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XAFS Study of Ce-Enhanced Stability of Pt/KL Catalyst

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Abstract. The stability of the Pt/KL catalyst can be greatly enhanced by the presence of the rare earth Ce. The analysis of the X-ray absorption edges indicates that some electronic differences may indeed exist in the state of Pt supported on the Ce-KL compared to that on the unpromoted KL zeolite. Although the Pt particle size and location inside the zeolite is very similar in the two zeolites, the presence of the Ce seems to have influence on the electronic potential around Pt, which may be responsible for the observed enhanced stabilization of the small metal clusters. The presence of Ce in the zeolite also greatly affects the reducibility of Pt.

1. Introduction

In catalysis engineering, a third component is often added into the catalyst in order to improve either thermal stability or activity and selectivity. For example, in the design of high performance diesel catalysts, there have been several attempts to increase the sulfur-tolerance of the catalyst. Besides different methods of preparation and pretreatment,^{1,2} promoters is often used to increase the sulfur tolerance.^{3,4} Addition of rare earth to Pt/KL catalysts prepared by liquid impregnation could increase the sulfur resistance and aromatization selectivity.⁵ Tiny amount of Ce can also improve the thermal stability of Ni-P amorphous alloy catalysts for the selective hydrogenation.⁶ However, it is still poorly understood how the promoters can alter the chemical and physical properties of the catalyst.

Due to the small particle sizes and the lackness of long-range order in supported catalysts, X-ray absorption spectroscopy is best suited for the characterization. In this work, Pt/KL catalysts were synthesized with and without Ce promotion. Preliminary structural characterization of the catalysts was assessed by *in-situ* X-ray absorption fine structure spectroscopy (XAFS) in order to get a more comprehensive insight into the apparent catalyst structure. This technique offers the advantage that the catalysts can be investigated in the as-synthesized state, in which they are also tested for their chemical properties of the catalytic systems.

2. Experimental

2.1 Sample Preparation

Unpromoted 1 wt% Pt/KL catalyst and rare earth Ce-promoted catalyst were prepared by vapor phase impregnation (VPI). The KL zeolite (K-LTL, BET area=292 m²/g, SiO₂/Al₂O₃ ratio = 6)

was used as support. Before adding the metals, the zeolite was dried in an oven at 110 °C for 12 h and calcined at 350 °C in flow of dry air of 100 cm³/(min g_{cat}) for 5 h. The metal precursors were platinum(II) acetyl-acetonate (Pt(C₅H₇O₂)₂), and cerium(III) 2,4-pentanedionate hydrate (C₁₅H₂₁CeO₆·xH₂O). The weighed metal precursors and the calcined support were physically mixed under inert atmosphere of He. The mixture was then heated up slowly to 40 °C and held at that temperature for 3 h, heated again to 60 °C holding it for 1 h, and further heated to 100 °C, at which temperature the mixture was held for 1 h to complete the sublimation of the metal precursor. After sublimation, the mixture was heated under flowing He to 130 °C and held for 30 min. In the last step, the mixture was calcined at 350 °C in flow of dry air at 100 cm³/(min g_{cat}) for 2 h. In the Ce-containing sample, prior to the loading of the Pt precursor, the Ce/KL support was prepared using the same VPI and calcination procedure as described for the loading of Pt, using the same temperatures and heating times.

2.2 X-ray absorption analysis

The absorption spectra at the Pt L_{2,3} edges for fresh and spent Pt/KL and Pt/Ce-KL catalysts were measured fluorescence mode. The measurements were conducted in a *homemade* stainless steel sample cell (similar to that in Ref. 7) that allowed *in situ* pretreatments at temperatures ranging from liquid nitrogen to 500 °C. Prior to each measurement, the catalysts, previously reduced *ex situ* at 500 °C, were re-reduced *in situ* at 300 °C (heating rate of 10 °C/min) for 30 min in flowing H₂. After the reduction step, the sample was cooled down under flowing He. The X-ray absorption spectra were recorded at liquid nitrogen temperatures under He flow. Six scans were recorded and averaged for each sample. The pre-edge background was subtracted by using power series curves. Subsequently, the post-edge background was removed using a cubic-spline routine. The spectra were normalized to the height of the adsorption edge. The range in *k*-space used for the extended x-ray absorption fine structure (EXAFS) analysis was 3.0–15 Å⁻¹. Absorption data obtained on a Pt foil at liquid nitrogen temperature was used as an experimental reference for the Pt–Pt bond (coordination number N = 12; R = 0.275 nm).

