

# THE STATE OF THE PLATINUM IN ZEOLITIC CATALYSTS

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The CaY and Na-mordenite supported Pt with 0.1—5 wt. % Pt showed a linear increase in the specific Pt surface area with increasing amount of metal. The sintering of Pt between 773 and 1073 K is diffusion controlled whereas it is sintering controlled at higher temperatures. The former becomes faster with higher metal content and temperature, being slower with Pt/Na-mordenite than with Pt/CaY. The specific activity for hydroisomerization of *n*-hexane with 2% Pt/CaY varies with the time of calcination at 1073 K and with Pt particle size.

## Introduction

Catalytic active metals are commonly employed in the form of supported metal catalysts with the metal dispersed as small crystallites on high surface area supports. This good dispersion renders an optimal economical utilization of the mostly expensive metal. Besides the support separates physically the metal crystallites and thereby hinders the sintering.

Especially at high working temperatures growth of the metal crystallites still occurs. To investigate the influence both of the Pt content and of the structure of the support on the sintering of the noble metal, catalysts with different zeolitic supports — CaY and Na-mordenite — and different Pt contents have been prepared and sintered in air.

Furthermore, sintered catalysts with different Pt crystallite sizes were tested for the specific hydroisomerization activity.

## Experimental

### Catalyst preparation

As support for the catalysts a commercial Na-mordenite powder (Norton) and CaY zeolite powder were used. CaY zeolite was prepared from NaY (Linde SK-40) by exchanging 86% of the Na-ions by Ca<sup>2+</sup>. These supports were loaded with [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>·H<sub>2</sub>O. After drying at 393 K and a 2 h calcination at 673 K the catalyst was reduced 2 h at 473 K and 1 h at 673 K with 50 ml H<sub>2</sub>/min.

### Measurement of the metal surface area

The structural parameters of the metallic phase of the catalysts, *i.e.* the specific metal surface area, the metal dispersion and the mean metal crystallite size, have been determined by the O<sub>2</sub>/H<sub>2</sub>-titration at 573 K by the pulse method in a gas-chromatographic flow apparatus [1]. First the adsorbed water was removed at 673 K with 50 ml N<sub>2</sub>/min. Then the Pt was covered with oxygen 1 h at 573 K with 30 ml dried air/min. At the same temperature the formed Pt oxide was titrated by injection of several H<sub>2</sub> pulses (0.664 cm<sup>3</sup> each) into the carrier gas stream of 20 ml N<sub>2</sub>/min. The non-oxidized H<sub>2</sub> was determined by a heat conductivity cell. A following chemisorption of H<sub>2</sub> on Pt could be neglected at this temperature [1, 2]. This gave good agreement with electron microscopy results.

### Catalytic activity measurements (procedure)

The activity for the hydroisomerization of *n*-hexane was tested in a fixed bed tube reactor [3]. For activation the pelletized catalysts were treated in the reactor in flowing H<sub>2</sub> 2 h at 473 K and 2 h at 673 K with final cooling down to 473 K. The reaction parameters were the following:

Temperature:	583 K
Pressure:	27.5 bar
Weight of catalyst:	3 g
Feed ( <i>n</i> -hexane):	6 g/h
Feed (H <sub>2</sub> ):	0.4 mol/h

### Results and discussion

#### Influence of the amount of zeolite supported platinum on the metal surface area

The metal surface area per g of catalyst (*S*) and the degree of dispersion (ratio of surface to total metal atoms) was measured for CaY and Na-mordenite supported Pt catalysts all prepared in the same way. Fig. 1 shows that *S* increases linearly with increasing metal content according to

$$\begin{aligned} S &= 0.96 \cdot c_{\text{Pt}} && \text{for Pt/CaY and} \\ S &= 1.46 \cdot c_{\text{Pt}} && \text{for Pt/Na-mordenite.} \end{aligned}$$

So for the same Pt content the mordenite catalyst has a 50% higher metal surface area than the CaY catalyst.

This can be explained by the different crystal systems and pore structures, respectively, of the supports. Whereas CaY has a relatively open 3 dimensionally accessible pore system with 0.9 nm wide pores, the diffusion of Pt atoms for forming bigger particles is more hindered in the Na-mordenite by the parallel elliptical pores of the size 0.57 × 0.69 nm which cannot be passed crosswise.

