wavelength part, called Kossel absorption (*6*), is due to the excitation of a 2*p* inner electron to the outer 5*d* and 6*s* levels of the platinum that are electron-deficient. The characteristics of these levels and hence the Kossel part are primarily affected by platinum chemical state. The shorter wavelength Kronig absorption (*7*) is due to the excitation of the 2*p* electron to the extent that it moves away from its parent atom and interacts with its parent's neighbor atoms. The Kronig absorption is characterized by undulations with peaks B and C and valleys α, β, and γ.

In working with L_3 absorption edge spectra a wavelength reference point *M* is defined as that at which the absorption of platinum metal in the Kossel region has increased to a value half way between its maximum at *P* and the value at the long wavelength foot of the absorption edge. A similar reference point is used for L_1 absorption edge data. The reference point *L* is the wavelength corresponding to the platinum Fermi level as determined from the shape of the absorption edge by Beeman and Friedman (*5*).

Feasibility of Studying Platinum in a Catalyst

Figure 2 is the L_3 absorption edge spectrum of pure platinum metal. Consider the problem of obtaining the same spectrum if the metal is present to the extent of 0.5% on a zeolite support. In order to obtain a useful spectrum over this region it is necessary to obtain sufficient data at closely spaced intervals to define the Kronig structure and to obtain each point with sufficient precision to demonstrate the peaks and valleys. The number of data points required would be of the order of 200. To obtain these 200 points with a

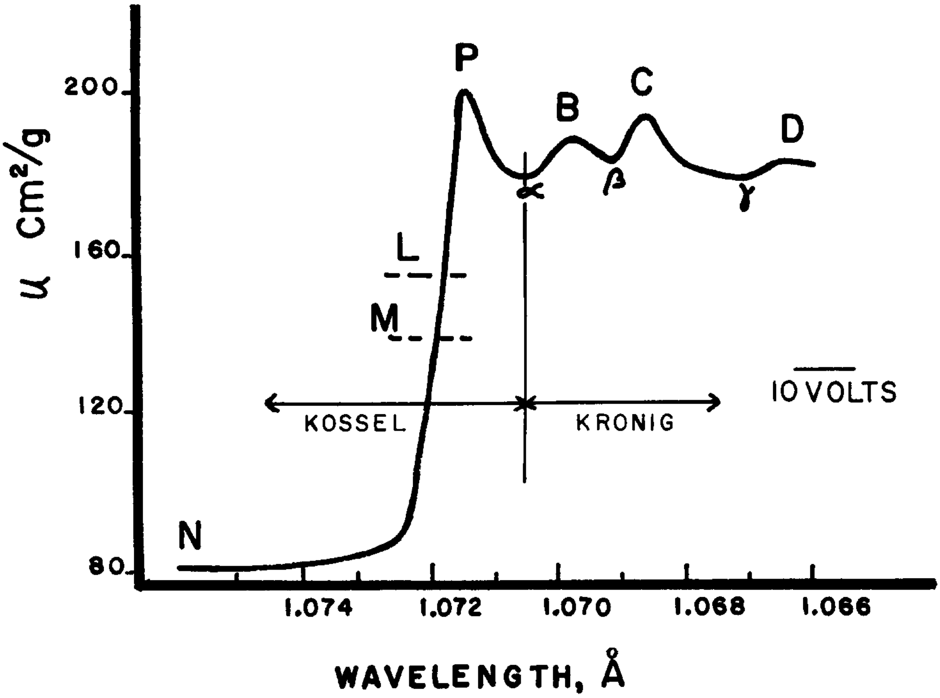

FIG. 2. L_3 absorption edge of platinum.

precision equal to one-fifth of the difference in absorption between B and β is estimated (see Appendix I) to require a total time of about 3400 hr, and even then one would have a rather poor Kronig spectrum. It is unfortunate that it is not feasible to obtain a Kronig edge spectrum since it is sensitive to the size of the dispersed platinum. If the platinum were atomically dispersed in the zeolite, this spectrum would be expected to be almost completely flat and similar to that observed by Parratt (*8*) for argon gas. Materials whose atoms are aggregated exhibit Kronig region spectra with undulations of the type shown in Fig. 2.

The problem is nearly as bad if one attempts to obtain a complete Kossel spectrum where about 60 monochromator settings would be required. It is desirable to find a way in which determining data at but a few monochromator settings will enable one to obtain a useful characterization of the absorption edge spectra of low platinum content catalysts.

A method for accomplishing this has been described in part previously (*2*). It is based on the empirical observation that when catalyst L_3 absorption edge data are measured at small wavelength intervals, corrected for the wavelength dependence of the zeolite absorption, and then plotted versus absorption data for a platinum metal foil, part of the data forms a straight line regardless of the chemical state of the platinum. This is an unusual and a fortunate occurrence. The linearity of such a plot can generally be expected when the catalyst constituent metal is in the same state as that of the reference foil. One cannot, however, foretell that this will occur when the catalyst metal has been combined with other elements. In the case of nickel, for example (*9*), the linear plot that one observes when one studies well-reduced metal is badly distorted when the metal is combined with oxygen. This linearity can be seen in plots of absorption edge data for platinum in combination with oxygen, hydrogen, and chlorine (*2*). Experience at this laboratory has been that this linearity is also observed when platinum is combined with bromine or iodine. That the plots are linear within the experimental error was checked by using samples containing larger amounts of platinum and making absorption measurements at very small wavelength intervals.

