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Changes in Dispersion of Platinum Deposited on LaY and CeY during Heating at High Temperatures in Oxygen, Hydrogen, Carbon Dioxide, and Water Vapour

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Sintering of platinum deposited on CeY and LaY zeolite has been studied during heating at high temperatures in different gases. Small angle X-ray scattering and X-ray diffraction studies have led to the conclusion that the nature of the gas atmosphere in which the Pt^o/CeY and Pt^o/LaY are heated is the most important factor influencing the sintering of the platinum. The sintering of Pt^o in Pt^o/CeY and Pt^o/LaY samples occurs most intensively in oxygen, is slower in carbon dioxide, and very slow in hydrogen and water vapour. There are small differences between the sintering of the platinum on CeY and LaY zeolite. For all gases except oxygen, the sintering of Pt^o is greater on LaY than on CeY. In oxygen, sintering of Pt^o is visibly greater on CeY zeolite; this is probably related with the oxidation of the Ce^{3-} ions which takes place during heating in oxygen. The usefulness of the SAXS method for the investigation of the size distribution function of metal supported on zeolite has been demonstrated.

INTRODUCTION

A detailed characterization of metals supported on zeolites is needed to interpret the catalytic properties of these materials which are involved in many catalytic processes of present and potential interest.

A very important property of all supported metal catalysts is the dispersion of the metal and also its stability while heating at high temperature in different gas atmospheres. The sintering of Pt^o supported on many different carriers has been examined in detail, but only a few papers were dedicated to the sintering of the Pt^o/zeolite system (*1–4*). However, there are many papers which describe the influence of pretreatment and reduction conditions on the dispersion of Pt^o in Pt^o/zeolite systems (*5–15*). It is known from these papers that it is possible to obtain Pt^o/zeolite samples in which the sizes of platinum particles are in the range of 0.7–1.2 nm and it was also noted (*11, 16, 17*) that cerium ions favour the formation of smaller and more homogeneous particles of metal.

It is of interest to investigate whether there is an influence of cerium ions on the sintering of Pt^o. The purpose of the present paper is to describe the sintering of Pt^o supported on CeY and LaY when the systems are heated in different gases. The platinum dispersion has been studied by small angle X-ray scattering (SAXS) and X-ray diffraction methods. The SAXS method allows one to measure the size of very small clusters and crystallites and also provides the possibility to obtain a distribution of crystallite sizes. For these reasons the SAXS method is well suited for the investigation of the sintering process of metal/zeolite systems.

EXPERIMENTAL

Materials

The starting material for preparation of CeY and LaY was pure crystalline NaY zeolite (produced in Poland) in which the ratio SiO_2/Al_2O_3 was 5.4. CeY and LaY were made by conventional ion-exchange using $Ce(NO_3)_3$ and $La(NO_3)_3$ (analytical reagent grade). The following two zeolites were ob-

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tained: $Ce_{12}Na_{16}Al_{52}Si_{140}O_{384}$ and $La_{12}Na_{16}Al_{52}Si_{140}O_{384}$. Platinum was introduced into the CeY and LaY by ion-exchange from a solution containing $Pt(NH_3)_4^{2+}$ complex ions. $Pt(NH_3)_4Cl_2$ of high purity was prepared from H_2PtCl_6 acid according to the procedure described in Ref. (*18*). The amount of platinum introduced both to CeY and LaY was about 4.1 wt.%.

Procedure of Pt^{2+} Reduction

Zeolite samples were heated at a very low heating rate (1°C/min) up to 300°C, in the presence of a very rapid continuous flow of oxygen through the sample. After achieving this temperature, platinum was reduced by hydrogen for 2 h and the samples were then cooled to room temperature in nitrogen atmosphere.

Procedure of Pt^o Sintering

Both Pt^o/CeY and Pt^o/LaY samples were heated from room temperature to a chosen temperature at a heating rate of about 10°C/min; they were then held at this temperature for 5 h, all the time in the presence of a flow of pure gas through the sample. After this time samples were cooled to room temperature in a flow of the same gas. Pt^o/CeY and Pt^o/LaY samples were heated at temperatures of 500, 600, 700 and 800°C. In this paper the nomenclature "zeolite type/sintering temperature/gas" is used. For example, for sample Pt^o/LaY sintered in hydrogen at 500°C the designation is PtLaY/500/H_2.

