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Chemisorption of H_2 on supported Pt clusters probed by ^{129}Xe NMR

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The surface of Pt clusters with average size between 1 and 8 nm supported on SiO_2, γ-Al_2O_3 or Y-zeolite was probed by ^{129}Xe NMR as the Pt surface coverage with hydrogen, θ, was increased. A distinct change in the structure of the hydrogen overlayer at $\theta \approx 0.3$ was inferred from the NMR spectra. This change is believed to take place when the chemisorbed hydrogen fills all the next nearest neighbor metal sites and the nearest neighbors start to be occupied. These new observations clarify previously reported determinations of the average number of Pt atoms in supported clusters by means of Xe NMR and other techniques. It also appears that interfacial metal–support interactions may be probed by Xe NMR.

Keywords: Chemisorption of H_2 on Pt; Xe NMR; metal–support interaction

1. Introduction

The large size (0.44 nm), spherical symmetry, and large polarizability of the xenon atom make it an incisive probe of the surface of solids. Thus, nuclear magnetic resonance (NMR) of adsorbed ^{129}Xe, called Xe for short, has been used to study microporous solids [1,2], clathrate hydrates [3], as well as the distribution of adsorbed species during penetration and reaction in microporous solids [4–7] or porous solids [8–10] with and without supported metallic clusters. In particular, Xe NMR has been used to estimate the average number of Pt atoms per cluster for samples of Pt contained in a NaY zeolite (Pt/NaY) [7]. Thus, an average of four to eight Pt atoms per cluster was estimated when the

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progressive chemisorption of H_2 at room temperature (rt) in a bed of Pt/NaY powder was followed by Xe NMR. These results agree with an average value of six Pt atoms per cluster which has been inferred earlier from the rapid exchange with D_2 of OH groups in a Pt/CaY zeolite as followed by infrared spectroscopy [11].

The determination in these two studies of the number of Pt atoms per cluster attracted attention as it was the first time that the number of atoms in a supported metallic cluster less than ≈ 1 nm in size had been reported [12]. However, the study of similar or identical samples of Pt/Y zeolites by transmission electron microscopy (TEM) [13], small angle X-ray scattering (SAXS) [14], wide angle X-ray scattering (WAXS) [15], and extended X-ray absorption fine structure (EXAFS) [16], indicates Pt clusters of about 1 nm in size in the supercages of the Y-zeolite (1.3 nm in diameter), with about 16–40 Pt atoms per cluster [17]. In particular, a combined investigation of Pt/Y samples by TEM, SAXS, WAXS, and EXAFS suggested that the Pt clusters were substantially larger than those probed by IR and Xe NMR. The results of the present study suggest a way to reconcile both types of observations.

First, let us review the previous work on the probing of Pt clusters by Xe NMR. The chemical shift, δ, of Xe adsorbed on a Pt/NaY-zeolite is an average over all sites visited by Xe during the characteristic time of the NMR experiment [2]. Xenon gas adsorbed on a Pt/NaY sample with bare Pt clusters at rt generally gives a single Lorentzian Xe NMR peak as a result of rapid averaging over many adjacent Y-zeolite crystallites of 1 μm size [18]. As H_2 is introduced at rt to a bed of Pt/NaY zeolite grains, a second peak is observed in the Xe NMR spectrum and its intensity increases at the expense of the first peak as more H_2 is dosed (ref. [7]). However, the two peaks can be explained by the progressive penetration of H_2 into the bed layer by layer [9]. By contrast, when the temperature of the closed cell is raised to 450 K between successive doses of H_2 at rt, H is uniformly distributed on the Pt surface in the pores of the Y-zeolite all over the bed, and only one Xe NMR peak is observed [18,19]. We will refer to this situation as that of uniform chemisorption. In addition, δ shifts linearly with increasing surface coverage, θ, of Pt by H, with an abrupt change in the slope of the δ versus θ line at a value of θ that will be called an endpoint [19]. In principle, from the endpoint, the average number of Pt atoms per cluster in the sample can be determined. To do that, the number of H atoms chemisorbed per cluster at the endpoint must be assumed. One assumption is that the endpoint corresponds to one H_2 or two H atoms per cluster. This assumption gives four to eight Pt atoms per cluster [7]. Another interpretation is that the Pt clusters are large enough to fill the supercages of the Y-zeolite, with Xe interacting only with the Pt atoms exposed through the four windows of the supercages. Then, at the endpoint, there are two H atoms chemisorbed per window, or eight per cluster, resulting in 16–32 Pt atoms per cluster, as concluded from the use of other techniques [19].