Furthermore, it was shown that the slope of this line increases or decreases as the chemical state of the platinum is varied. Because data at only a few points are needed to determine a straight line, and because of the response of the line to the chemical state, one has an opportunity to use X-ray absorption edge spectroscopy to characterize the chemical state of low platinum content catalysts.

Treatment of Catalyst Absorption Data

The essence of the method adopted in this work is to compare the absorption by the platinum in a catalyst sample at each X-ray wavelength with the absorption by a reference sample of platinum foil. It is necessary to be able to treat the catalyst data in a manner such that differences in its absorption properties from that of the foil which arise from its chemical or physical state can be recognized and differentiated from absorption differences due to the amounts of platinum in the two samples.

The absorption by a catalyst sample of a beam of X-rays of wavelength λ is related to the incident beam intensity, $I_0(\lambda)$, and the transmitted intensity $I_s(\lambda)$ by the equation

$$2.30 \log[I_0(\lambda)/I_s(\lambda)] = u_s(\lambda)\rho_s t_s \quad (1)$$

where u, ρ, and t are the mass absorption coefficient, density, and sample thickness and the subscript s denotes that these quantities refer to the catalyst sample as a whole. For a homogeneous sample the catalyst absorption is equal to the sum of the absorptions of its platinum and zeolite components; that is;

$$u_s(\lambda)\rho_s t_s = u_{\mathrm{Pt}}(\lambda)\rho_{\mathrm{Pt}} t_{\mathrm{Pt}} + u_z(\lambda)\rho_z t_z \quad (2)$$

If one measures the absorption of a platinum foil and a wafer of zeolite containing no platinum one can write as the most general expression for sample absorption

$$u_s(\lambda)\rho_s t_s = A(\lambda)u_f(\lambda)\rho_f t_f + C(\lambda)u_{z'}(\lambda)\rho_{z'}t_{z'} \quad (3)$$

where the subscripts f and z′ denote quantities measured for the platinum foil and zeolite wafer reference samples. Over the wavelength range considered in this paper, 0.893–1.080 Å, and over the range of compositions and states of hydration in Linde-zeolites (*10*) SK-20, SK-40, and SK-200, C is a constant to within 0.3%. The effect of this small variation will be considered in a later section.

If $u_{\mathrm{Pt}} = u_f$, then $A = (\rho t)_{\mathrm{Pt}}/(\rho t)_f$ and A is also independent of wavelength. This situation will exist if the chemical and physical states of the platinum are identical in the catalyst and foil samples. It is also expected, regardless of the chemical or physical state of the platinum, at wavelengths near but on the long wavelength sides of the platinum edges (*3*, *4*). This is a rational expectation since the absorption event entails the excitation of an inner electron to infinity. Equation (3) can be written in its equivalent form

$$\log(I_0/I_s) = A \log(I_0/I_f) + C \log(I_0/I_{z'}) \quad (4)$$

One solves Eq. (4) for A and C by setting up two simultaneous equations. The first contains absorption measurements for catalyst sample, platinum foil, and zeolite wafer measured at a wavelength 0.003 Å on the long wavelength side of the platinum L_1 edge; the second is based on absorption measurements for the three made 0.003 Å on the long wavelength side of the L_3 edge. These values of A and C will be designated hereafter as A_3 and C_3. They are referred to as bulk state parameters for the sample and are proportional to the amount of platinum and zeolite in the sample.

As reported previously (*2*), over the wavelength region from about 1.0715 to 1.074 Å, or from the foot of the absorption edge to a point on the long wavelength side of peak P in Fig. 2, A in Eq. (3) is found to be independent of wavelength but to be affected by the chemical state of the platinum. Over this narrow wavelength region the sample absorption, corrected for the wavelength dependence of its zeolite absorption, is plotted versus the platinum foil absorption. The slope of this plot is designated A_2 and is given by

$$A_2 = \frac{\Delta(u\rho t)_{\mathrm{Pt}}}{\Delta(u\rho t)_f} = \frac{\rho_{\mathrm{Pt}} t_{\mathrm{Pt}} \Delta u_{\mathrm{Pt}}}{\rho_f t_f \Delta u_f} \tag{5}$$

A_2 is the change in absorption of the catalyst platinum per change in platinum foil absorption for a given change in X-ray wavelength. A_2 equals A_3 when $u_{\mathrm{Pt}} = u_f$; that is, when the catalyst platinum is identical with the platinum foil in its chemical properties. The quantity $\Delta A/A_3$ is a measure of the fractional difference in absorption coefficient of the catalyst and foil platinum in the long wavelength part of the Kossel spectrum

$$\frac{\Delta A}{A_3} \equiv \frac{A_2 - A_3}{A_3} = \frac{\Delta u_{\mathrm{Pt}} - \Delta u_f}{\Delta u_f} \tag{6}$$

It is evident that if the catalyst platinum has the same chemical state as that of the platinum metal $\Delta A/A_3$ is zero. It has been found in the past (*2*) experimentally that $\Delta A/A_3$ is positive-valued if the catalyst platinum is oxidized; if the platinum be converted to a negative valence state then $\Delta A/A_3$ is found to be negative.

