

THE INFLUENCE OF HYDROGEN PRETREATMENT ON THE STRUCTURAL AND CATALYTIC PROPERTIES OF A Pt/K-LTL CATALYST

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ABSTRACT

A platinum, non-acidic K-LTL catalyst, reduced at 300, 450, and 600°C, was characterized by extended X-ray absorption spectroscopy (EXAFS), hydrogen chemisorption, hydrogen temperature programmed desorption (H₂-TPD) and methylcyclopentane hydrogenolysis. Reduction at 300°C produces small platinum crystallites with an interfacial layer of hydrogen. Reduction at 450°C increases the particle size, releasing interfacial hydrogen. This irreversible hydrogen desorption is observed in the TPD around 300°C. Reduction at 600°C results in further growth of the platinum cluster with the loss of the remaining interfacial hydrogen. In the TPD, a second high temperature H₂ desorption is observed at around 610°C. Because of the confined space within the zeolite pore, as the platinum particle size approaches the pore size, there is a reduction in hydrogen chemisorption capacity and catalytic activity compared to a particle of equivalent size on an amorphous support.

INTRODUCTION

The effect of reduction temperature on the structure and behavior of catalysts has been the subject of numerous investigations [1-5]. Many studies have shown both reduced catalytic activity and reduced hydrogen chemisorption capacity after reduction in hydrogen at high temperatures (>500°C) [1-5]. However, a clear understanding of the phenomena involved is still lacking. Reduction at high temperatures may induce sintering [6], but may also bring about changes in the morphology of the metal crystallite and the structure of the metal-support interface [7].

Temperature programmed desorption of hydrogen from supported and unsupported platinum typically shows multiple peaks above 100°C: one at low temperature (ca. 150°C) assigned to hydrogen chemisorbed to the metal surface [6,8], and one or more higher-temperature peaks (ca. 300-500°C) [6,8-10]. These higher-temperature peaks have been assigned by various authors to hydrogen in sub-surface layers of the platinum [1,3,10-11], formation of a superficial Pt-Al alloy [12], or oxidation of the reduced platinum by support protons [13-14]. In this study, the structural characterization by EXAFS of a non-acidic Pt/K-LTL catalyst reduced at 300, 450, and 600°C, in

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combination with H_2 -TPD and catalytic measurements, provide insight into the phenomena occurring during high temperature hydrogen treatment.

EXPERIMENTAL

The K-LTL was obtained from Linde. Excess alkali was reduced by water wash until the pH of the wash solution was 9.5. The Pt was deposited by impregnation using tetraammine platinum(II)nitrate followed by drying at 120°C. Platinum loading was 1.2 wt%. The crystallinity of the zeolite did not change during the TPD experiments as has been checked by XRD.

Self-supporting wafers were reduced in H_2 at 300 or 450°C in a controlled atmosphere *in-situ* EXAFS cell [15]. A third sample was reduced *ex-situ* at 600°C and rereduced in the EXAFS cell at 450°C. The EXAFS data were obtained at liquid nitrogen temperature in the presence of H_2 . The EXAFS measurements were carried out at the Synchrotron Radiation Source in Daresbury, U. K., Wiggler Station 9.2 at the Pt L_{III} edge (11564 eV). Standard procedures were used to extract the EXAFS functions [16]. Phase shifts and backscattering amplitudes extracted from experimental data on Pt foil and $Na_2Pt(OH)_6$ were used in the analysis for the Pt-Pt and Pt-O contributions, respectively.

Hydrogen Temperature Programmed Desorptions (TPD) were programmed at 10°C/min to 700°C in flowing N_2 . The H_2 and N_2 gases were purified by oxygen and hydrocarbon traps.

