

ATOMIC AND ELECTRONIC STRUCTURE AND CHEMICAL REACTIVITY OF METAL CLUSTERS

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Platinum clusters were introduced into the crystals of a Y-zeolite, a porous silicoaluminate containing internal cavities called supercages with a diameter of 1.3 nm. Two kinds of samples were prepared by finishing their preparation at a low (490 K) or high (673 K) temperature. The corresponding clusters are denoted as L and H respectively. It was determined by transmission electron microscopy (TEM) that the L clusters contain 20 atoms on the average. This critical finding by TEM led to a new interpretation of results obtained by means of a technique developed recently by the Fraissard group and based on ^{129}Xe NMR. According to the Fraissard technique, the same L clusters contain 16 atoms on the average. These values are compatible with the size determination of L clusters by X-ray techniques, EXAFS and WAXS. From the Fraissard technique, the H clusters contain 30 atoms. The X-ray techniques also confirm that the H clusters are larger than L clusters. The atomic and electronic structure of these clusters is discussed, together with their chemical and catalytic reactivity.

1. Introduction

Metal clusters with a size less than 1.5 nm and containing less than 100 atoms show properties deviating from those of the bulk metal. Thus, as compared to bulk metal, such clusters show higher ionization potential, lower melting point, shorter nearest neighbor distance, and possibly a different icosahedral structure [1]. It is also of interest to study if such clusters with less than 100 atoms show catalytic activity different from that of bulk metal. For such clusters, along with measurement of catalytic activity, it is essential to determine the number of atoms per cluster, the atomic and electronic structure of the clusters, and assess the possible effect of the support on the properties of the clusters. We have undertaken such a study, and report general findings in this paper. All details will be published elsewhere.

The system chosen consisted of Pt clusters contained in a porous crystalline silicoaluminate support Y-zeolite. It is easy to prepare [2,3] Pt clusters in the size range < 1 nm in the so-called

supercages 1.3 nm, in diameter, of the Y-zeolite. The supercages are interconnected through four windows 0.75 nm in diameter. The building blocks of the Y-zeolite structure are silica and alumina tetrahedra sharing corners. These are sodalite cages opening up into the supercages through 0.22 nm openings, and even less accessible hexagonal prisms connecting the sodalite cages as shown in fig. 1 [4]. For each aluminum ion in the framework, a charge-compensating cation must be present, normally sodium. These cations occupy various positions in the zeolitic framework. As sodium is exchanged for multivalent cations or protons (as in H-Y-zeolites) the chemical acidity of the framework increases. This ability to change the charge-compensating cation in the Y-zeolite provides the means to study the possible effect of the support on the properties of the metal clusters. It must be also noted that it is possible to achieve high loading of Pt in a Y-zeolite ($\sim 15\%$ by weight). This, together with the crystallinity of the support, greatly improved the results of the various physical probes used in our work.

The size of the Pt clusters in Y-zeolite as determined by different physical techniques by dif-

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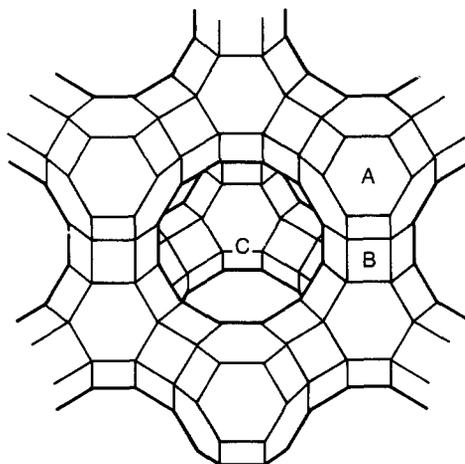


Fig. 1. The framework of the Y-zeolite. (A) Sodalite cage. (B) Hexagonal prism. (C) Supercage. Vertices represent oxygen bridges between silica and alumina tetrahedra. The silicon and aluminum atoms are located at the intersections of these vertices [4].