An explanation for the changes in slope goes like this. Mott and Jones (*11*) interpret the magnitude of a mass absorption coefficient in the Kossel section as being determined by the number density of empty energy levels available to an excited electron and the transition probability of an absorption event. To the approximation that in the case of platinum the transition probability is invariant, the platinum mass absorption coefficient measured just on the long wavelength side of P of Fig. 2 is directly dependent in part on the number of electron-empty $5d$ and $6s$ energy levels available to receive an excited L_3 electron. At N, X-ray quanta are not sufficiently energetic to excite an L_3 electron. The absorption event involves an excitation of an electron to states that are not affected by the physical or chemical characteristics of the platinum. If the platinum is oxidized and electrons are removed from the $5d$ and $6s$ levels, the absorption coefficient measured near P increases while that measured near N does not change. Thus oxidation causes the slope of a line joining P and N to increase. It is evident that the reverse argument explains the decrease in slope if platinum metal accepts electrons from a chemical species. The relationship between the charge on the platinum atom and this change in slope has been successfully demonstrated.*

A parameter D_{96} is defined as the difference between the mass absorption of platinum metal and the catalyst platinum:

$$D_{96} = [u_f - u_{\mathrm{Pt}}]_{-96} \tag{7}$$

It is measured near the boundary between the Kronig and Kossel parts of the spectra, at a monochromator setting 96 sec smaller than that at M. It has been correlated in the past (*2*) with the size of the catalyst platinum particles. The larger D is, the smaller the platinum particles. This decrease in platinum absorption is believed to be due to the fact that with small particles a large number of the absorption events result in an L_3 electron being excited to a state outside of its parent atom's particle. Such an event is considered to be less probable than one in which the excitation results in the excited electron moving away from its parent atom but remaining within a large particle.

EXPERIMENTAL

a. X-ray system and procedures. Polychromatic radiation was obtained from a molybdenum General Electric CA-7H X-ray tube operated at 50 kV and 40 mA. The tube output was held constant with a General Electric XRD-6 unit. The X-rays were collimated by a 1/6° divergence slit and then monochromatized using a von der Hyde double crystal attachment mounted on a Philips spectrometer. The attachment was fitted with germanium crystals cut so as to have their surfaces parallel to the (111) plane. Stray radiation was blocked by mounting molybdenum sheets just above the crystals and by placing a 4° scatter slit in front of a scintillation counter detector. The Hamner amplifiers, pulse-height analyzer, and scaler used to measure X-ray intensities all have dead times of the order of 1 μsec. Since the maximum intensities

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* To be described in a forthcoming paper.

were less than 1000 cps, there was no need to correct the observed intensities for lost counts.

Intensities were measured in terms of the times required to accumulate 10 000 counts. The intensities were corrected for "noise" by shutting off the X-ray beam and counting the number of pulses accumulated in 50 sec. The noise was 0.1–0.3 count/sec.

The observed catalyst absorption data is subjected to small but necessary corrections. To determine A_2 it is necessary to compensate the catalyst absorption data for the decrease in zeolite absorption with decreasing X-ray wavelength. This is done by adding the term, $-8.6 \times 10^{-5} C_3 \log (I_0/I_{z'}) \Delta\beta/2$, to the observed L_3 absorption edge data. The term is derived in Appendix II. $\Delta\beta$ is the change in angular setting of the X-ray monochromator from position M. Sample I, which will be described, was supported in the cell in a carbon container. The absorption of this container must be added to $C_3 \log(I_0/I_{z'})$ when making the compensation. Sample II, also to be described, was placed in the cell without the container. Over the wavelength range 1.0715–1.074 Å the compensation term is never more than 0.010. The compensated catalyst absorption will be called $\log(I_0/I_s)$.* To determine A_3 for Sample I it is necessary to subtract from the observed $\log(I_0/I_s)$ the absorption of the carbon container.

b. Vacuum system. This has been adequately described (*2*).

c. Materials. The SK-200 catalyst used was a commercial preparation obtained from the Linde Division of Union Carbide and bore the lot number 11060-21. Platinum-free zeolites used were identified by Linde as being: SK-20, a NaX zeolite; SK-40, a NaY zeolite. A 0.0001 inch thick platinum metal foil, obtained from A. D. MacKay, New York was used as a reference absorber. Electrolytic hydrogen was used in preparing the catalysts for examination. The hydrogen was purified by passage through a hot palladium-silver alloy thimble.

The powdered zeolite samples were pressed into sheets under 30 000–40 000 lb. Wafers were cut from these sheets having dimensions of roughly 2.5 × 2.5 × 0.2 cm.

RESULTS

X-Ray Absorption Edge Studies

Two samples of SK-200 catalyst were studied. Sample I was the catalyst as received from the manufacturer. Sample II was prepared from I by calcining a pressed wafer according to a procedure similar to that recommended by the manufacturer:

Temperature of sample raised in 2 hr to 204°C.

Temperature of sample held 1 hr at 204°C.