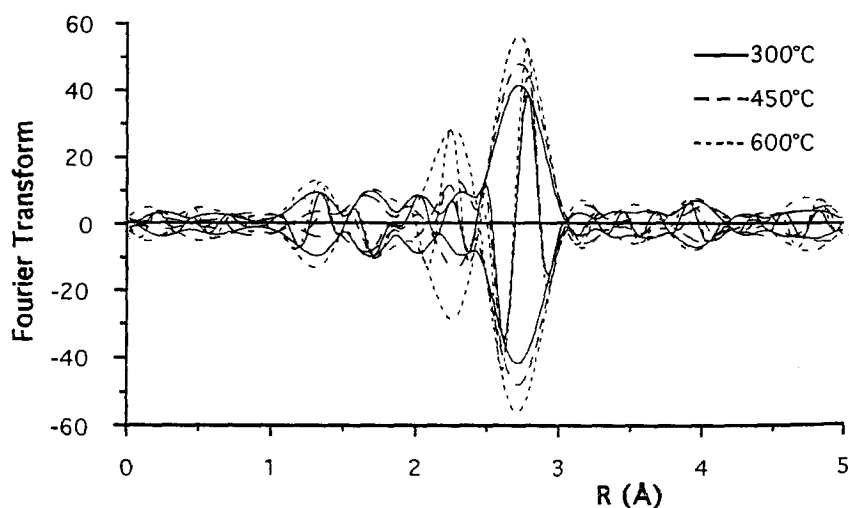


Figure 1 Magnitude and Imaginary part of the k^3 weighted, Pt-Pt phase and amplitude corrected (Δk : 3.1-15.0 \AA^{-1}) Fourier transform of Pt-K/LTL. Sample reduced at 300°C solid line (—), 450°C dashed line (---), 600°C dotted line (·····).

Table 1 Results of Fitting of EXAFS data.

Reduction Temperature	Backscatterer	N	R (Å)	$\Delta\sigma^2$ ($\times 10^{-3} \text{ \AA}^{-2}$)	E_0 (eV)
300°C	Pt	4.0	2.75	4.0	5.0
	O	1.2	2.72	7.5	-1.7
450°C	Pt	4.4	2.75	4.0	4.6
	O	0.7	2.76	2.0	-1.7
	O	0.6	2.22	2.8	-13.5
600°C	Pt	4.9	2.75	4.3	1.8
	O	1.3	2.24	-1.5	-14.1

Cryogenic traps containing 5A molecular sieve were placed before and after the furnace for water trapping. Desorbed gases were monitored by a thermal conductivity detector and checked by gas chromatographic analysis for H₂.

The conversion of MCP was carried out at atmospheric pressure in a fixed-bed reactor. The reaction temperature was 272°C, with a H₂/MCP ratio of 13.6. The conversion was adjusted to be in between 2 and 10% by changing the space velocity at constant temperature. Activity of this catalyst in *n*-hexane aromatization has been reported earlier [17].

RESULTS AND DISCUSSION

EXAFS

The Pt-Pt phase and amplitude corrected k^3 weighted Fourier transform (Δk : 3.1–15.0 Å⁻¹) of the EXAFS data is presented in Figure 1. Qualitative inspection of Figure 1 shows that metallic Pt is present in all samples as indicated by the main peak around the Pt-Pt bond distance of 2.77 Å. In addition, as the reduction temperature is raised the amplitude of the Pt-Pt peak increases, indicating a growth of the platinum particle size (coordination number). For all reduction temperatures, however, the platinum particles are relatively small as denoted by the absence of higher Pt-Pt shells. The peak at 2.77 Å in the Fourier transform of the EXAFS data has an asymmetrical magnitude and imaginary part, indicating the presence of additional backscatterers.

The EXAFS spectra were fitted in both k - and r -space over a k -range of 3.3 – 13 Å⁻¹ and a r -range of 1.4 – 3.2 Å. The results of this fitting procedure are given in Table 1. The full analysis of the data, including Goodness of Fit and errors on the parameters, will be presented elsewhere.

As discussed above, the Pt-Pt coordination number increases steadily with increasing reduction temperature. The lowest coordination number of 4.0 for 300°C reduction corresponds to an average cluster size of 6 atoms. Increasing the reduction temperature to 450°C results in a

raise in coordination number to 4.4. This corresponds to addition of 2 atoms to the average platinum cluster. Raising the reduction temperature to 600°C results in an increase in coordination number to 4.9 (average cluster size: 11 atoms).

In all samples we observed backscattering from the oxygen in the zeolite lattice. Assuming a spherical particle on a flat support the relative contribution from the metal–support interface steadily decreases as the particle size increases. As LTL pores are cylindrical and have sidepockets the relative contribution from the metal–zeolite interface will not decrease necessarily when the particles grow.

In the samples reduced at 300°C and 450°C we observed oxygen at a distance of 2.7 Å. This distance, however, is longer than the sum of the covalent radii of the two atoms (1.37 Å for Pt + 0.74 Å for O). Previously, it has been suggested that the long Pt–O distance results from the presence of hydrogen between the platinum atoms and the support oxide–surface [18]. This interfacial hydrogen may be either chemisorbed hydrogen trapped at the interface during reduction or surface hydroxyl groups on the support.

For the samples reduced at 450°C and 600°C, another oxygen contribution to the EXAFS is observed. The observed distance of 2.2 Å suggests that this contribution arises from platinum atoms in direct contact with the zeolite lattice. The very low E_0 values associated with these oxygen contributions suggest that they should be fitted with another backscatterer, for example potassium. However, in studies on other systems where only oxygen is present as a backscatterer we also observe these very low E_0 values [19] for the short (2.2 Å) Pt–O distance.