3. Results

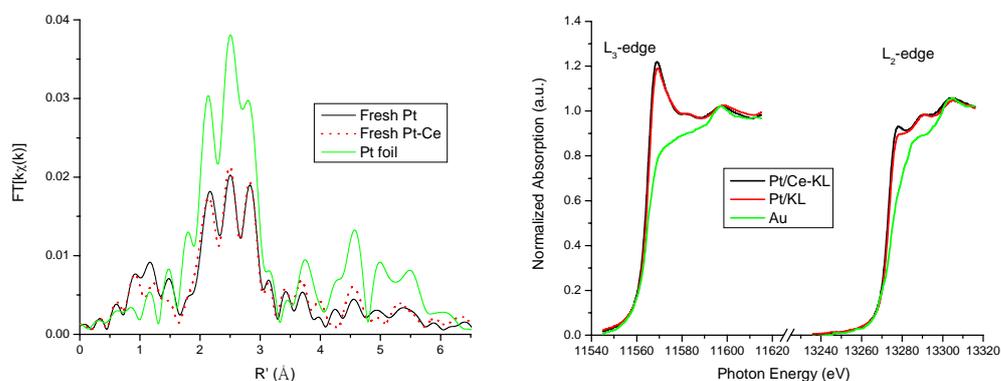


Figure 1. (left) The Fourier transform amplitudes of *k*-weighted EXAFS data of the Pt/KL and Pt/Ce-KL samples after reduced at 500 °C. (right) the L_{3,2} edges of the unpromoted Pt/KL and Ce-promoted Pt/KL after reduced at 500 °C. The Au spectra was expanded and aligned in energy with the Pt spectra on the fine structure, see the text.

The local structure of Pt atoms in the Pt/KL and Pt/Ce-KL catalysts was investigated by EXAFS at liquid nitrogen temperature after reduction in H₂ at 500 °C. Fig. 1(left) shows the Fourier transforms of the X-ray absorption data collected on the two samples. The spectra were almost identical, indicating that the Pt clusters in the two catalysts are very similar. In agreement with

this qualitative observation, the quantification of the EXAFS data indicates that the structural parameters of the Pt clusters are very similar in both catalysts in the freshly reduced state (see Table 1).

Table 1. Structural parameters obtained from the fitting of the EXAFS data on the unpromoted Pt/KL and promoted Pt/Ce-KL after reduction at 500 °C.

	N	$R(\text{Å})$	$\Delta \sigma^2 (\text{Å}^2)$	$\Delta E (\text{eV})$
Pt/KL	5.2±1.0	2.77(5)	0.0067(6)	0.27±1
Pt/Ce-KL	5.4±1.0	2.76(5)	0.0094(9)	2.21±1

The X-ray absorption near-edge structure (XANES) provides information about oxidation states, vacant orbitals, electronic configuration, and site symmetry of the absorbing atom.⁸ The L_3 and L_2 edges for Pt on the unpromoted and Ce-promoted Pt/KL catalysts are compared in Fig. 1(right). As pointed out by Ramaker *et al.*,⁹ there are significant differences among the transitions involved in each of the two edges. Specifically, the L_3 edge takes account of transitions from the $2p_{3/2}$ level to the $5d_{5/2}$ and $5d_{3/2}$ levels, but the L_2 edge only includes a transition from the $2p_{1/2}$ level to the $5d_{3/2}$. As can be observed for the L_2 edge, the first peak after the edge (whiteline) is much smaller on the Pt/KL sample than on the Pt/Ce-KL. In very small Pt clusters, the $5d_{3/2}$ level falls below the Fermi level due to band narrowing, inhibiting the corresponding $2p_{1/2} \rightarrow 5d_{3/2}$ transition.⁷ However, the difference between the unpromoted and the Ce-promoted Pt/KL catalysts cannot be explained in those terms, since both catalysts have comparably small Pt clusters as shown in Table 1. The enhanced absorption in the whiteline would indicate that the $2p_{1/2} \rightarrow 5d_{3/2}$ transition occurs to a greater extent on the Pt/Ce-KL catalyst than on the Pt/KL catalyst. This enhancement could be due to either an electron transfer from the Pt to the Ce-promoted zeolite, which would depopulate the $5d_{3/2}$ level, or a shift in the Fermi level, not associated with an electron transfer, but only due to a change in the Madelung potential of the zeolite around the Pt particles.^{10,11} Similar changes have been proposed for Pt supported on La^{3+} -containing zeolites.¹² Interestingly, since L_3 edges also contain a transition to the $5d_{3/2}$ level, the same difference between Pt/KL and Pt/Ce-KL is carried along to this edge (see Fig. 1). Clearly, the analysis of the X-ray absorption edges indicates that some electronic differences may indeed exist in the state of Pt supported on the Ce-KL compared to that on the unpromoted KL zeolite.

To further investigate the effect of Ce in enhancing the interaction of Pt with the zeolite, we monitored the evolution of the XANES spectra at increasing reduction temperatures to see how the presence of Ce affects the reducibility of the supported Pt, since it is directly associated with the enhancement of the stability of the catalyst by Ce promotion in reaction. The XANES of the Pt L_3 -edge was obtained after holding the sample under pure H_2 for 30 min at the indicated temperature. This comparison is illustrated in Fig. 2a and b, which show only a few of all the spectra taken. It is clearly seen that as the reduction proceeds the size of the whiteline in the L_3 edge decreases, reflecting the increase in the electron occupancy of the d levels when the Pt oxide is reduced to metallic Pt. The integrated area of the whiteline is a direct measurement of the oxidation state of Pt. However, the Pt $L_{3,2}$ edges do not exhibit a strong “whiteline” and the errors in the determination of the step-like background might now as large as 40%. For an accurate analysis, we have therefore compared the Pt $L_{3,2}$ edges with those of Au (Au has similar structure with Pt so the structures at higher energies are very similar for both samples, and the whiteline is due to $2p \rightarrow 5d$ transitions, are caused by transitions to pd and df hybridized states.), measured the same experimental conditions in Au foil.¹³ The energy scale of the Au spectra was expanded by a factor of 1.08 to account for the difference in the lattice parameter, then aligned in energy with the Pt spectra on the fine structure and finally normalized to the edge jump.¹⁴ The whiteline area is calculated by integrating the difference spectrum over the whiteline region (*i.e.*, between its initial rise and its first node). The values of this area for all the measured spectra are summarized in Fig. 2c as a function of reduction temperature for the Pt/KL and Pt/Ce-KL catalysts. A clear