Temperature of sample raised in 1 hr to 371°C.

Temperature of sample held 1 hr at 371°C.

Temperature of sample raised quickly to 538°C.

Temperature of sample held at 538°C for 3 hr.

The sample was then placed in the X-ray cell while hot.

The wafer pressed from Sample I was mounted in the X-ray cell and evacuated. The necessary X-ray absorption measurements were made for the determination of A_2 and A_3. Figure 3 shows a plot of the wavelength-compensated catalyst absorption data taken at the L_3 edge versus the absorption data of the platinum foil. The data were taken at the three relative angular settings of the germanium monochromator crystal listed above each swarm of points. The settings are relative to that at M, the midpoint of the L_3 edge shown in Fig. 2. The settings are in seconds of arc and can be converted to volts by dividing by 6. Each swarm contains 15 or more data points. Each data point was determined by measuring the time to accumulate 10 000 counts for I_0, I_s, and I_f. The scatter of the individual points is large because of the normal statistical fluctuations; however, the averages marked by error flags are quite precise. They are based on accumulations of more than 150 000 counts and have the small errors shown by the flags. The bulk state line has been drawn with slope A_3 and positioned vertically to intersect the solid line at foil absorbance of 0.400. This was done to demonstrate the difference in slope to be observed.

TABLE 1
SUMMARY OF EXPERIMENTAL DATA

Condition of catalyst	A_2	A_3	$\Delta A/A_3$	$(u\rho t)_z$, L_3	D_{96} (cm²/g)
Sample I					
Unreduced	0.088 ± 0.003	0.071 ± 0.004	+(0.24 ± 0.06)	2.605	—
Sample II					
Reduced at 300°	0.101 ± 0.004	0.101 ± 0.004	+(0.02 ± 0.07)	3.217	+40 ± 4
evac. at 500°	0.100 ± 0.008		+(0.01 ± 0.90)		+34 ± 4
Reduced at 300°, evac. at 500°, reexposed to H₂ at 100° for 1 hr	0.080 ± 0.003	0.095 ± 0.004	−(0.16 ± 0.05)	3.330	+36 ± 4
Reduced at 300°, evac. at 500°, reexposed to H₂ at 300° for 1 hr	0.070 ± 0.005	0.095 ± 0.004	−(0.26 ± 0.07)	3.344	+44 ± 4
Reduced at 300°, evac. at 500°, reexposed to H₂ at 300° for 20 hr	0.070 ± 0.005	0.095 ± 0.004	−(0.26 ± 0.07)	3.319	+48 ± 4

Table 1 lists absorption edge results obtained for Sample I. The difference between A_2 and A_3 is four times the root-mean error. The table and Fig. 3 show that A_2 is larger than A_3. The validity of the A_3 measurement was tested by calculating the platinum weight fraction, X_{Pt}, using formula (8)

$$X_{\mathrm{Pt}} \equiv \frac{(\rho t)_{\mathrm{Pt}}}{(\rho t)_{\mathrm{Pt}} + (\rho t)_{\mathrm{z}}} = \frac{A_3(\rho t)_{\mathrm{f}}}{A_3(\rho t)_{\mathrm{f}} + (\rho t)_{\mathrm{z}}} \quad (8)$$

For this calculation $(\rho t)_{\mathrm{f}}$ was measured to be 0.0115 g/cm²; $(\rho t)_{\mathrm{z}}$ was calculated from the $(u\rho t)_{\mathrm{z}}$ value measured at the L_3 edge that is listed in Table 1 by dividing it by the value for u_{z}, 14.9 cm²/g. One obtains 0.175 g/cm² for $(\rho t)_{\mathrm{z}}$. This u_{z} was calculated using the composition of a dehydrated Ca-Y zeolite (*10*) and from literature values (*4*) for the mass absorption coefficients for its constituent elements. The calculated platinum content, 0.47%, is close to that reported by the manufacturer for the sample, 0.50 ± .02%.

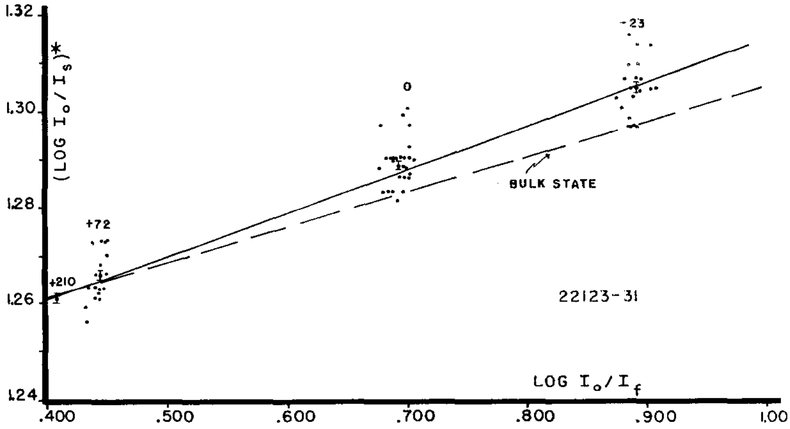


FIG. 3. Unreduced SK-200.

Sample II was prepared for X-ray study using the following procedure:

Sample degassed in a vacuum at 500° for 45 min.