Experimental Methods

(*a*) *SAXS measurements*. Measurements were performed on a slit-collimated Kratky camera using a Cu anode tube as the radiation source. A scintillation counter with a nickel filter and a pulse-height analyser were used to measure the scattered intensity. The scattering curves of Pt^o/CeY and Pt^o/LaY samples were measured as well as the scattering curves of the CeY and LaY carriers (CeY and LaY zeolites were heated in the same way as Pt^o/CeY and Pt^o/LaY samples). Next, after properly smoothing the scattering curves, subtracting the value of the scattering curve of the carrier from that of the scattering curve of the sample and another smoothing of the curve, the chord distribution function was calculated from the Mering–Tchoubar formula for a beam of infinite length and then the function of crystallite size distribution was calculated (*15, 19–21*).

For almost all of the investigated samples the crystallite distribution function was discontinuous, i.e. $f_v(D)$ has two or more maxima and between these maxima the values of $f_v(D)$ should be equal to zero. In practice, this is very difficult to obtain; usually the $f_v(D)$ curve shows many oscillations around the zero line. To minimize these oscillations, very precise measurements of the scattering curves are required and proper calculating procedures, especially smoothing procedure should be used. For these reasons the scattering curves for a given sample as well as the blank scattering from the carrier were measured several times and also many calculations with different parameters for smoothing were used. In the final $f_v(D)$ function the oscillations around the zero line were no larger than ±3% of the value of the highest maximum of $f_v(D)$ for a given sample. This criterion was assumed because $f_v(D)$ was then sufficiently oscillation-free.

Samples for SAXS measurements were prepared by sedimentation in a benzene–paraffin oil solution (*22, 23*). Small regular pores of the zeolite yield very weak scattering, mainly in the diffraction part of the spectrum, but use of this procedure of sample preparation for SAXS experiments additionally reduced scattering from the pores and also allowed samples to be obtained with the optimum thickness.

(*b*) *X-ray diffraction measurements*. Diffraction measurements were performed using a DRON-3 (USSR) X-ray apparatus with a Cu tube and Ni filter. All investigated samples contained silicon powder as an internal standard. A more precise recording was made in the region of the Pt^o lines by mea-

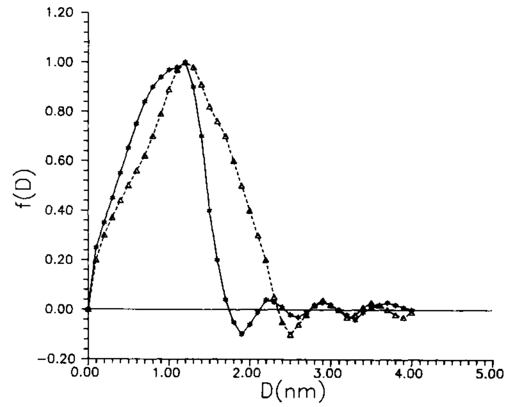

FIG. 1. Size distribution function of Pt° particles obtained by SAXS for initial samples: (*) Pt°/CeY; (△) Pt°/LaY.

suring the number of impulses within a given angle over 40 seconds. The measurements were taken every 0.02°. The intensities of diffraction peaks were estimated by means of a computer program which had been written as specified in the paper by Toraya (*24*).

RESULTS

The procedure of Pt^{2+} reduction employed favoured the obtaining of a very high dispersion of Pt° (*9, 10, 15*). Figure 1 shows the volume distribution function of Pt° obtained by the SAXS method for samples of Pt°/CeY and Pt°/LaY (after reduction and before sintering). These results for both samples showed the existence of very small platinum clusters and also a small difference between Pt°/CeY and Pt°/LaY; clusters in Pt°/CeY were smaller, confirming that Ce^{3+} ions favour the formation of smaller and more homogeneous particles of metal. X-ray diffraction patterns were in agreement with SAXS results; there were no diffraction peaks originating from Pt°. Taking into account the results obtained by Gallezot and co-workers (*10*) we can assume that these platinum clusters are located within the zeolite pores.