The present work extends the Xe NMR technique to probe Pt clusters larger than 1 nm in size, supported on non-zeolitic materials, as the size of such clusters can be determined without any ambiguity. Besides, with the larger pore size of non-microporous oxides, as opposed to that in zeolites, Xe is able to interact more freely with supported Pt clusters. The results obtained with non-zeolitic supports resemble closely those reported previously in the case of zeolites. They reveal overlayers of hydrogen as they grow by Xe NMR with details that have not been obtained thus far by other techniques.

2. Experimental

The samples used in this work consisted of Pt supported on SiO_2, γ-Al_2O_3, or Y-zeolite. A batch of powdered 5.95 wt% Pt/SiO_2 was prepared by incipient wetness impregnation of an acid-washed [20] silica gel (Davison, grade 62, code number 62-08-08-226) with an aqueous solution of H_2PtCl_6. The sample was dried in air at 380 K for 10 h. One portion of the sample was exposed to flowing H_2 (Matheson, Hydrogen Generator, model 8325) at atmospheric pressure with a contact frequency (number of molecules per Pt atom per second) of $\approx 1.3\ s^{-1}$ as the temperature was raised from rt to 465 K at a rate of 0.033 K s^{-1}, to 515 K at 0.017 K s^{-1}, to 560 K at 0.012 K s^{-1}, and maintained at 560 K for 2 h. This portion of the sample was then reduced in flowing H_2 from rt to 670 K at a rate of 0.127 K s^{-1} and maintained at 670 K for 2 h. The resulting powder is called sample I. The remaining portion of the sample was reduced in flowing H_2 at 670 K for 2 h; it is called sample II. Before transferring the samples to the NMR cell [21], the powders were pressed at about 85 MPa for 0.5 h and subsequently cut into pellets 10 mm wide, 10 mm long and 5 mm thick.

The percent metal exposed, D, for each sample, was measured by titration of pre-chemisorbed O by H_2 [22], by irreversible H chemisorption, and by irreversible O chemisorption at rt in a standard volumetric system equipped with a differential pressure gauge (Texas Instrument, model 145-01). Prior to chemisorption, the samples were reduced for 1 h and evacuated for 2 h at 570 K. The results are shown in table 1. The average size, d, for the Pt clusters was

Table 1
Percent Pt exposed, D, as measured by titration of pre-chemisorbed oxygen or hydrogen chemisorption and estimated cluster size, d

Sample	Support	D (%)	d (nm)
I	SiO_2	36	3.1
II	SiO_2	14	8.1
III	γ-Al_2O_3	62	1.6
IV	NaY	100	1.5 [a]

[a] Estimated by TEM, WAXS and EXAFS [19].

obtained from the percent metal exposed, assuming a spherical shape and an average Pt surface number density of 1.10×10^{19} m^{-2} [14]. Nitrogen (Matheson, 99.998%) adsorption isotherms of SiO_2 and (sample I) were measured at 78 K up to atmospheric pressure.

The preparation and characterization of Pt/γ-Al_2O_3 (sample III) and Pt/NaY-zeolite (sample IV) have been described elsewhere [19,23]. Prior to the NMR experiment, samples I, II, and III were reduced at 570 K for 1 h and evacuated at 670 K for 2 h, while sample IV was reduced and evacuated at 670 K for 1 h.

All NMR spectra were taken at rt under xenon (Matheson, 99.995%) at atmospheric pressure for samples I, II, and III, and at 26 kPa for sample IV, respectively. Successive doses of H_2 that were adequate to cover $\approx$ 10–25% of the exposed Pt surface were introduced into the evacuated cell at rt followed by heating of the closed cell at 450 K for 0.25 h to redistribute the chemisorbed H on the Pt surface throughout the sample, so as to achieve uniform chemisorption [9]. The closed cell was cooled to rt, and Xe was then introduced to the sample from a storage bulb containing MnO/SiO_2 to remove traces of O_2.