ferent researchers is reported in table 1. Indirect techniques such as uptake of H_2 , O_2 , or CO [3] simply tell us that essentially all the atoms in the cluster seem to be exposed. This suggests less than ~ 30 atoms per cluster. Two even more circumstantial techniques, infrared spectroscopy (IR) [3] and ^{129}Xe nuclear magnetic resonance spectroscopy (NMR) [5], assign less than 10 atoms to each Pt cluster. By the more direct techniques such as transmission electron microscopy (TEM) [6], small-angle X-ray scattering (SAXS) [7], wide-angle X-ray scattering (WAXS) [8], and extended X-ray absorption fine structure (EXAFS) [9], it is concluded that the Pt cluster size is around 1 nm. This corresponds to about 40 atoms per Pt cluster.

Table 1
Size of the Pt/Y clusters

Method	Particle size	Reference
Gas uptake	< 1 nm	Dalla Betta and Boudart [2]
O-H, O-D	6-10 atoms	Dalla Betta and Boudart [2]
^{129}Xe NMR	4-8 atoms	De Ménorval et al. [5]
TEM	0.8-1.3 nm	Gallezot et al. [6]
SAXS	0.6-1.3 nm	Gallezot et al. [7]
WAXS	1 nm	Gallezot et al. [8]
EXAFS	1 nm	Weber [9]

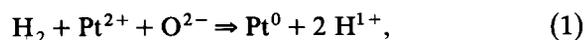
Thus there exists a discrepancy between the results of the direct and indirect techniques. As regards the structure of Pt clusters, Gallezot et al. [7] have shown by WAXS that these clusters have a face centered cubic structure with a normal lattice parameter in the presence of adsorbed hydrogen and that the Pt structure is disrupted when exposed to O_2 at room temperature (RT) but restored by treatment with H_2 at RT. Further, Gallezot and Bergeret [10] found that the Pt-Pt nearest neighbor distance is sensitive to the nature of the gas adsorbed on the clusters, and in the case of bare metal clusters the Pt-Pt distance showed a contraction of ~ 7 pm. One drawback of these interesting conclusions is that they were all reached on the basis of work on different samples in spite of the fact that cluster size is known to be quite sensitive to details in the accepted method of their preparation [2].

In the present work the atomic structure, electronic structure, and the chemical reactivity of the Pt clusters were all studied on the same samples taken from a large batch of ~ 6 g, especially prepared for the study. The techniques used included chemical probes and physical probes. The chemical probes included chemisorption and catalysis. The chosen catalytic reaction was the hydrogenation of ethylene, a structure-insensitive reaction, i.e., a reaction whose turnover rate is independent of the surface atomic structure as expressed by different crystal planes or dimensions in the range between 1 and 10 nm. The physical probes used here include TEM, ^{129}Xe NMR, EXAFS, and WAXS, providing information on the size and atomic structure of the Pt clusters. Information on the electronic structure was obtained by chemisorption and FTIR. All experimental details will be published [11-13].

2. Sample preparation

The preparation of Pt clusters in Y-zeolite followed the procedure of Dalla Betta and Boudart [2]. The Na^{1+} cations in Y-zeolite were exchanged by $\text{Pt}^{2+}(\text{NH}_3)_4$. This sample was then oxidized at 573 K in O_2 . The final reduction was done at a low temperature, 490 K, designated as L, or at a

high temperature, 673 K, designated as H. The samples will be called Pt/Y(L) and Pt/Y(H) respectively. They contain variable amounts of Pt as noted in wt% [11]. The reduction step followed the stoichiometry shown below:



The reduction of each Pt^{2+} gave rise to two acidic hydroxyl groups as shown in eq. (1).