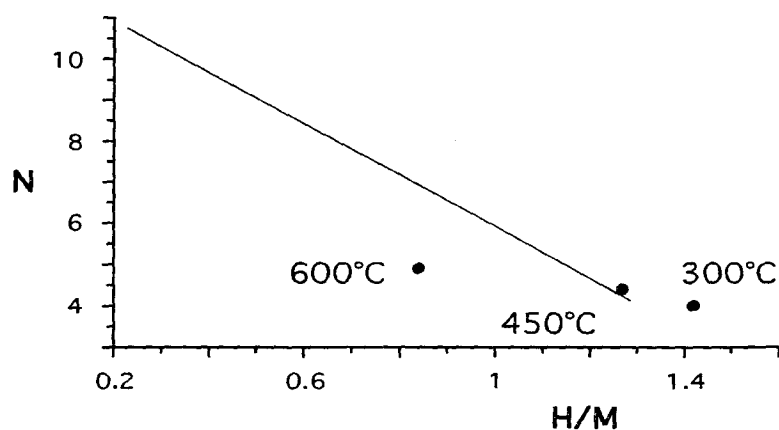


Figure 2 Comparison between EXAFS Pt-Pt coordination number (N) and H_2 chemisorption for Pt/K-LTL after reduction at 300°C, 450°C or 600°C. Line from correlation by Kip, et al [19] as extended by Vaarkamp et al [20].

Hydrogen Chemisorption

The EXAFS analysis indicates that the catalysts differ in platinum particle size. The hydrogen chemisorption of each catalyst was determined in order to estimate the exposure of platinum atoms. The values are reported in Table 2. Previously, a correlation between the EXAFS Pt–Pt coordination number (N) and the H/Pt value was established for Pt/Al_2O_3 catalysts [20] and extended to include a $Pt/BaK-LTL$ catalyst [21]. For the $Pt/K-LTL$ catalysts reduced at 300°C or 450°C, the H/Pt value is consistent with the previous correlation (Figure 2). Reduction at higher temperatures increases the Pt–Pt coordination number and decreases the H/Pt value, but the measured H/Pt value for the sample reduced at 600°C falls below the correlation. There is, therefore, a suppression in the chemisorption capacity following reduction at 600°C [1–5]. Additionally, because of the finite space within the zeolite pores, as the platinum particle grows, less of the platinum surface is exposed compared to a particle of identical size on an amorphous support. In the limiting case where the platinum particle fills the pore, only those atoms exposed through the pore windows will chemisorb H_2 . As a result, for metal particles in zeolites which occupy the available pore volume, the particle size can not be accurately determined by H_2 chemisorption.

Hydrogen TPD

Hydrogen TPD of $Pt/K-LTL$ reduced at 300°C shows three distinct features (Figure 3a). Two broad, overlapping peaks are observed at about 150°C and 275°C with some H_2 desorbing up to 400°C. In addition, there is a distinct desorption peak at about 610°C. The total H_2 desorption was 2.16 ml/g. After the first TPD, the catalyst was exposed to H_2 at 700°C for 1 hr and cooled in H_2 . A second TPD (Figure 3b) revealed only the desorption at 150°C, 1.3 ml/g. The second TPD indicates that the H_2 associated with the desorption peak at 150°C is reversible, while the higher

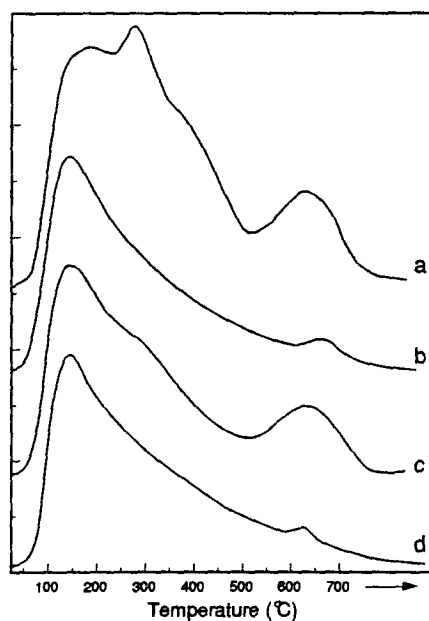


Figure 3 TPD of $Pt/K-LTL$: a) reduced at 300°C; b) second TPD of 3a after rereduction in H_2 1 hr. at 700°C, cooled to RT in H_2 ; c) reduced at 500°C; d) reduced at 650°C

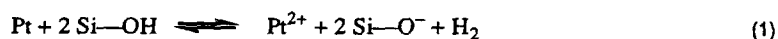
Table 2 Hydrogen Chemisorption and Catalytic Results

Reduction Temperature	H/Pt	TOF ($\times 10^{-4} \text{ s}^{-1}$)	nC ₆ /3MP	2MP/3MP
300°C	1.42	3.5	0.9	1.1
450°C	1.27	6.2	1.0	1.2
600°C	0.84	6.5	1.1	1.5

temperature desorptions are irreversible.