Two NMR instruments were used: a Nicolet NMC-300 operating at 83.0 MHz for ^{129}Xe and a Varian VXR-400S at 110.7 MHz. Neither sample spinning nor field locking was employed. For each spectrum, the pulse width was between 22 and 29 μs, the delay time between 0.1 and 2.5 s and the number of transients between 5000 and 20000. The chemical shift was referenced to the Xe gas extrapolated to zero pressure by the equation of Jameson et al. [24] by using a secondary reference sample, xenon in KY zeolite with $\delta = 95.1$ ppm received from the Fraissard group.

3. Results

The microporosity of SiO_2 and sample I was obtained from the shape of the N_2 adsorption isotherm by the *n*-method [25]. The micropores contribute less than 5% of the BET surface area, with the majority of the pores in both samples in the range of mesopores. The average pore size [26], the maximum in the pore size distribution [27], the range of pore diameter, and the BET surface area are given in table 2. A similar analysis was done for sample III [8], and led to similar results: the texture of that sample also exhibits negligible microporosity.

The Xe NMR spectra were taken at various values of nominal surface coverage, H/Pt_s, corresponding to repeated doses of H_2 gas for samples I, II, and III. The nominal surface coverage is defined as the total number of H atoms dosed in per surface Pt atom, Pt_s, as obtained from the percent metal exposed. The Xe NMR spectra of Pt/NaY were taken at increasing values of H/Pt_t, the ratio of the number of hydrogen atoms to the total number of Pt atoms in the sample. All spectra show two peaks: one with $\delta \approx 0.5$ ppm, assigned to Xe in the

Table 2
BET surface area and pore size for SiO_2 and sample I [a]

Sample	S_{BET} (m^2 g^{-1})	d_a (nm)	d (nm)	Range of pore diameter (nm)
SiO_2	233	4.6	5.4	2–10
sample I	249	5.4	6.0	2–14

[a] d_a: average pore diameter ($d_a - 4\,V/S_{BET}$, where V is the N_2 volume adsorbed at $P/P_0 = 0.95$). d^*: pore diameter at maxima in the plot of pore volume versus pore radius.

gas phase [8], and another *single peak* with δ between 85 and 285 ppm, corresponding to the average interaction of adsorbed Xe with the Pt surface and the support [9].

When H is uniformly chemisorbed on Pt/SiO_2 samples, δ of Xe decreases linearly with H/Pt_s (fig. 1, I and II), with a distinct change in slope at $H/Pt_s \approx 0.3$ on both samples. Most of the drop in δ ($\approx$ 60–80%) occurs for $0 < H/Pt_s < 0.3$, while at full coverage ($H/Pt_s = 1.1$), δ is near the value of δ for SiO_2.

The change in δ with H/Pt_s for sample III (fig. 1, III) is similar to that observed for samples I and II. Thus, the change in slope of the linear decrease also occurs at $H/Pt_s \approx 0.3$, with a decrease in δ of about 60% of the total variation of $0 < H/Pt_s < 0.3$. The variation in δ with H/Pt_t for sample IV (Pt clusters of 1.5 nm in size) [19] is also linear, the change in slope occurring at ≈ 0.3 H/Pt_t (fig. 1, IV). However, the extrapolated value of δ to zero H/Pt_s for the region $0 < H/Pt_s < 0.3$ does not coincide with δ obtained for bare sample III, whereas it does for samples I, II, and IV. This observation has been reported briefly [28] and will be discussed in more detail following the discussion of our main data.

4. Discussion

Our main observation is the break in the straight line of Xe chemical shift versus hydrogen coverage when the latter is approximately equal to 0.3. This is so for samples I, II, and III, for which hydrogen coverage is expressed as the number of H atoms chemisorbed per number of surface Pt atoms, Pt_s (fig. 1, I–III). It is also the case for sample IV where hydrogen coverage is expressed as the number of H atoms per total number of Pt atoms, Pt_t (fig. 1, IV). Thus we observe the same phenomenon on three different supports and for Pt clusters between $\approx$ 1 and 8 nm in size.