Sintering in Hydrogen

Heating of Pt°/CeY samples in a hydrogen atmosphere at 500, 600, 700, and even 800°C caused no growth of platinum clusters; they were still as small as in the initial sample (see Fig. 2, PtCeY/800/H_2 curve), and certainly are all located inside the zeolite pores. Figure 2 shows also size distribution curves (*f*(*D*)) for two samples of PtLaY heated in hydrogen at 500 and 800°C. The *f*(*D*) curve for PtLaY/500/H_2 sample shows beside a sharp peak in the range of 0–2 nm also small peaks in the range of 15–24 nm. The *f*(*D*) curves for PtLaY/600/H_2 and PtLaY/700/H_2 samples are nearly identical with the *f*(*D*) curve for PtLaY/500/H_2 (for that reason they are not presented in Fig. 2), except that the *f*(*D*) curve for PtLaY/800/H_2 has a small additional peak in the range of 30–35 nm. It is clear that crystallites which have sizes of 15–35 nm are situated outside the zeolite grains.

The existence of very small clusters (up to 2 nm) and much larger crystallites (12–50 nm) as well as the absence of 2–12 nm crystallites allow one also to calculate from the X-ray diffraction patterns the amounts of the platinum in the form of larger crystallites or very small clusters. The areas of the X-ray diffraction peaks originating from Pt° depend on the quantity of the larger crystallites of platinum (in practice greater than 2.5 nm). For this reason the area of the diffraction peak of Pt(111) for all samples was estimated.

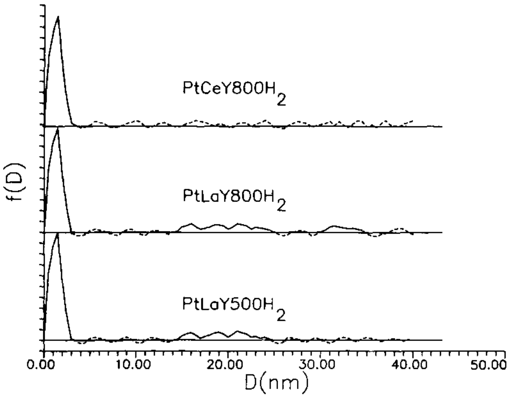

FIG. 2. Size distribution function of Pt° particles obtained by SAXS after sintering Pt/LaY and Pt/CeY in hydrogen at different temperatures.

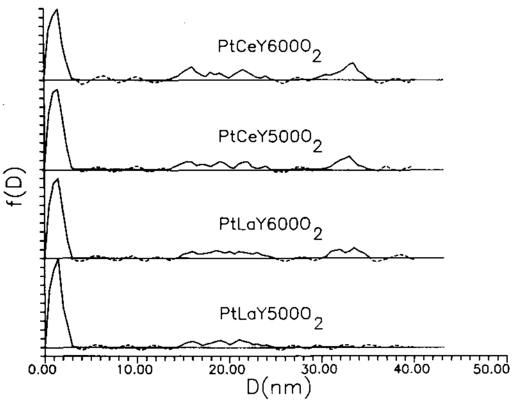

FIG. 3. Size distribution function of Pt^0 particles obtained by SAXS after sintering in oxygen.

For all the investigated samples the Pt(111) diffraction peak is very sharp without broadening near the base, which is characteristic for the presence of large crystallites. Thus the area of this peak corresponds with the amount of the larger platinum crystallites and moreover this area can be estimated with good accuracy. This permits in a simple way calculations with good precision for the amount of the platinum whose size is greater than 2.5 nm (indeed, greater than 10 nm because there are no crystallites in the 2.5–10 nm range). The area of the Pt(111) peak of the PtCeY/800/O_2 sample was assumed to correspond to the platinum crystallites greater than 2.5 nm. For other samples the amount of the Pt > 2.5 nm fraction was calculated by dividing the area of the Pt(111) peak by the area of the Pt(111) peak of the PtCeY/800/O_2 sample.

Table 1 gives the amount of the platinum which exists in the form or large crystallites calculated from X-ray diffraction as well as from SAXS results. Additionally Table 1 contains the sum of the heights of the 15 highest peaks which originate from the zeolite structure. This value allows one to estimate approximately the degree of destruction of the zeolite structure which takes place during the heating in different atmospheres.

For PtLaY samples heated in hydrogen at 500, 600, 700, and 800°C the amount of the large crystallites of platinum calculated from X-ray diffraction measurements is about 17–18% (Table 1), which is in very good agreement with the results obtained by the SAXS method.