Sample reduced in hydrogen at 300° for 15 hr.

Sample degassed at 500° for 2 hr.

Sample reduced again in hydrogen at 300° for 22 hr.

A typical plot of absorption edge data for for the reduced and evacuated zeolite catalyst is shown in Fig. 4. In drawing the solid line to determine A_2 one must make a choice of what data are to be used in its calculation. It is quite evident from examination of the figure that the data at −96 sec cannot be on the same straight line that fits the remaining data and are, therefore, not included in the least-squares determination of A_2. If one uses the data at monochromator settings −12 to +78 sec to obtain a least-squares line one finds that the data at −36 sec deviate from it by 0.008–0.009 whereas the other points are found to be off the line by the expected ± 0.002−0.003. Because of this, the data at −36 sec will not be used to calculate A_2. Table 1 lists the results of this run and a second run that show the reproducibility of the determination of the A_2 and the parameter D_{96}. Figure 4 and the data in Table 1 show that by excluding the two data points one obtains a near equality of A_2 and A_3. The exclusion will be considered further in the discussion section.

The validity of the determination of A_3 and $(u_z \rho_z t_z)$ was again checked by using formula (8) to calculate the platinum content, 0.49—0.54%, which also agree well with that reported by the manufacturer (*10*). The agreement supports the validity of the determination of A_3.

In determining A_3 and C_3 a hydrated SK-20 zeolite was used as the platinum-free zeolite instead of Linde anhydrous CaY. If one solves Eq. (4) using the two simultaneous equations one sees that the value of A_2 is dependent on the ratio, R, of the absorption of the platinum-free zeolite at the platinum L_3 edge to its absorption at the platinum L_1 edge

$$A_3 = \frac{R \log(I_0/I_s)_{L_1} - \log(I_0/I_s)_{L_3}}{R \log(I_0/I_f)_{L_1} - \log(I_0/I_f)_{L_3}}$$

The calculated value of R for Linde anhydrous CaY is 1.682; for hydrated SK-20, 1.678. The use of hydrated SK-20 with a lower value of R leads to a determined A_3 that is low by 0.002. This is negligible.

The reduced degassed catalyst was exposed to hydrogen in various ways. Figure 5 shows the absorption edge data for the zeolite-supported platinum subsequent to exposure to 1 atm hydrogen at 100° for 1 hr; Fig. 6 after exposure to 1 atm hydrogen at 300° for 1 hr. In each plot the least-squares line that fits the L_3 absorption edge data (+78 to −36 sec) has a slope smaller than that measured by the bulk state procedure, A_3. Figures 5 and 6 also show that the depression of the slope below

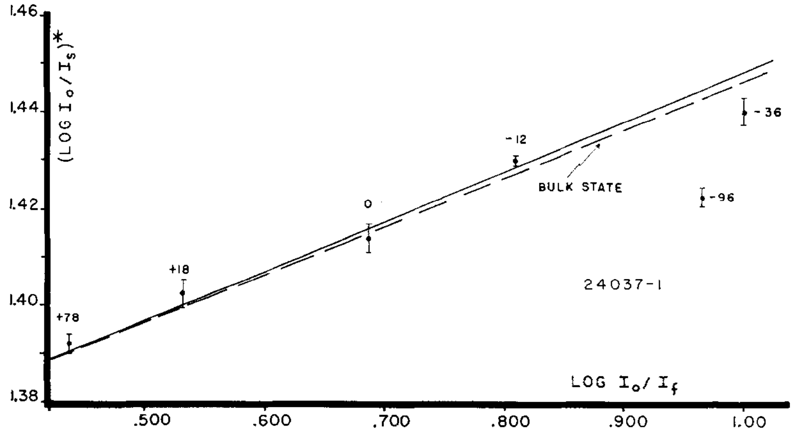


FIG. 4. Sample reduced at 300°C, evacuated at 500°C.

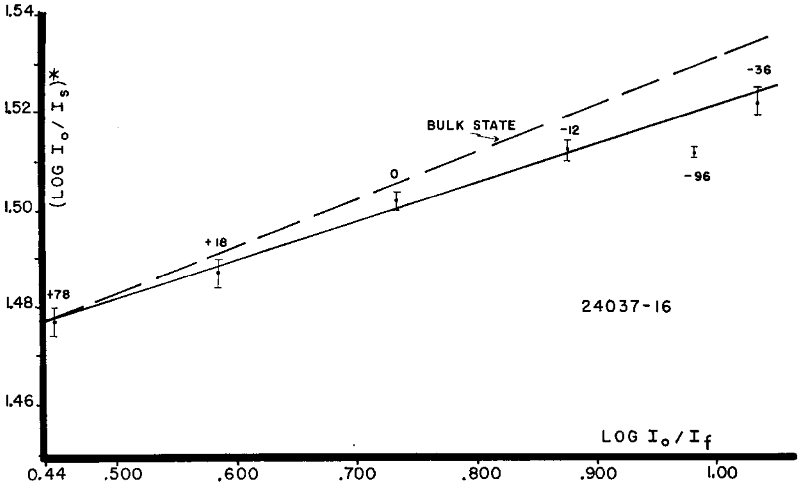


FIG. 5. Sample heated in hydrogen at 100° C, subsequent to pump-off.

the bulk state line is the greater, the higher the temperature of exposure to hydrogen. Table 1 lists quantitative data. The data in this table show that $\Delta A/A_3$ is the same, -0.26, regardless of whether the platinum has been exposed at 300° to hydrogen for 1 hr or 20 hr.