In attempting to explain this apparently simple phenomenon observed on structurally undefined metal surfaces, we decided to look for general features of hydrogen chemisorption on large single crystals of metals [29]: quite generally, it

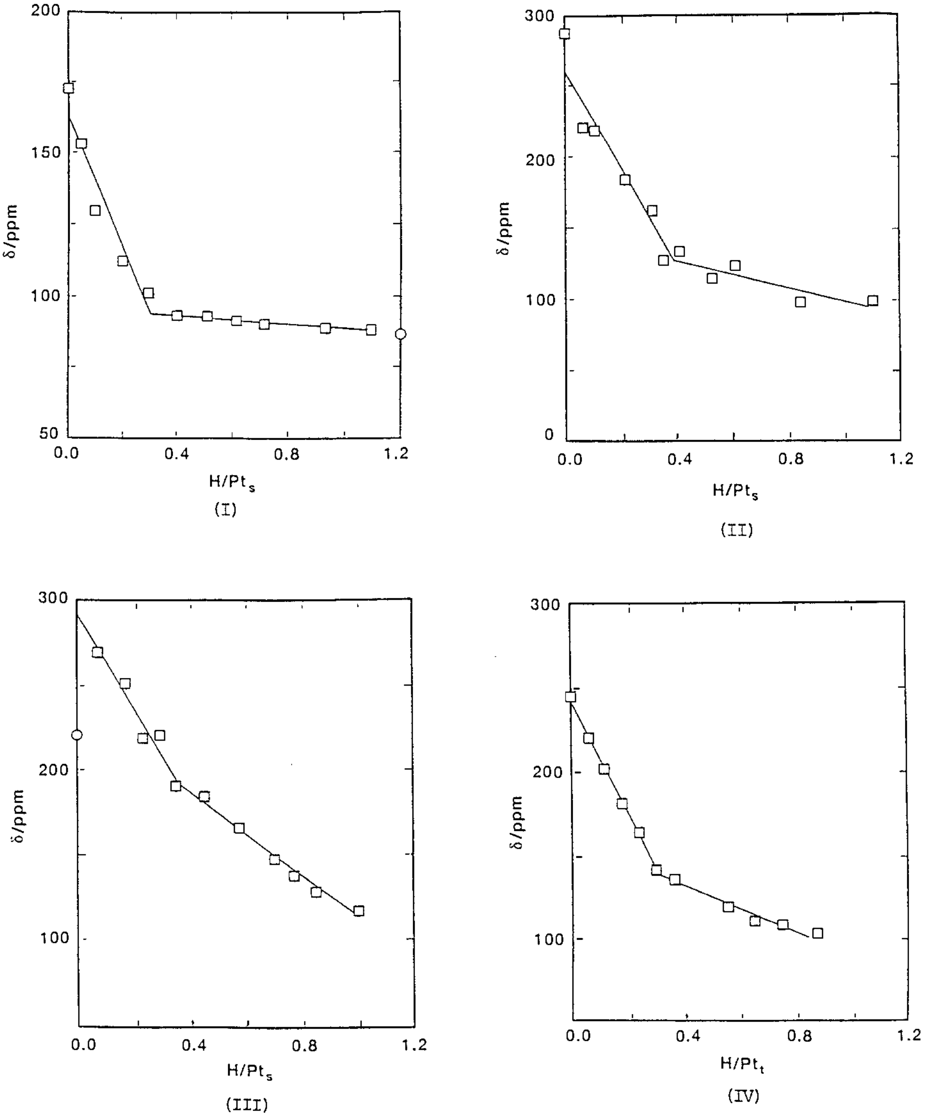

Fig. 1. Change of chemical shift δ of Xe NMR with surface coverage: H/Pt_s or H/Pt_t where Pt_s is the number of surface Pt atoms and Pt_t is the total number of Pt atoms in the sample. The average size of Pt clusters is d. (I) Pt/SiO_2, $d = 8.1$ nm; point O is for SiO_2 without Pt. (II) Pt/SiO_2, $d = 3.1$ nm. (III) $Pt/\gamma\text{-}Al_2O_3$, d – 1.6 nm; point O for Pt without H. (IV) Pt/Y-zeolite $d = 1.5$ nm.

is found that H atoms attract each other at low coverage to form ordered overlayers with H atoms occupying next nearest neighbor hollow sites, while they repel each other when occupying nearest neighbor sites at high coverage [30]. The transition from low to high coverage in the above sense occurs at 1/4, 1/3, or 1/2 of a monolayer [31]. On this basis, we speculate that when Xe NMR probes structurally undefined surfaces as H coverage increases, it senses the transition occurring when next nearest neighbor occupancy is followed by nearest neighbor occupancy. In the absence of any information on surface morphology, the simplest assumption is that this transition occurs at a H coverage averaging $1/3\ (1/4 + 1/3 + 1/2) \approx 0.3$. This transition is reflected by the end points shown in fig. 1, I–IV.