Another reason might be the statistically smaller distance between the freshly reduced Pt atoms in the Pt/CaY as CaY has a higher density of exchangeable cations compared with Na-mordenite. Fig. 1 also shows that the dispersion degree of the Pt in both zeolite catalysts approaches unity for very small metal contents and is decreas-

ing mainly between 0 and 1 wt.% Pt. At higher Pt contents the degree of dispersion and the mean Pt particle size are almost constant with 2.4 nm for Pt/CaY and 1.6 nm for Pt/Na-mordenite, respectively.

Many of the industrially used non-zeolitic Pt catalysts are Pt-on- $\text{Al}_2\text{O}_3$  which mostly are prepared by impregnation with  $\text{H}_2\text{PtCl}_6$ . These catalysts have Pt surface areas increasing only by a lower power function, e.g., by  $c_{\text{Pt}}^{2/3}$  [4] or by  $c_{\text{Pt}}^{0.3}$  [5].

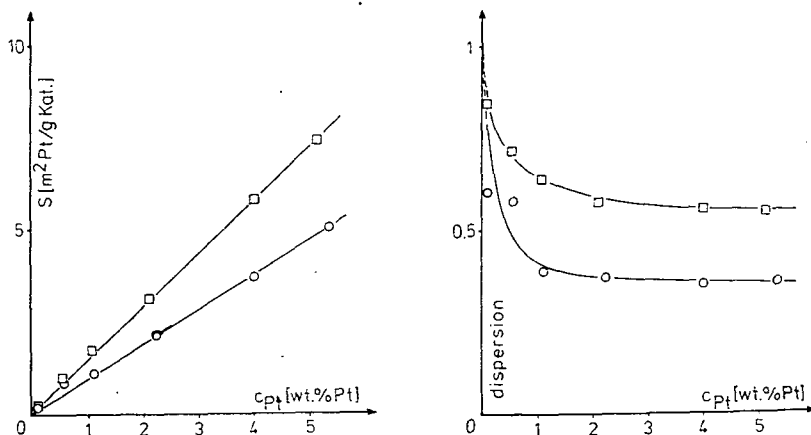


Fig. 1. Specific surface area  $S$  and dispersion of Pt as function of content of Pt on CaY (○) and on Na-Mordenit (□)

### The sintering of zeolite supported Pt

For testing the influence of the temperature on the sintering of zeolite supported Pt the catalyst 0.5% Pt/CaY was sintered up to 60 h between 773 and 1073 K. Fig. 2 shows little sintering of the Pt at a temperature of 773 K whereas at higher temperatures the rate of sintering is strongly accelerating. For these sintering rates ( $dS/dt = -k \cdot S^n$  [6],  $k$ : rate constant) the power-law order  $n$  showed to be between 6 and 8 for 773–873 K and to be 2 and 3 for 973 and 1073 K, respectively.

Therefore, according to RUCKENSTEIN AND PULVERMACHER [7], the first region means a diffusion controlled sintering whereas at higher temperatures it is sintering controlled. Similar results were found for the 2% Pt/CaY catalyst.

For the investigation of the influence of the support and the metal content on the sintering behaviour Pt/CaY and Pt/Na-mordenite have been sintered in air at 873 K, i.e. under diffusion controlled conditions. With increasing metal content and the same initial Pt dispersion (cf. Fig. 1) an increasing sintering rate was found for

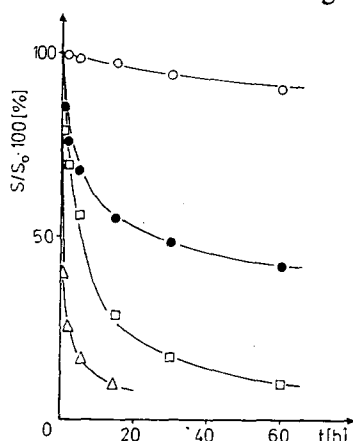


Fig. 2. Relative decrease of Pt surface area by sintering of 0.5% Pt/CaY in air at 773 K (○), 873 K (●), 973 K (□) and 1073 K (△)

both catalysts (see Fig. 3), being explainable by the increasing surface concentration of Pt crystallites. But whereas the sintering rate at Pt/CaY has become very small after 5–10 h this holds for Pt/Na-mordenite only after 30–40 h, presumably also a result of the better diffusion of Pt in CaY.