Hydrogen Desorption Studies

Volumetric hydrogen desorption measurements were initiated by heating the catalyst to temperature in hydrogen at 1 atm pressure for certain times. Subsequent to the exposure, the sample was cooled to 25° and excess hydrogen was removed by evacuating the cell. The cell was then closed off to the pumps, the sample was heated, and the amount of hydrogen that was desorbed was measured by the pressure rise in the cell. The desorption of the hydrogen was obtained when the sample had been heated to 430°. No further desorption was observed when the sample was heated to 500°. To avoid a pressure rise in the cell due to zeolite water evolution, the cell was connected to a trap cooled with liquid nitrogen. The desorption data were corrected for the hydrogen desorbed from the zeolite itself by running the above experiments using a Linde platinum-free Na-X zeolite.

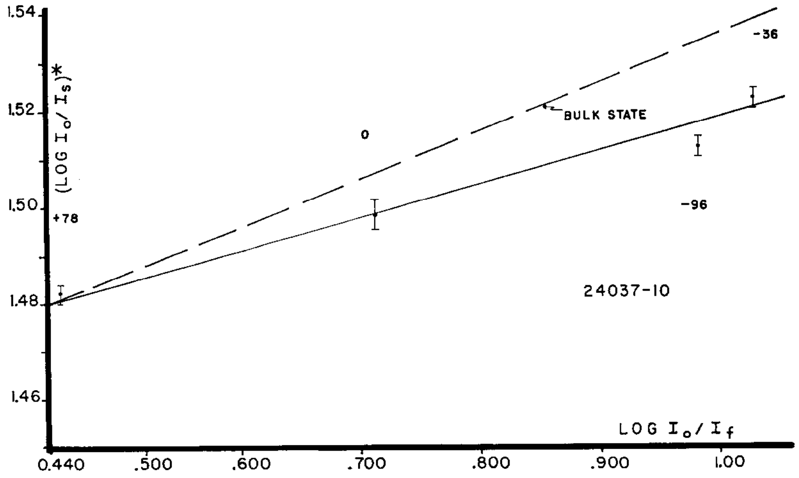


FIG. 6. Sample exposed to hydrogen at 300°C, after pump-off.

TABLE 2

HYDROGEN DESORPTION RESULTS

Time of exposure (hr)	Gram atoms hydrogen desorbed		
	100°	300°	
		Uncorrected	Corrected
2	1.5×10^{-5}	2.4×10^{-5}	1.4×10^{-5}
3	—	2.4×10^{-5}	1.4×10^{-5}
21	2.4×10^{-5}	—	—
23	—	5.4×10^{-5}	4.4×10^{-5}
88	—	5.3×10^{-5}	4.3×10^{-5}

Table 2 lists the number of gram-atoms of hydrogen that can be desorbed from the sample containing 2.7×10^{-5} g-atom of platinum at 430° subsequent to the exposure to hydrogen at the stated temperatures and for the stated lengths of times. The results are corrected for the hydrogen adsorption by the support at 300°. No correction is necessary at 100°.

After the sample has been exposed to hydrogen for 3 hr at 300°, only about half the hydrogen can be desorbed by heating to 300°. In contrast, 87% of the hydrogen adsorbed after an exposure at 100° for 2 hr can be desorbed at 200°.

Acid Solubility Studies

The reduced SK-200 sample was removed into the air and treated first with cold HF and then cold, concentrated HCl. The zeolite dissolved leaving a platinum black residue and some platinum dissolved in the acid. The amount of dissolved platinum was measured by saturating the acid solution with H_2S and then firing in air the resultant precipitate. Sixty percent of the zeolite-supported platinum was found to be soluble in the acid. The remaining 40% of the platinum was found by X-ray diffraction line-broadening to be 60 Å metal crystals.

DISCUSSION

In Fig. 3 the absorption edge data for an unreduced sample were presented. That the slope of the least-squares line, A_2, was larger than that of the bulk state line, A_3, was interpreted as showing the platinum to bear a net positive charge. This is entirely reasonable since the catalyst was prepared by substituting $Pt(NH_3)_4^{2+}$ for Ca^{2+} followed by a calcination which would be expected to decompose the ammine leaving Pt^{2+}. In Fig. 4 the absorption edge data for the reduced and degassed sample are presented. The equality of A_2 and A_3 indicates that the platinum has been converted to a zero-valent state. This is the expected result. The deviation of the data at -96 and -36 sec from the straight line is interpreted to be due to the very small size of the catalyst platinum. The deviation of the datum at -96 sec has been frequently observed (*2*) when the platinum is small in size. The deviation of a datum at -36 sec has not previously been observed. Because the experimental evidence indicates that the zeolite platinum is smaller than any hitherto observed this last deviation has also been attributed to platinum size.