Sintering in Oxygen

Figures 3 and 4 present the size distribution curves obtained by means of the SAXS method for Pt^0/CeY and Pt^0/LaY samples which were heated in an oxygen atmosphere. As is shown in Fig. 3, after heating in oxygen at 500 and 600°C only a small amount of Pt^0 clusters have grown and they form quite large crystallites (13–35 nm). This process takes place both for Pt^0/LaY

TABLE 1

SAXS and X-ray Diffraction Results

Sample	% Pt > 2.5 nm		Sum of heights of 15 highest zeolite peaks (relative units)
	SAXS	X-ray diffraction	
PtLaY/500/H_2	17	18	572
PtLaY/600/H_2	17	18	564
PtLaY/700/H_2	17	18	548
PtLaY/800/H_2	19	17	547
PtCeY/500/O_2	20	18	514
PtCeY/600/O_2	28	23	489
PtCeY/700/O_2	87	75	453
PtCeY/800/O_2	100	100	397
PtLaY/500/O_2	17	20	530
PtLaY/600/O_2	23	26	538
PtLaY/700/O_2	80	63	525
PtLaY/800/O_2	97	92	476
PtLaY/500/CO_2	13	16	343
PtLaY/600/CO_2	20	27	336
PtLaY/700/CO_2	32	46	330
PtLaY/800/CO_2	67	94	310
PtCeY/500/CO_2	7	6	408
PtCeY/600/CO_2	8	6	378
PtCeY/700/CO_2	27	31	367
PtCeY/800/CO_2	61	73	305
PtLaY/500/H_2O	14	15	285
PtLaY/600/H_2O	22	26	284
PtLaY/700/H_2O	23	26	241
PtLaY/800/H_2O	20	25	0
PtCeY/800/H_2O	0	6	0
LaY/500/O_2			543
LaY/800/O_2			482
CeY/500/O_2			523
CeY/800/O_2			402

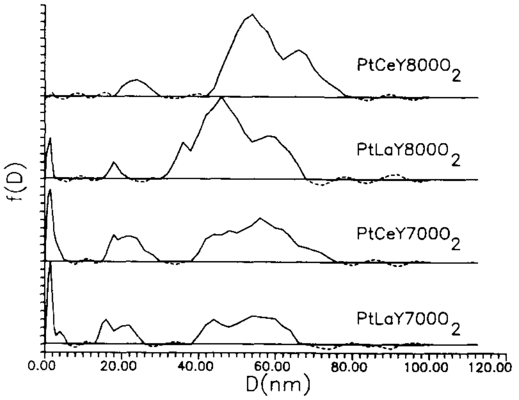

FIG. 4. Size distribution function of Pt^0 particles obtained by SAXS after sintering in oxygen.

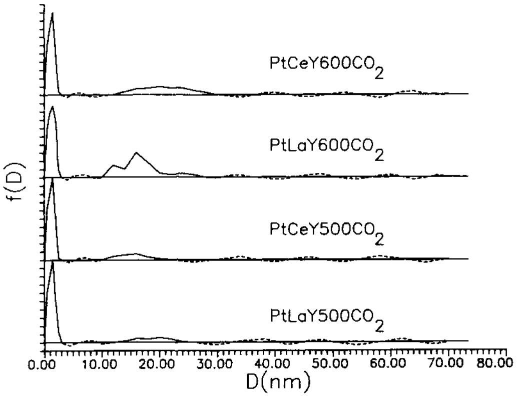

FIG. 5. Size distribution function of Pt^0 particles obtained by SAXS after sintering in carbon dioxide.

and Pt^0/CeY samples, but for samples with cerium ions it was a little stronger. After heating at 700 and 800°C the situation was fundamentally changed, most of the platinum being in the form of larger crystallites (see Fig. 4) whose diameter was in the range of 15–25 and 38–80 nm. The amount of these crystallites and their diameter is also much greater for the Pt^0/CeY samples than for the Pt^0/LaY ones. For the PtCeY/800/O$_2$ sample the size distribution curve (Fig. 4) does not show any maximum in the region of very small clusters (1–2 nm). This means that all the platinum has grown to large crystallites which are situated outside the zeolite grains.

X-ray diffraction data give similar results (see Table 1). X-ray diffraction peaks of the Pt^0 are high and narrow; they can only originate from large crystallites of Pt^0. Pt-oxides were never detected by X-ray diffraction.