3. Results and discussion

Hydrogen, oxygen, and carbon monoxide chemisorption was measured on 9.77% Pt/Y(L) and 10.79% Pt/Y(H) samples [11], and the results are listed in table 2. The ratio of the total number of chemisorbed H atoms and CO molecules to the total number of Pt atoms, H/Pt, was greater than unity for both samples. These ratios were substantially higher for Pt/Y(L) than for Pt/Y(H), indicating a possible change in the stoichiometry of adsorbed species on the Pt surface associated with a smaller size of the clusters reduced at the lower temperature. This assessment of relative cluster size is consistent with the results obtained by WAXS and EXAFS, as presented later.

The O/Pt ratio for Pt/Y(L) was lower than that for Pt/Y(H). This suggests that the Pt clusters reduced at the lower temperature have a greater ionization potential, probably because they are smaller than those reduced at high temperature, as already noted above. As to absolute size, in the absence of better information on adsorption stoichiometries, all that can be said is that all ratios observed are consistent with clusters of about 1 nm in size or smaller, again in accord with other results discussed below.

Table 2
Number of H or O atoms, and of CO molecules adsorbed per Pt atoms in Pt/Y

	9.77% Pt/Y(L)	10.79% Pt/Y(H)
H/Pt	2.2	1.1
O/Pt	0.43	0.60
CO/Pt	2.0	1.4

The high resolution transmission electron micrograph (TEM) shown in fig. 2 was obtained on 9.77% Pt/Y(L) [12]. The cluster size histogram obtained from the negative of this picture is shown in fig. 3. A mean diameter is defined as follows:

$$d_m = (\sum n_i d_i) / (\sum n_i), \quad (3)$$

where d_m is the mean diameter and n_i is the number of clusters with diameter d_i . The value of d_m for this distribution is 0.75 nm. The number of Pt atoms, N , per cluster with diameter, d , was estimated following Van Hardeveld and Hartog [14], and the histogram in fig. 3 was converted to one relating number of clusters to number of atoms per cluster as shown in fig. 4. The mean number of atoms per cluster can be defined as follows:

$$N_m = (\sum n_i N_i) / (\sum n_i), \quad (4)$$

where N_m is the mean number of atoms per cluster and n_i the number of clusters with N_i number of atoms per cluster. The value of N_m for this sample is 20 Pt atoms per cluster.

Another technique used to study the clusters was WAXS, from which radial electron distribution functions (REDF) were obtained (fig. 5). The WAXS data were obtained in the presence of H_2 . The positions in ppm of the major maxima in the REDF are indicated by the number next to the maxima with the number in parentheses indicating the intensity of these maxima. Since the last major maxima in the REDF appear at 736 pm, it is suggested that the size of these clusters is about 1000 pm or 1 nm, i.e., $736 + 276$, since 736 pm corresponds to center-to-center distance, and size corresponds to that distance plus twice the radius of a platinum atom. The positions of the various maxima are at distances corresponding to distances in bulk Pt, implying that the Pt clusters have the fcc structure of bulk Pt. As before [8], there is no indication of an icosahedral structure. The comparison of the REDF for the two samples shows that the various maxima lie at identical positions with the intensity of the maxima for Pt/Y(H) being higher than that of the maxima for Pt/Y(L). This indicates that the Pt clusters in Pt/Y(H) are larger than the Pt clusters in the