difference is observed, showing that the presence of Ce in the zeolite greatly influences the reducibility of Pt, *i.e.*, the reduction temperature of Pt was aroused by more than 120 °C after the KL support was promoted by Ce. This clear metal-support interaction may in fact be responsible for the enhanced resistance to metal agglomeration displayed by the Ce-promoted catalysts under reaction conditions.

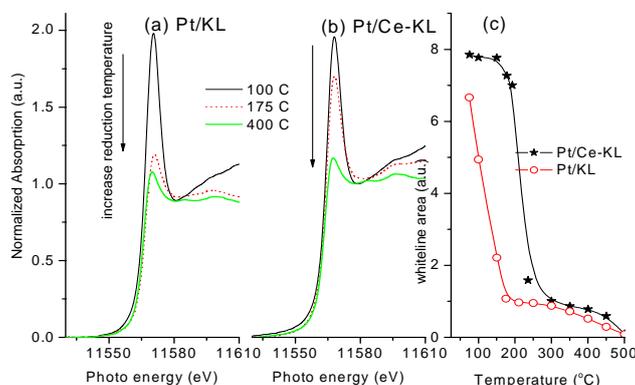


Figure 2. The L_3 edges of the unpromoted Pt/KL (a) and promoted Pt/Ce-KL (b) after reduction at different temperature. (c) Variation of the area under the first peak in the XANES spectra (whiteline) as a function of reduction temperature. The decrease in the size of the whiteline indicates the reduction of Pt.

4. Conclusions

In summary, we studied the XAFS properties of the Pt nano-clusters supported on the Ce-promoted and pristine KL zeolites. It was found that, although the Pt particle size and location inside the zeolite is very similar in the two zeolites, the presence of the Ce seems to have influence on the electronic potential around Pt, which may be responsible for the observed enhanced stabilization of the small Pt clusters. The presence of Ce in the zeolite also greatly affects the reducibility of Pt. We have ascribed the improved stability to an inhibition in the agglomeration of Pt particles, which normally occurs on the unpromoted Pt/KL catalysts. This inhibition can be linked to metal-support interactions that are enhanced by the presence of rare earth oxides and are made evident by XANES analysis.

Reference

- [1] Manninger I., Zhan Z., Xu X. L., Paal Z., 1991 *J. Mol. Catal.* **65** 223.
- [2] Ostgard D. J., Kustov L., Poepelmeier K. R., Sachtler W. M. H., 1992 *J. Catal.* **133** 342.
- [3] Fang X., Li F., Lao L., 1996 *Appl. Catal. A* **146** 297.
- [4] Grau J. M., Daza L., Seoane X. L., Arcoya A., 1998 *Catal. Lett.* **53** 161.
- [5] Fang X., Li F., Zhou Q., Luo L., 1997 *Appl. Catal.* **161** 227.
- [6] Chen C., Bian G., Jiang M., Li Z., and Wei S., 1999 *Chinese Journal of Catalysis*, **20** 659.
- [7] Hannemann S., Casapu M., Grunwaldt J.-D., Haider P., Trüssel P., Baiker A., and E. Welter, 2007 *J. Synchrotron Rad.* **14** 345.
- [8] Stöhr, J. NEXAFS Spectroscopy; Springer: Berlin, 1996.
- [9] Ramaker D. E., Mojet B. L., Garriga Oostenbrink M. T., Miller J. T., Koningsberger D. C., 1999 *Phys. Chem. Chem. Phys.* **1** 2293.
- [10] Grunert W., Muhler M., Schroder K.-P., Sauer J., Schlögl R., 1994 *J. Phys. Chem.* **98** 10920.
- [11] Koningsberger D. C., de Graaf J., Mojet B. L., Ramaker D. E., Miller J. T., 2000 *Appl. Catal. A* **191** 205.
- [12] Okamoto Y., Ogawa M., Maezawa A., Imanaka T., 1988 *J. Catal.* **112** 427.
- [13] Grange, W.; Maret, M.; Kappler, J. P.; Vogel, J.; Fontaine, A., *Phys. Rev. B* **1998**, *58*, 6298.
- [14] Vogel J., Fontaine A., Cros V., Petroff F., Kappler J.-P., Krill G., Rogalev A., and Goulon J., 1997 *Phys. Rev. B* **55**, 3663.