The effect of exposing platinum to hydrogen at 100° and 300° is shown in Figs. 5 and 6. At both temperatures A_2 is smaller than A_3, showing that the platinum has been converted to a negative state.

As yet the D_{96} absorption observation has not been calibrated so that particle sizes can be obtained. One can, however, compare the D_{96} observed for the SK-200 catalyst with those observed for other low platinum content catalysts. Table 3 lists the data. The higher value of D_{96} found for the Linde SK-200 sample indicates that it contains platinum particles that are smaller in size than those found in the other catalysts.

TABLE 3

SIZE DATA

Catalysts	D_{96} (cm²/g)
Linde SK-200	34–48
U.O.P. R-8	22
Sinclair-Baker RD-150	17

One can proceed to obtain a reasonable estimate of the sizes of the platinum in the SK-200 catalyst in the following way. The hydrogen adsorbed by the platinum in the sample will be reported as the number of gram-atoms of hydrogen adsorbed, H, per gram-atom of platinum, Pt, in the sample. We shall be concerned with three adsorptions. The first, $(H/Pt)_t$, is that measured for all the platinum in the sample. The second, $(H/Pt)_c$, is the measure of the hydrogen adsorbed by that platinum in the form of crystals that can be observed by X-ray diffraction. One obtains $(H/Pt)_c$ from crystal sizes determined using X-ray diffraction line-broadening measurements made on the acid-insoluble platinum. One uses a size–H/Pt relationship previously given (*2*) and assumes

(1) The platinum crystals are cubes.

(2) Each platinum atom on the crystal surface adsorbs but one gas atom.

The third adsorption measurement, $(H/Pt)_s$, is that for the platinum small enough to dissolve in the acid. This measurement assumes that the platinum that does dissolve does so because of its size and not because of its chemical state. That this is so is confirmed by these X-ray absorption edge studies which show reduced platinum is in the zero-valent state when under a vacuum. We shall not go into the mechanism of solution in acid. It is conceivable that the small platinum particles oxidize upon exposure to air and acid and then dissolve.

The three adsorption measurements are related by:

$$(H/Pt)_t = X(H/Pt)_s + (1 - X)(H/Pt)_c$$

X is the fraction of platinum soluble in acid. Since X, $(H/Pt)_t$, and $(H/Pt)_c$ are measured, $(H/Pt)_s$ can be calculated.

This procedure can be tested by comparing $(H/Pt)_t$ with $(H/Pt)_c$ for catalysts containing negligible amounts of soluble platinum. Table 4 lists the results. It is apparent that the total hydrogen adsorption runs from more than 1 to 4 times that expected from the X-ray platinum metal crystal size measurements. It is possible that the excess hydrogen is activated by platinum so as to adsorb on the support, so some care will have to be exercised to make sure that hydrogen adsorption measurements are stopped when the platinum surface is saturated and before appreciable hydrogen adsorption by the support begins.

TABLE 4

CORRELATION OF GAS ADSORPTION AND X-RAY DIFFRACTION MEASUREMENTS OF PLATINUM SIZE

Sample	Hydrogen atoms adsorbed per platinum $(H/Pt)_t$	$(H/Pt)_c$	$(1 - X)$
0.55% Pt/Al_2O_3	0.40	0.17	1.00
1.7% Pt/Al_2O_3	0.4–0.6	0.14	0.91
U.O.P. R-8	0.20	0.17	1.00

While Table 2 shows that the hydrogen adsorption by the SK-200 catalyst as a whole increases with time, the X-ray absorption data in Table 1 show that hydrogen adsorption by its platinum has ceased after 1 hr, since there is no further change in A_2 after 1 hr. The 2.7×10^{-5} g-atom of platinum in the catalyst therefore adsorb but 1.4×10^{-5} g-atom of hydrogen. $(H/Pt)_t$ is then 0.5. Since X is measured to be 0.6, and $(H/Pt)_c$ is calculated from the Pt crystal size to be 0.15, one can determine $(H/Pt)_s$ to be 0.7. This hydrogen adsorption corresponds to platinum particles that are 10 Å in size.

This type of analysis leads to the conclusion that platinum in the SK-200 catalyst is present as two sizes. The larger 60 Å crystals are too large to fit inside a zeolite crystal. There is no direct experimental evidence that the platinum particles that are estimated to be 10 Å are within the zeolite cages. It is, however, reasonable to expect them to be so. Zeolite crystals are 0.1–10 μ in size (*12*). Their external surface area is but 5 m²/g compared to 500 m²/g for an internal surface area. The area external to the zeolite crystals would not be expected to be large enough to prevent approximately 10 Å crystals from growing to larger sizes when the catalyst is heated to 500°.

It is interesting to speculate that 10 Å is close to the largest size for a platinum crystal to just fit the inside diameter of the zeolite α-cage. The platinum crystal can not leave the cage through the cage window with a smaller diameter and hence would be stable towards growth.