In all of our work, hydrogen was uniformly distributed on the metal surface. The surface Xe NMR spectra exhibited a single peak. Thus at room temperature, adsorbed xenon was mobile on the surface of the metal and of the support. The value of δ is an average of its value on four different surface environments available to the xenon atoms: support; free metal surface; metal surface increasingly covered with H occupying next nearest neighbor metal sites; and finally, beyond the transition at 0.3 H/Pt_s or H/Pt_t, metal surface increasingly covered with H atoms filling the nearest neighbor sites.

A related study provides additional information pertaining to the above speculation [32,33]. This study deals with photo-electron spectroscopy of xenon adsorbed on the reconstructed Pt(110)(1 × 2) surface. This surface has a missing row and consists of parallel valleys and ridges separated by (111) microfacets. Several peaks of the $5p_{1/2}$ level of adsorbed Xe could be assigned to Xe adsorbed in the valleys, on the ridges, and on the microfacets. When hydrogen was admitted at 97 K to this Pt surface covered with adsorbed Xe, changes in the spectra of Xe could be interpreted to show that hydrogen displaces Xe and is first chemisorbed in the valley sites (next nearest neighbor sites), and then only after saturation of the latter, on the facet and ridge nearest neighbor sites.

Yet there is an important difference between photo-electron spectroscopy at 97 K and NMR at rt of adsorbed xenon, because for the first technique xenon samples local environments, whereas for the latter technique xenon samples environments averaged over the surface visited by Xe. The difference is similar to that between differential and integral heats of adsorption.

In Xe NMR, provided that Xe is mobile enough, only one peak is observed, as was the case in all of our work. Thus, as hydrogen is added to the undefined Pt surface, Xe probes different types of sites on the free Pt surface that is filling up with hydrogen in next nearest neighbor positions. Different platinum sites would probably give different values of δ but the measured value of δ is an average over all available types of sites. Thus δ decreases linearly with coverage until the transition takes place and new types of sites, the nearest neighbor sites, are occupied by hydrogen. Then the δ–H coverage line changes slope, as observed.

5. Interaction between Pt and γ-Al_2O_3

In this section, we discuss a puzzling observation that has been repeated many times in our laboratory by two investigators working independently. This observation is the discrepancy between the value of the chemical shift δ measured on pre-reduced Pt samples without any hydrogen. With all details of the reduction and evacuation procedure being the same (this paper and refs. [9,19]), straight lines for δ versus H coverage extrapolate to the value measured for zero H coverage for samples I, II, and IV. But this is not so for sample III. For sample III, the value of δ on the sample without H is considerably lower than that extrapolated to zero coverage from the δ versus H coverage line. Particularly striking is the fact that for as little as 10% coverage by H, the measured value of δ is exactly on the δ versus H coverage line.

This anomaly is difficult to explain. The first explanation that comes to mind is the contraction of the lattice parameter of Pt clusters without any adsorbed gas as opposed to the normal bulk Pt lattice parameter observed following H adsorption on the same clusters. This phenomenon has been reported in particular for Pt/Y-zeolite samples [19,34]. But this explanation cannot explain the anomaly reported here since the anomaly is found for Pt/γ-Al_2O_3 but not for a Pt/Y-zeolite with clusters of a size similar to those in a Pt/Y-zeolite sample for which the contracted lattice was reported [35].

The only tentative explanation that we retain as of now is based on the following rather meager facts. In a study of Pt clusters supported on silica or γ-Al_2O_3, Adams et al. comment on TEM pictures [36]. They note that "much of the platinum has been dislodged from the silica support by the ultrasonic treatment" used for the preparation of the TEM specimen. They further note that "a similar treatment of platinum supported on alumina does not dislodge the particles of platinum." A reason for the difference in sticking of Pt clusters on SiO_2 and γ-Al_2O_3 may be found in the different morphology of the two supports as revealed by high resolution TEM [37]. The silica particles show no or little evidence of structure, while the γ-Al_2O_3 particles are sheets normal to a [111] direction. Thus Pt clusters seem to be more strongly held on the platelets of γ-Al_2O_3 than on the poorly structured SiO_2. As to the interaction between Pt clusters and the framework of the supercage of a NaY zeolite, with its four windows, it also appears to be relatively weak, as judged by the equality of turnover rate for the hydrogenation of ethene on a Pt/NaY sample and on a Pt/SiO_2 catalyst under identical conditions [19].