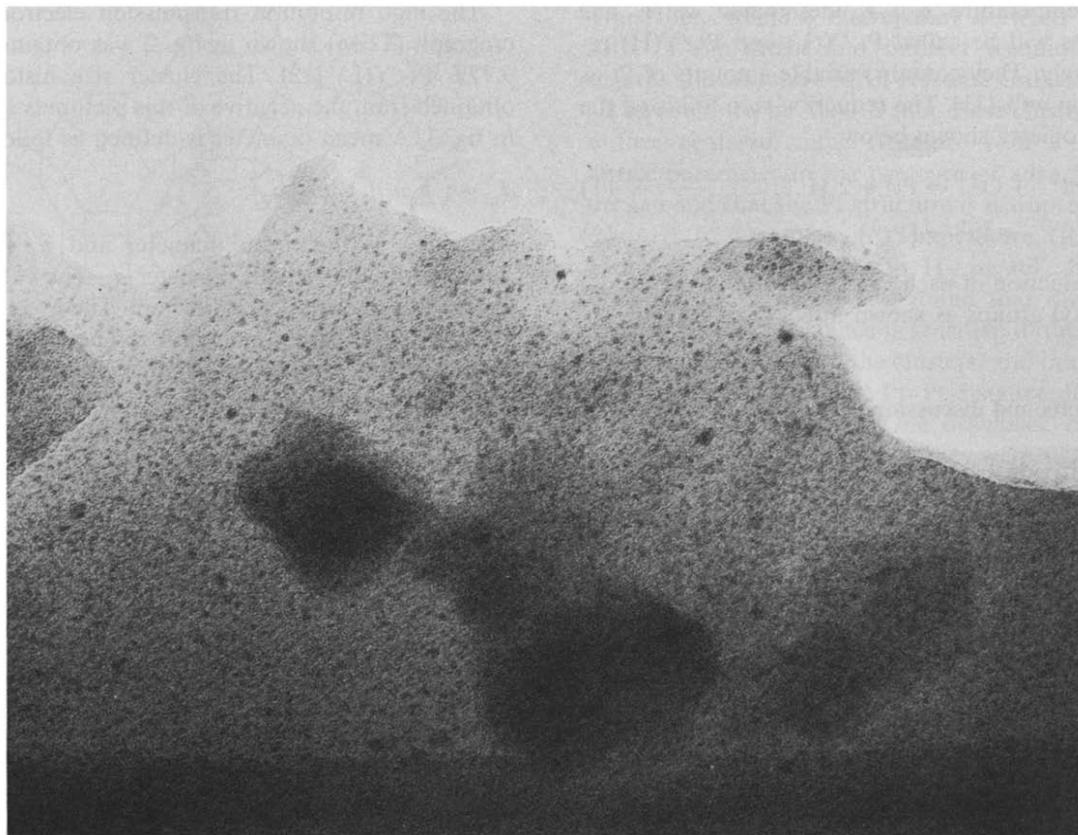


Fig. 2. High resolution transmission electron micrograph of the 9.77% Pt/Y(L) sample.

Pt/Y(L), as previously inferred from the chemisorption data.

For the same samples, EXAFS data were also collected (table 4) [12]. In the presence of H_2 , the coordination number for Pt/Y(H) was 8.8, whereas the coordination number for Pt/Y(L) was 7.0, which is in agreement with all the evidence presented earlier that the lower-temperature-reduced sample has Pt clusters with smaller size. The coordination numbers suggest that the size of the Pt clusters is ~ 1 nm. The nearest neighbor distance for the Pt–Pt pair in these samples was 276 pm in the presence of H_2 , in agreement with Pt–Pt distance of 277 pm in Pt foil. By contrast, in the absence of adsorbed hydrogen, a contraction of the lattice is clearly seen, as reported earlier [10].

The same samples were also studied with ^{129}Xe

NMR spectroscopy [11]. This method determines the number of clusters by titration of the clusters with H_2 . The chemical shift of ^{129}Xe varies linearly with the amount of adsorbed hydrogen (fig. 6). The first endpoint is indicated by the point at which the slope of the chemical shift of ^{129}Xe changes. In order to obtain from this endpoint the number of clusters present in the sample, an assumption has to be made about the distribution of hydrogen on the clusters. One such assumption is that the clusters are small enough so that Xe colliding with them “sees” the first two hydrogen atoms adsorbed on the clusters no matter where it strikes them. Then the endpoint corresponds to one H_2 per cluster in the sample [5]. This leads to the result that there are about 4 to 8 atoms per cluster, depending on the samples. The other assumption says that the Pt clusters are large so that