Reduction of Pt/K-LTL at 500°C decreases the total H₂ desorption to 1.5 ml/g, a 30% reduction. After reduction at 500°C (Figure 3c) the peaks between 275–400°C are absent, but the 610°C peak is not affected. Reduction at 650°C removes all the higher-temperature peaks, and only the peak at 150°C remains (Figure 3d). The total H₂ desorption following reduction at 650°C was 1.3 ml/g. In all cases, the amount of reversibly adsorbed H₂ associated with the 150°C peak was approximately equal to the amount of chemisorbed H₂ measured volumetrically (Table 2).

Comparison of the EXAFS with the H₂ TPD shows that the irreversible H₂ desorptions from 275–400°C occur over the same temperature range as the changes in platinum particle size and coordination environment. This strongly suggests that the hydrogen desorbed at these temperatures is formed from hydrogen at the platinum-zeolite interface, which is exposed by migration or rearrangement of the platinum particles. If the interfacial hydrogens originate from support hydroxyl groups, then desorption of this hydrogen also requires oxidation of platinum [14]:



During reduction at high temperature, oxidized platinum would be rereduced. The desorptions of interfacial hydrogen are irreversible because the sintering of platinum is irreversible (in hydrogen).

The H₂ desorption at 610°C in the TPD also corresponds to structural changes observed in the EXAFS. At these high reduction temperatures it is possible that migrating platinum particles react with zeolite silanol groups, (reaction 1 above). The H₂ desorption at 610°C in the TPD is irreversible since sintering of the platinum particle is irreversible in hydrogen.

Catalytic Reactions (MCP)

The H/Pt values, turnover frequencies, nC₆/3MP and 2MP/3MP selectivities for MCP ring opening are given in Table 2. At a reaction temperature of 272°C, the Pt/K-LTL reduced at 300°C

was less active than the catalysts reduced at 450 and 600°C. Calculation of the turnover frequencies in Table 2, assumes that a site capable of chemisorbing hydrogen is an active site.

Since the changes in platinum cluster size are not accompanied by corresponding changes in activity, we conclude that the specific activity of these catalysts is not a strong function of particle size. Rather, the higher activity after higher temperature reduction might be the result of changes in the electronic structure of platinum induced by the zeolite.

The hexane isomer distribution is also shown in Table 2. Isomer selectivity was invariant with conversion. The distribution was non-statistical (approximately 1:1:1) [22], but did change slightly with reduction temperature with the amount of 2MP steadily increasing relative to the other isomers. The isomerization activity of the catalyst was negligible as was shown by *n*-hexane isomerization experiments (conversion < 1%).

CONCLUSIONS

During the low temperature reduction of Pt/K-LTL small platinum particles of approximately six atoms are formed. The platinum atoms are supported by oxygen atoms from the support at a distance which suggests the presence of interfacial hydrogen between the platinum and the oxide support. At reduction temperatures of 450°C, there is an increase in the platinum particle size and a change in the platinum-zeolite interface, releasing some of the interfacial hydrogen. The release of interfacial hydrogen can be seen in the TPD at temperatures from 275–400°C. The desorptions observed with TPD are irreversible since the structural changes are irreversible in a hydrogen atmosphere. A further increase in reduction temperature to 600°C results in the growth of the platinum particles to approximately eleven atoms. In addition, there is no "long" Pt-O coordination, and the "short" Pt-O coordination increases. A peak in the TPD at about 650°C indicates the evolution of hydrogen during the sintering process. It is proposed that during the sintering of the platinum particles, migrating platinum can be oxidized by the zeolite hydroxyl (silanol) groups. This hydrogen desorption is irreversible since particle growth is irreversible.

The structural changes induced by reduction at higher temperatures affect the catalytic performance. At low reduction temperatures the smaller platinum particles have lower activity. Selectivity also changes with increasing reduction temperature, but the observed changes do not correspond with those reported in the literature for particle size effects [23]. We therefore conclude that changes in the local platinum environment may be responsible for the observed differences in activity and selectivity. As the platinum particle size increases to fill the available pore volume, a large fraction of the surface platinum is blocked from reacting molecules by the

pore walls, thereby lowering catalyst activity.

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