The anomaly reported here can then be rationalized by the following speculation. In vacuo, the shape of Pt clusters on SiO_2 or in Y-zeolite is approximately spherical, and the interface between metal and support is minimal. But with a γ-Al_2O_3 support, clusters of platinum about 1 or 2 nm in size probably have the shape of a pillbox or raft in vacuo as a result of the high interfacial energy. Indeed, high resolution TEM reveals epitaxial growth of 2 nm clusters of Pd on γ-Al_2O_3 [34] and it must be noted that the lattice parameters of Pt and Pd are very close to each other so that both metals should behave similarly on γ-Al_2O_3. In the raft-like shape, xenon interacts with the free Pt surface but senses the surface of the cluster in contact with the Al_2O_3 platelets. At this contact, there are *weak* bonds between Pt and oxygen ions of the Al_2O_3. Hence the chemical shift of Xe is smaller than that corresponding to bare Pt just as δ of Xe decreases as oxygen is added to bare Pt clusters [9]. When hydrogen is introduced to the sample, the *weak* bonding between the metal and the support disappears as a result of chemisorption of hydrogen.

The speculative nature of these considerations needs to be stressed. Yet they suggest further studies. In any event, as first shown by Fraissard and co-workers [2,7,8], Xe NMR appears again as an unusually incisive physical probe of subtle effects such as metal–support interactions that are difficult to detect by other techniques.

Reviewing results from X-ray absorption spectroscopy bearing on the nature of the metal–support interface in supported metal catalysts, Koningsberger and Gates [38] conclude that EXAFS spectroscopy, temperature programmed reduction and desorption, and infrared spectroscopy together with chemisorption and catalytic testing would be helpful in clarifying the situation. In this Letter, the Xe NMR also appears as a promising simple technique to continue the search.

6. Conclusion

Our data lead us to reexamine the use of Xe NMR to determine the number of Pt atoms per cluster, when the cluster size is of the order of 1 nm. Because of the similarity in the four figures of fig. 1, we conclude that with Pt clusters in NaY with size of – 1 nm, *i.e. with essentially all Pt atoms exposed*, the break in the δ–H/Pt_t plot occurs when $\approx 1/3$ of the atoms in the cluster have chemisorbed hydrogen on their surface. Of course the value of the ratio H/Pt_t must be even. But on the whole, by analogy with the Pt/SiO_2 and Pt/Al_2O_3 samples, the break in the δ–H/Pt_t curve may occur *not* when 2 H atoms are adsorbed per cluster [7] but when about 0.3 H atoms per total number of atoms in the cluster are adsorbed, if almost all atoms in the cluster are surface atoms. Clearly, Xe NMR does not provide information on the average number of Pt atoms per cluster.

Yet, the difficulty discussed in the introduction disappears. When a Pt cluster exposes all of its atoms, Xe NMR does not yield values, say, of 6 Pt atoms per cluster but about three times as much, say, 18. All results from Xe NMR, TEM, EXAFS, and WAXS are now self-consistent [19]. The contradictory interpretation from IR spectroscopy [11] must now be considered as suspect, probably because it was based on a kinetic argument. This argument relied on the amount of OH groups in the zeolite framework that could exchange *rapidly* with deuterium spilling over from neighboring Pt clusters. While the average number of atoms in the clusters was about the same as inferred from IR [11] and Xe NMR measurements [7], our new interpretation of the latter casts serious doubt on the interpretation of the IR data.