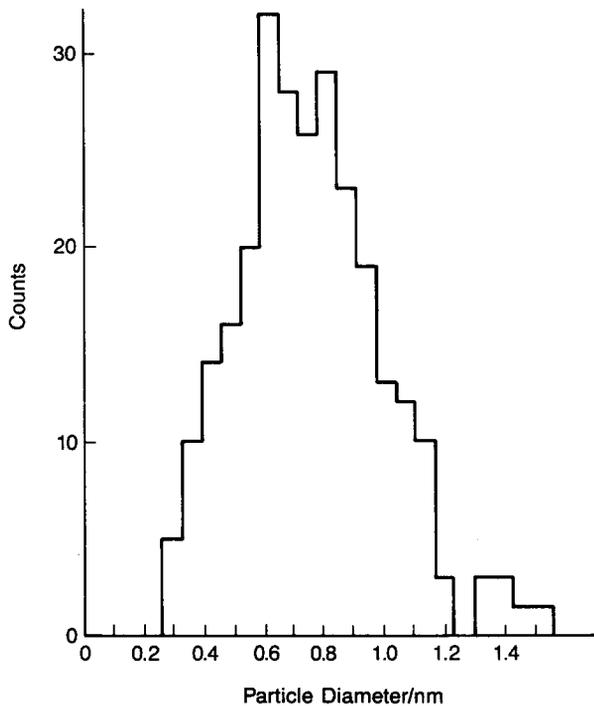


Fig. 3. Cluster size histogram for the 9.77% Pt/Y(L) sample, obtained from the micrograph shown in fig. 2.

they almost fill the supercages of Y-zeolite. Then Xe will interact only with Pt atoms exposed in each of the four windows of the supercages. If, in addition, the first two H atoms adsorbed on Pt facing a window stay at that window, the endpoint indicates the point at which there is one H₂ adsorbed per window of the supercage [12]. Accordingly, there are four times as many Pt atoms per cluster as obtained by the first assumption. The second assumption gives results which are compatible with the results obtained from other physical techniques such as TEM, WAXS, and EXAFS as listed in table 3. It should be pointed out that at this stage of development of the ¹²⁹Xe NMR technique it is not possible to choose a priori one or the other assumption. The choice rests on an independent assessment by another physical technique of the rough size of the clusters as compared to the size of the supercage. But once this knowledge is available, the Xe NMR method is capable of giving an average number of atoms per cluster. The good agreement shown in table 3 between values obtained for this quantity by TEM and Xe NMR on the basis of this second assumption is particularly interesting.

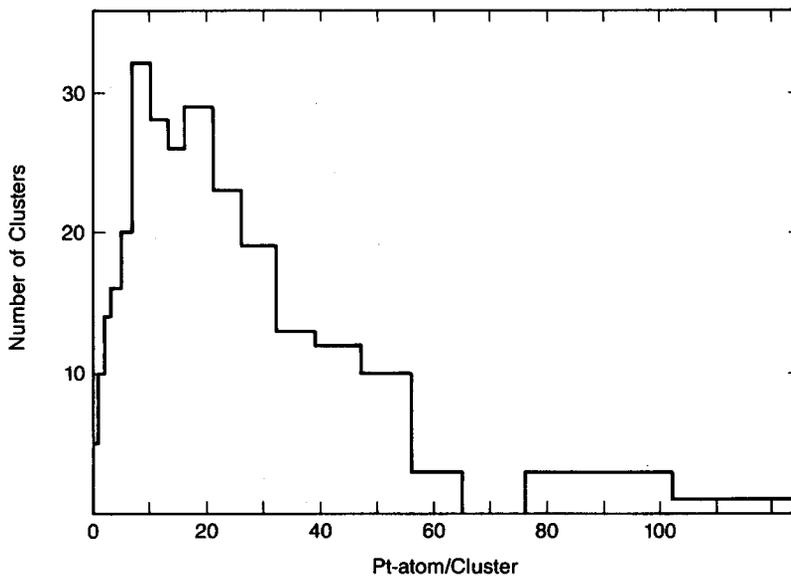


Fig. 4. The number of clusters versus number of Pt atoms per cluster from 9.77% Pt/Y(L) sample, obtained from fig. 3.