Rabo *et al.* (*1*) interpreted their hydrogen adsorption data as indicating that virtually all the zeolite platinum is atomically dispersed. Quite possibly the difference between this characterization and that described in this paper might be due to sample preparation. However, our sample seems to adsorb about as much hydrogen as Rabo's sample. The hydrogen desorption characteristics are similar. The difficulty is believed to be just which hydrogen adsorption measurement should be interpreted to give a meaningful measurement of platinum surface area: one made after a few hours exposure to hydrogen at 300°, or one made after a 20-hr exposure at 300°. The interpretation used in this paper can be defended in two ways:

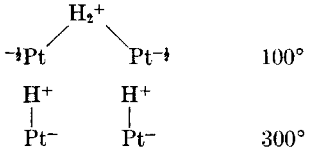
(1) Absorption edge spectra show that little or no hydrogen is adsorbed by the platinum after the first few hours of hydrogen exposure.

(2) The $(H/Pt)_t$ ratio of 1.7, which was measured after keeping the sample at 300° for 23 hr, is inconsistent with the presence of a relatively large fraction of 60 Å platinum crystals.

On the basis of the above interpretation the zeolite part of SK-200 has been found to adsorb 3×10^{-5} g-atom of hydrogen. A gram of platinum-free zeolite can adsorb but 1×10^{-5} g-atom of hydrogen. It is a logical deduction then that the platinum in the SK-200 catalyst is capable of activating the hydrogen so that it can be reversibly adsorbed. One now faces a problem of how to study this.

If one adopts the shorter time measurement of hydrogen uptake as a valid measure of the number of platinum hydrogen bonds formed, then the $\Delta\ A/A_3$ per hydrogen–platinum bond formed at 300° is −0.5. This is interpretable in simple terms. L_3 absorption edge spectroscopy involves the excitation of a $2p$ electron into a d or an s orbital. This is so because of the selection rule that requires the change in angular momentum states in a transition to be ± 1. For a neutral platinum atom the lowest energy electron-deficient s and d orbitals available are one $5d$ and one $6s$ orbital. Each of these contains one electron (*13*). If one assumes that the magnitude of the Kossel absorption is due to the holes in these two orbitals, then the filling of one of them by a hydrogen-contributed electron will lead to a reduction of the absorption coefficient by a factor of 0.5, equal to that observed.

One should note that the greater effect of hydrogen on the platinum absorption edge spectrum at 300° compared with that at 100° correlates well with the hydrogen desorption properties. The ratio of $\Delta\ A/A_3$ observed after the 300° exposure to that observed after the 100° exposure, 1.6 ± 0.5, is consistent with but does not prove the following pictures of the hydrogen chemisorption:



The two pictures show what are believed to be the dominant forms of adsorbed hydrogen at the two temperatures.

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APPENDIX I

One can show that the difference in absorption between peak B and trough β of Fig. 2, $\Delta \log(I_0/I_s)_{B\beta}$, is a constant fraction of the absorption of the sample at the peak B, $\log(I_0/I_s)_B$. Thus

$$2.3 \log(I_0/I_s)_B = u_{Pt,B}(\rho t)_{Pt} + u_{z,B}(\rho t)_z \quad (1)$$

$$2.3\Delta \log(I_0/I_s)_{B\beta} = (\Delta u_{Pt})(\rho t)_{Pt} \quad (2)$$

From the platinum content one knows that

$$0.005 = \frac{(\rho t)_{Pt}}{(\rho t)_{Pt} + (\rho t)_z} \quad (3)$$

To the approximation that the first term in Eq. (1) is small compared to the second and that $(\rho t)_{Pt}/(\rho t)_z \approx 0.005$, one can write

$$\Delta \log(I_0/I_s)_{B\beta} = (\Delta u_{Pt})(0.005)(1/u_z)$$

Now Δu_{Pt} is 5.7 cm^2/g and u_z is 14.9 cm^2/g. So

$$\Delta \log(I_0/I_s)_{B\beta} = 0.0019 \log(I_0/I_s)_B$$

For the extreme case where the transmitted intensity is just equal to the detector noise, 0.2 cps, and using a normal incident beam intensity of 770 cps, $\Delta \log(I_0/I_s)_{B\beta}$ is 0.007. For a more reasonable sample thickness giving an I of 6 cps, $\Delta \log(I_0/I_s)_{B\beta}$ would be 0.005. To obtain $\log I_0/I$ to at least a precision of ± 0.001 one would have to wait 6×10^4 sec at each monochromator setting.

APPENDIX II

The wavelength dependence of the absorption of a sample is given by

$$u = D\lambda^3$$

Its change with wavelength is then

$$du/d\lambda = 3D\lambda^2$$

Combining

$$du/u = 3\, d\lambda/\lambda$$

Converting from wavelength in Å to X-ray energy in volts

$$du/u = -3\, dV/V$$

Now

$$dV = \Delta\beta/6$$

and

$$V = 12.4 \times 10^3/\lambda$$

Hence $\Delta u = -8.6 \times 10^{-5} u(\Delta\beta/2)$ for 1.07-Å X-rays. Multiplying by $(\rho t)_z$

$$(\Delta u\rho t)_z = -8.6 \times 10^{-5}(u\rho t)_z(\Delta\beta/2)$$

or using the relationship between catalyst reference zeolite absorptions of Eqs. (3) and (4) of the main text

$$\Delta \log(I_0/I_z) = -8.6 \times 10^{-5} C_3 \log(I_0/I_{z'})(\Delta\beta/2)$$

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