Sintering in Carbon Dioxide

In Figs. 5 and 6 are presented the size distribution curves of platinum obtained by means of the SAXS method for samples heated in a carbon dioxide atmosphere, whereas in Table 1 the X-ray diffraction results are presented. Results obtained from both methods clearly show that substantial changes in platinum dispersion take place after heating at 800°C; up to this temperature only about 15–30% of the platinum clusters have grown to large crystallites. This process is occurring faster for Pt^0/LaY samples than for Pt^0/CeY ones.

As shown in Table 1, for the samples heated in carbon dioxide atmosphere there are greater differences between results obtained by SAXS and the X-ray diffraction method than for the samples heated in oxygen or hydrogen atmosphere. This is probably caused by the partial destruction of the zeolite framework which takes place during heating of the samples in a carbon dioxide atmosphere (see in Table 1 the values of the sum of the zeolite diffraction peaks for the

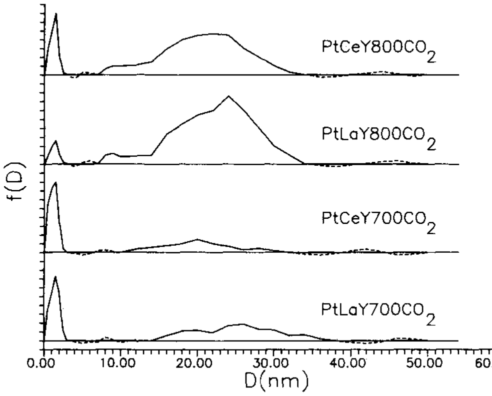

FIG. 6. Size distribution function of Pt^0 particles obtained by SAXS after sintering in carbon dioxide.

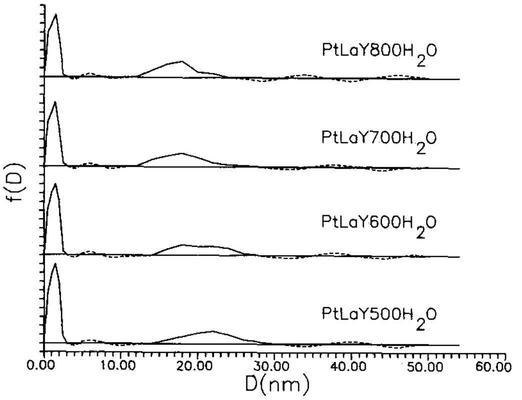

FIG. 7. Size distribution function of Pt^0 particles obtained by SAXS after sintering Pt/LaY in H_2O vapour.

samples heated in hydrogen and in carbon dioxide atmospheres) and the resulting influence on the precision of the SAXS results.

Sintering in Water Vapour

Figure 7 shows SAXS distribution curves for the Pt^0/LaY samples heated in water vapour. There are no curves presented for the Pt^0/CeY samples because for all these samples (even for sample which was heated at 800°C) the size distribution curve is the same as for the initial Pt^0/CeY sample. X-ray diffraction results largely confirm the SAXS results, but only for the PtCeY/800/H_2O sample is there a very small peak of the platinum (see Table 1).

DISCUSSION

Metals in zeolites can be detected as:

—metals dispersed on the external surface of zeolite grains

—metal particles occluded inside the zeolite matrix but with sizes which are larger than the pores and cages of the zeolite

—metal clusters (metal aggregates and molecular metal clusters) situated inside the zeolite cages.

In the initial samples, especially for the Pt^0/CeY, platinum is in the form of very small particles (Fig. 1), almost all of which are situated inside the zeolite cages. For the Pt^0/LaY sample, the size distribution function is spread up to the range of 2–2.5 nm, which suggests that for this sample a small amount of the platinum particles can be treated as particles occluded inside the zeolite matrix (their size is greater than the size of the largest cages of the zeolite).