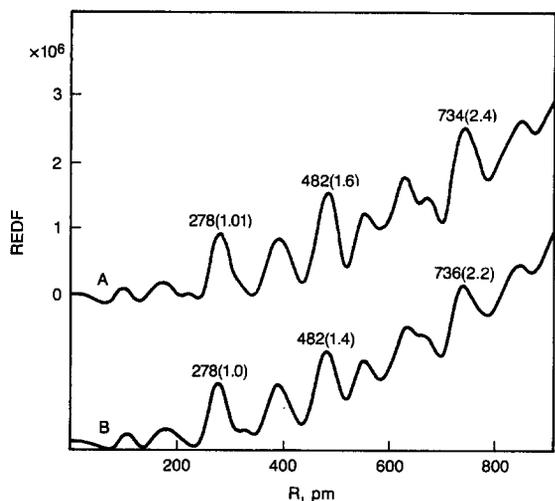


Fig. 5. The radial electron distribution function (REDF) in the units of e^2/nm . (A) Pt/Y(H) sample and (B) Pt/Y(L) sample. The ordinate axis is the radial distance r in nm.

In addition, the Xe NMR technique provides information on the distribution of the clusters inside the zeolite crystals. The ^{129}Xe NMR signal shown in fig. 7 (Pt/Y sample when no hydrogen is chemisorbed on the cluster) is a narrow line that can be fitted with a Lorentzian function. This indicates that the clusters are uniformly distributed in the Y-zeolite crystallite. Otherwise peak broadening or even the appearance of a second peak would have been observed.

The atomic and electronic structures were also probed by X-ray absorption spectroscopy (XAS) on another set of samples, and the results obtained are listed in table 4 [13]. The coordination number obtained for Pt/NaY(H), 8.4, is larger than the coordination number, 7.3, for the Pt/NaY(L) sample, and both are in reasonable agreement with the values listed for the samples in

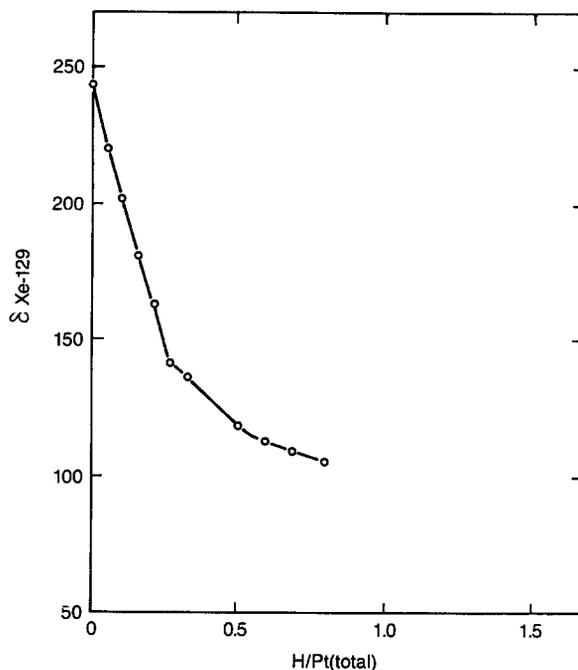


Fig. 6. Chemical shift of ^{129}Xe adsorbed in the Pt/Y(H) sample versus the number of hydrogen atoms chemisorbed per total number of Pt atoms. Chemical shift was obtained at 83 MHz at RT.

table 3. The nearest neighbor Pt–Pt distance in the presence of H_2 is identical to 276 pm, and this agrees with 277 pm for Pt foil. In the absence of H_2 , the nearest neighbor distance contracts by 8–9 pm from the bulk value, in agreement with previous results [10]. This contraction suggests that the Pt clusters are small enough so that most of the Pt atoms are on the surface. This interpretation is suggested by observations made at the surface of large single crystals of platinum [15]. In that work, the distance between the two outermost planes was found to be shorter than the distance between deeper-lying planes.