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References

[1] T. Ito and J.P. Fraissard, in: *Proc. 5th Int. Conf. Zeolite*, Naples, June 1980, ed. L.V.C. Rees (Heyden, London, 1980) p. 510.
[2] J.P. Fraissard and T. Ito, Zeolites 8 (1988) 350.
[3] J.A. Ripmeester, C.I. Ratcliff and J.S. Tse, J. Chem. Soc. Faraday Trans. I 84 (1988) 3741.
[4] L.-C. de Ménorval, D. Raftery, S.-B. Liu, K. Takegoshi, R. Ryoo and A. Pines, J. Phys. Chem. 94 (1990) 27.
[5] E.W. Scharpf, R.W. Crecely, B.C. Gates and C. Dybowski, J. Phys. Chem. 90 (1986) 9.
[6] A. Gedeon, J.L. Bonardet, T. Ito and J.P. Fraissard, J. Phys. Chem. 93 (1989) 2563.
[7] L.-C. de Ménorval, T. Ito and J. Fraissard, J. Chem. Soc. Faraday Trans. I 78 (1982) 403.
[8] M. Boudart, L.-C. de Ménorval, J.P. Fraissard and G.P. Valença, J. Phys. Chem. 92 (1988) 4033.
[9] M. Boudart and G.P. Valença, J. Catal. 128 (1991) 447.
[10] D.J. Suh, T.-J. Park, S.-K. Ihm and R. Ryoo, J. Phys. Chem. 95 (1991) 3767.
[11] R.A. Dalla Betta and M. Boudart, in: *Proc. 5th Int. Cong. on Catalysis*, Vol. 2, ed. J.W. Hightower (North-Holland, Amsterdam, 1973) p. 1329.
[12] M. Boudart and G. Djéga-Mariadassou, *Kinetics of Heterogeneous Catalytic Reactions* (Princeton Univ. Press, Princeton, 1984).
[13] P. Gallezot, I. Mutin, G. Dalmai-Imelik, A.J. Renouprez and B. Imelik, J. Microsc. Spectrosc. Electron 1 (1976) 1.
[14] P. Gallezot, A. Alarcon-Diaz, J.A. Dalmon, A.J. Renouprez and B. Imelik, J. Catal. 39 (1975) 334.
[15] P. Gallezot, A.I. Bienenstock and M. Boudart, Nouv. J. Chim. 2 (1978) 263.
[16] R.S. Weber, PhD Dissertation, Stanford University, USA (1985).
[17] R. van Hardeveld and G. Hartog, Surf. Sci. 15 (1969) 189.
[18] R. Ryoo, C. Pak and B. Chmelka, Zeolites 10 (1990) 790.
[19] M. Boudart, M.G. Samant and R. Ryoo, Ultramicroscopy 20 (1986) 125.
[20] S. Ladas, R.A. Dalla Betta and M. Boudart, J. Catal. 53 (1978) 356.
[21] R. Ryoo, PhD Dissertation, Stanford University, USA (1986).
[22] J.E. Benson and M. Boudart, J. Catal. 4 (1965) 704.
[23] F.J. Rivera-Latas, R.A. Dalla Betta and M. Boudart, AIChE J. 38 (1992) 771.
[24] A.K. Jameson, C.J. Jameson and H.S. Gutowski, J. Chem. Phys. 53 (1970) 2310.
[25] A.J. Lecloux, in: *Catalysis: Science and Technology*, Vol. 2, eds. J.R. Anderson and M. Boudart (Springer, Berlin, 1981) ch. 4.
[26] S.J. Gregg and K.S.W. Sing, in: *Adsorption, Surface Area and Porosity* (Academic Press, London, 1967) ch. 3.
[27] D. Dollimore and G.R. Heal, J. Colloid Interf. Sci. 33 (1970) 508.
[28] R. Van Grieken, G. Valença and M. Boudart, in: *Proc. XIII Ibero-American Symp. on Catalysis*, Segovia, July 1992.

[29] G.A. Somorjai, in: *Chemistry in Two Dimensions* (Cornell University Press, Ithaca, 1982).
[30] T.L. Einstein and J.R. Schrieffer, Phys. Rev. B7 (1973) 3269.
[31] C.M. Chan, M.A. Van Hove and W.H. Weinberg, in: *Low Energy Electron Diffraction: Experiment, Theory and Surface Structure Determination* (Springer, Berlin, 1986).
[32] R. Ducros, J.J. Ehrhardt, J. Fusy and B. Mutaftschiev, Phys. Rev. B38 (1988) 10035.
[33] R. Ducros and J. Fusy, Surf. Sci. 207 (1988) 943.
[34] H. Dexpert, E. Freund, E. Lesage and J.P. Lynch, Stud. Surf. Sci. Catal. 11 (1982) 53.
[35] M. Boudart and M.G. Samant, J. Phys. Chem. 95 (1991) 4070.
[36] C.R. Adams, H.A. Benesi, R.M. Curtis and R.G. Meisenheimer, J. Catal. 1 (1962) 336.
[37] J.V. Sanders, in: *Catalysis: Science and Technology*, Vol. 7, eds. J.R. Anderson and M. Boudart (Springer, Berlin, 1985) pp. 134, 135.
[38] D.C. Koningsberger and B.C. Gates, Catal. Lett. 14 (1992) 271.