The stability of metal situated inside zeolite pores or occluded in the zeolite matrix depends upon many factors, but the more important of these are the following: vapor pressure of the metal, geometry of the porous network, nature of the sintering atmosphere and interaction between metal atoms and the zeolite support. The results presented here suggest that the nature of the sintering atmosphere is the most important factor. Differences between the sintering behaviour in different atmosphere are quite large. The fastest sintering of the platinum in both kinds of samples is occurring in an oxygen atmosphere; it is slower in a carbon dioxide atmosphere and in the case of the heating in hydrogen or water vapour atmosphere only for Pt^0/LaY does sintering take place. For Pt^0/CeY heating in hydrogen or water vapour atmosphere up to 800°C does not give rise to any substantial changes in the dispersion of the platinum. For all cases when sintering takes place, large crystallites in the size range of 10–60 nm are formed. Such large crystallites should be located outside the zeolite crystals; it is difficult to imagine that such large particles can be occluded inside the zeolite matrix. If it were to take place, many zeolite cages would be destroyed and it would decrease the sum of the X-ray diffraction peaks originating from the zeolite structure. Table 1 shows that this decrease for the samples heated in oxygen atmosphere (which are the samples with the fastest sintering to large crystallites) is similar to the samples without platinum but heated in the same way (compare the sum of the heights of the diffraction peaks for PtLaY/500/O_2, PtLaY/800/O_2 and LaY/500/O_2, LaY/800/O_2 or PtCeY/500/O_2, PtCeY/800/O_2 and CeY/500/O_2, CeY/800/O_2). This confirms that, under the conditions used, the sintering of platinum in oxygen does not cause the destruction of the zeolite network and additionally testifies to the suggestion that large platinum crystallites are located outside the zeolite grains. A similar situation arises for the samples after sintering in hydrogen; there is no decrease of the sum of the X-ray diffraction peak heights originating from the zeolite structure (Table 1).

The large Pt crystallites in samples after sintering in CO_2 or H_2O might not be located outside the zeolite grains. It is known that heating at high temperatures in H_2O or CO_2 causes reconstruction of the zeolite framework and the formation of mesopores (this is reflected by the decrease of the sum of the zeolite diffraction peaks), whose size can be even greater than 10 nm (*25*). Thus part of the large Pt crystallites could be situated in mesopores inside the zeolite grains. This is supported by the comparison of the SAXS- and X-ray diffraction results. As shown in Table 1, there are greater differences between results obtained by SAXS and the X-ray diffraction method for samples heated in CO_2 or H_2O (especially for samples PtLaY/700/CO_2, PtLaY/800/CO_2, PtCeY/700/CO_2, PtCeY/800/CO_2, PtLaY/800/H_2O) than for the samples heated in oxygen or hydrogen. Additionally, for all samples heated in CO_2 or H_2O lower amounts of particles larger than 2.5 nm are detected by the SAXS method than by the diffraction method, whereas the opposite is observed for samples heated in O_2 (for example, compare samples PtLaY/700/CO_2 or PtLaY/800/CO_2 and PtLaY/700/O_2 or PtLaY/800/O_2). Both these facts can be explained as follows: the SAXS method did not detect part of the platinum particles in mesopores because scattering from these particles and from the mesopore voids superimposed at the same angles.

There are some small differences between the sintering of the platinum on CeY and LaY. Only after heating in oxygen atmosphere is the sintering of the platinum greater and faster for the Pt^o/CeY form than for the Pt^o/LaY one. Heating of the Pt^o/CeY form in other gases up to 800°C either caused no sintering of the platinum (H_2, H_2O) or the sintering was less than for the Pt^o/LaY form.

Heating of the Pt^o/CeY form in oxygen is very exceptional. It is known that heating the CeY zeolite at high temperatures in an oxygen atmosphere causes the oxidation of the Ce^{3+} ions to Ce^{4+} and at 600°C this oxidation is almost complete. It is also known that sintering of supported Pt in oxygen undoubtedly occurs via the transport of platinum oxide species and that the nature of the interaction of the platinum oxides with the support governs the sintering behavior of Pt (*26*). Pt-oxides were never detected in our samples; this means that Pt-oxides on zeolite, just as Pt-oxides on alumina, are not stable at these temperatures. The faster and greater sintering of the platinum, especially at 700°C and 800°C, for Pt^o/CeY than for Pt^o/LaY can be explained by oxidation of the Ce^{3+} ions to Ce^{4+}. This oxidation probably changes the interaction of the platinum oxides with the zeolite support and consequently causes faster growth of Pt crystallites on CeY than on LaY zeolite.

Sintering in hydrogen and water vapour atmospheres up to 800°C do not cause any changes in Pt dispersion in the Pt^o/CeY case whereas in the Pt^o/LaY case a substantial percentage of the platinum sinters into large crystallites. Analysing this result one should remember that there are differences in the dispersion of the platinum in the initial samples of Pt^o/CeY and Pt^o/LaY. The platinum particles in the range size of 2–2.5 nm which exist only in the Pt^o/LaY should be treated rather as particles occluded in a zeolite matrix (their size is greater than the dimension of pores in zeolite Y) and they are less mobile than those clusters whose size is smaller than the size of zeolite pores.