Table 3

Cluster size, average coordination number, and number of atoms per cluster for Pt/Y samples

	Atoms/cluster		Average coordination number EXAFS	Cluster size (nm)	
	TEM	Xe NMR		EXAFS	WAXS
9/77% Pt/Y(L)	20	16	7.0	0.9 (± 0.2)	1
10.79% Pt/Y(H)	–	30	8.8	1.5 (± 0.5)	1

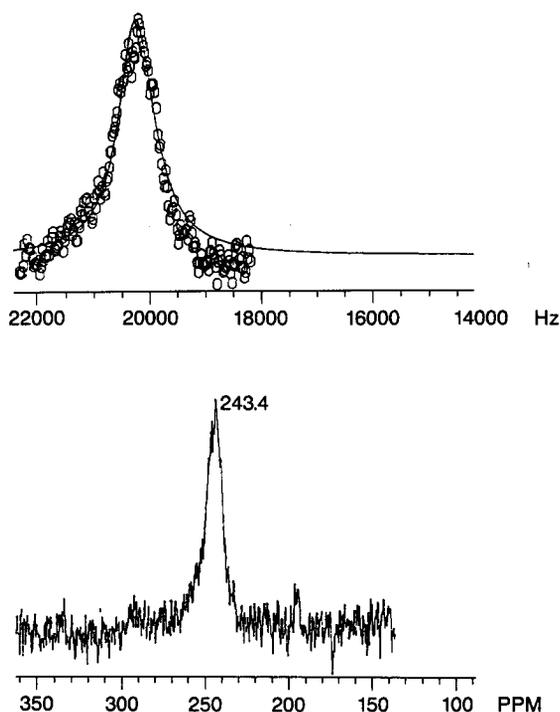


Fig. 7. ^{129}Xe NMR spectra for Pt/Y(H) sample in the absence of H_2 . (A) The experimental points are indicated by hexagons; the solid line indicates curve-fitting with Lorentzian distribution function. (B) The experimentally obtained spectrum.

The Pt L_{III} edge transition occurs at 11562 eV for a Pt foil, while both Pt/NaY samples exhibited the same value in the presence of H_2 . This supports the conclusion reached from WAXS and EXAFS that the lattice structure is that of metallic platinum in the presence of H_2 . But even in the absence of H_2 , the edge has its normal position so that the clusters must be fully reduced to the

metallic state. Hence, the lattice contraction observed for these clusters cannot be attributed to incomplete reduction of Pt atoms.

The results from FTIR are listed in table 5 [13]. With the exception of HY-zeolite, the various charge-compensating cations were ion-exchanged after the Pt clusters had already been formed. The CO stretching frequency, ν_{CO} , was obtained at room temperature, after adsorbing an amount of CO corresponding to 0.15 CO per total Pt for all samples. The value of ν_{CO} for Pt/NaY(H) sample is the same as that obtained for a similar Pt/Y sample by Primet et al. [16]. It seems that ν_{CO} is higher for smaller clusters, since Pt clusters reduced at a low temperature are smaller than those reduced at a high temperature, as concluded earlier. The value of ν_{CO} increases as the acidity of the Y-zeolite is increased for both the lower- and higher-temperature-reduced sample and could be indicative of the increase in the ionization potential of the Pt clusters as the acidity is increased.