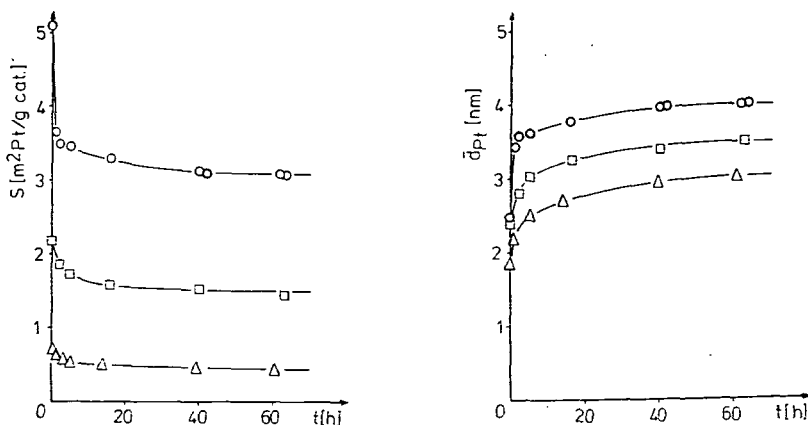


Fig. 3. Decrease of Pt surface area and increase of mean Pt particle size by sintering in air of 0.54% Pt/CaY ( $\Delta$ ), 2.23% Pt/CaY ( $\square$ ) and 5.36% Pt/CaY ( $\circ$ ), respectively

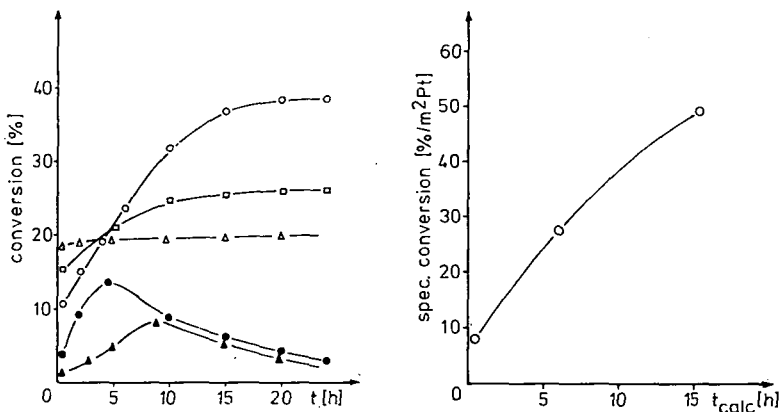


Fig. 4. Conversion and specific conversion of *n*-hexane at 583 K for 2% Pt/CaY (open symbols) and CaY (filled symbols) treated in air at 1073 K for 0.5 h ( $\circ$ ,  $\bullet$ ), 6 h ( $\square$ ) and 15.5 h ( $\Delta$ ,  $\blacktriangle$ ) corresponding to 4.1 nm, 9.1 nm, and 13.9 nm Pt particle size, respectively

### *Catalytic activity measurements*

The catalytic activity of 2% Pt/CaY treated in air at 1073 K between 0.5 and 15.5 h was tested (see Fig. 4). Whereas the supported Pt shows an increasing conversion of *n*-hexane with increasing reaction time becoming constant after about 24 h the activity of the support CaY alone has a maximum. The deactivation is mainly caused by coking. With supported Pt no other products than isomers of *n*-hexane are found. This means that Pt hinders the coking of the catalyst.

As in addition IR-spectroscopy [8] also showed a somewhat different behaviour of CaY and Pt/CaY treated in the same way it was not yet possible to relate the specific conversion exclusively to the metal phase. Instead, the specific conversion was plotted versus the time of heat treatment  $t_{\text{calc}}$  corresponding to increasing Pt particle sizes for relatively short reaction times (when the support still had only a relatively low activity).

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