Our experiments show that SAXS appears to be a versatile method for determining the size distribution of metal supported on zeolite, even for crystallites below 2.5–3 nm (where the application of many other methods becomes critical) and especially for samples in which no damage of the zeolite network takes place.

REFERENCES

1. Bergeret, G., Gallezot, P., and Imelik, B., *J. Phys. Chem.* **85,** 411 (1981).
2. Exner, D., Jaeger, N., and Schulz-Ekloff, G., *Chem. Ing. Technol.* **52,** 734 (1980).
3. Braun, G., Fetting, F., Haelsig, C. P., and Gallei, E., *Acta Chim. Phys.* **24,** 93 (1978).
4. Jacobs, P. A., *in* "Metal Microstructures in Zeolites" (P. A. Jacobs *et al.,* Eds.), p. 71, Stud. Surf. Sci. Catal., Vol. 12. Elsevier, Amsterdam, 1982.
5. Jacobs, P. A., "Carboniogenic Activity of Zeolites," p. 183. Elsevier, Amsterdam, 1977.
6. Uytterhoeven, J. B., *Acta Phys. Chem.* **24,** 53 (1978).
7. Minachev, Kh., and Isakov, Ya. I., *in* "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), p. 552. A.C.S., Washington, DC, 1976.
8. Gallezot, P., *Catal. Rev. Sci. Eng.* **20,** 121 (1979).
9. Gallezot, P., Alarcon-Diaz, A., Dalmon, J. A., Renouprez, A. J., and Imelik, B., *J. Catal.* **39,** 334 (1975).
10. Gallezot, P., Mutin, I., Dalmai-Imelik, G., and Imelik, B., *J. Microsc. Spectrosc. Electron.* **1,** 1 (1976).
11. Gallezot, P., *J. Chim Phys.* **78,** 881 (1981).
12. Jaeger, N. I., Ryder, P., and Schulz-Ekloff, G., *in* "Structure and Reactivity of Modified Zeolites" (P. A. Jacobs *et al.,* Eds.), p. 299, Stud. Surf. Sci. Catal., Elsevier, Amsterdam, 1984.
13. Sachtler, W. M. H., Tzou, M. S., and Jiang, H. J., *Solid State Ionics* **26,** 71 (1988).
14. Gallezot, P., and Bergeret, G., *in* "Metal Microstructures in Zeolites" (P. A. Jacobs *et al.,* Eds.), p. 167, Stud. Surf. Sci Catal., Vol. 12), Elsevier, Amsterdam, 1982.
15. Barcicka, A., and Pikus, S., *in* "Proceedings, Conference on Applied Crystallography, Kozubnik, 1978" (Z. Bojarski and T. Bold, Eds.), p. 543. Uniwersytet Slaski, Katowice, 1979.
16. Gallezot, P., and Bergeret, G., *J. Catal.* **72,** 294 (1981).
17. Barcicka, A., and Pikus, S., *Zeolites* **7,** 35 (1987).
18. Conard, F. W., "Inorganic Syntheses," Vol. II, p. 250. McGraw-Hill, New York, 1964.
19. Mering, J., and Tchoubar, D., *J. Appl. Crystallogr.* **1,** 153 (1968).
20. Donati, J. H., Pascal, B., and Renouprez, A. J., *Bull. Mineral Cristal.* **XC,** 452 (1967).
21. Vonk, C. G., *J. Appl. Crystallogr.* **8,** 340 (1975).
22. Vonk, C. G., *J. Appl. Crystallogr.* **9,** 433 (1976).
23. Pikus, S., *in* "Proceedings, X Conference on Applied Crystallography, Kozubnik, 1980" (Z. Bojarski and T. Bold, Eds.), p. 460. Uniwersytet Slaski, Kozubnik, 1980.
24. Toraya, H., *J. Appl. Crystallogr.* **19,** 440 (1986).
25. Zukal, A., Patzelova, V., and Lohse, U., *Zeolites* **6,** 133 (1986).
26. Wanke, S. E., *in* "Sintering and Heterogeneous Catalysis" (G. C. Kuczynski *et al.,* Eds.), p. 233, Materials Science Research, Vol 16. Plenum, New York, 1984.