The catalytic activity of these clusters for the hydrogenation of ethene was investigated [11]. Table 6 shows the results for the hydrogenation of ethene on Pt/Y samples with different Pt content along with the conditions used and size of the clusters. The rate listed is the turnover rate, v_t , defined as the number of ethene molecules hydrogenated per second per Pt atom exposed as measured by hydrogen chemisorption. The least active sample in this table is 0.54% Pt/Y [3] with a value of v_t close to that found on Pt/SiO₂ [17]. The most active sample is 10.79% Pt/Y (673 K) with a value of v_t close to that found on 0.59% Pt/CaY [3]. Both values are about 4 to 5 times higher than found on Pt/SiO₂. This variation in ethene hydro-

Table 4
Results from X-ray absorption spectroscopy

Sample with temperature of reduction	$N^{\text{a)}}$	In presence of hydrogen		In absence of hydrogen	
		$D^{\text{b)}}$ (pm)	$E^{\text{c)}}$ (eV)	$D^{\text{b)}}$ (pm)	$E^{\text{c)}}$ (eV)
Pt foil	12.0	—	—	277	11562.0
Pt/NaY(H)	8.4	276	11562.0	268	11561.7
Pt/NaY(L)	7.3	276	11562.3	269	11561.7

^{a)} Coordination number for the Pt/Pt pair.

^{b)} Nearest neighbor Pt-Pt distance.

^{c)} Threshold absorption energy.

Table 5
Tabulation of Fourier transform infrared spectroscopy results

Sample	CO stretching frequency (cm ⁻¹)
Pt/NaY(H)	2060
Pt/CeY(H)	2070
Pt/HY	2075
Pt/NaY(L)	2066
Pt/CeY(L)	2079

Table 6
Turnover rate v_t on Pt/NaY for $\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2 \Rightarrow \text{H}_3\text{C}-\text{CH}_3$ at 175 K with initial pressures of 20.3 and 3.1 kPa for H_2 and C_2H_4 respectively

Platinum loading (wt%)	Pt cluster size (nm)	$v_t/10^{-3}$ (s ⁻¹)
0.54	<1	0.81 ^{a)}
3.5	1	1.5
9.77	0.75	2.3
10	<1	2.5
10.79	<1	3.5 ^{b)}

^{a)} Compare with $(0.69-1.0) \times 10^{-3}$ s⁻¹ on Pt/SiO₂ (Stanford 1972).

^{b)} Compare with 3.8×10^{-3} s⁻¹ on 0.59% Pt/CaY (Stanford 1972).

generation activity can be explained on the basis of varying acidity of the Y-zeolite support [3]. As explained earlier, the acidity of the zeolite increases as the Pt content of the Y-zeolite increases. It also increases when a singly charged cation, say Na⁺, is replaced by a doubly charged cation, say Ca²⁺. Thus acidity of the support and v_t seem to go hand in hand. It is not possible at this stage to disentangle the effects on v_t of acidity or cluster size.

4. Conclusion

The most direct method to determine the average size of the metal clusters contained in the cavities of a crystalline silicoaluminat zeolite is TEM. The best method to assess the uniform spatial distribution of the clusters of the zeolite is ¹²⁹Xe NMR. Unfortunately, TEM also reveals a distribution of cluster size that should be further

narrowed in future work by improving their method of preparation. Yet, if we consider that ¹²⁹Xe NMR favors the detection of very small clusters of a few atoms, that TEM at the resolution used in this study focuses on medium size clusters of 20 atoms, and that X-ray methods are biased toward larger clusters, the agreement reported between results obtained by all of these techniques may be considered as satisfactory. The clusters investigated in this work are completely reduced to the metallic state, possess a normal fcc structure with a normal lattice parameter when covered with hydrogen but with a contracted lattice parameter if bare. Chemisorption of CO suggests an increase in their ionization potential with decreasing size and increasing acidity of the silicoaluminat. The latter, as it increases, seems also to be responsible for a modest increase in catalytic turnover rate for the test reaction chosen to probe their chemical reactivity. Further work on the nature of this metal support interaction remains to be done.

Acknowledgments

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