

XAFS analysis of PtGe supported catalysts for dehydrogenation reactions

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INTRODUCTION

A great variety of industrial reactions are catalyzed by systems base on Pt-group metals, in which the activity and selectivity are modified by the addition of a second metal. The characteristics and performance of these catalysts depend strongly on the preparation methods. Because of this reason, preparation methods that lead to reproducible solids are being developed. One of these is based on the application of the surface organometallic chemistry on metals (SOMC/M) [1].

In this work we study how the addition of Ge affects the selectivity to isobutene and the overall activity on Pt catalysts. In particular we characterized both the Pt and Ge phases present in catalyst supported on SiO₂ and studied the interaction between them by XAFS.

EXPERIMENT

For the preparation of the platinum monometallic catalysts a solution of H₂PtCl₄ was added onto the SiO₂ and a solution of [Pt(NH₃)₄]²⁺ was added on functionalized silica. In both cases the solution had a concentration so as to obtain 1 % w/w Pt exchanged on the support. Then, the solids were repeatedly washed, dried at 105 °C, calcined in air at 500 °C and reduced in flowing H₂ at the same temperature. The bimetallic systems have been prepared by reaction between the monometallic catalyst and Ge(C₄H₉)₄ following the methodology describes elsewhere [2]. The bimetallic phase is obtained after elimination of organic groups by activation in H₂ at 550 °C during 2 hours. Resulting catalysts are denominated PtGe_x, where x indicates the atomic relation Ge/Pt.

The XAFS experiments were performed at the D04B-XAS1 beam line at the LNLS, Campinas, Brazil. The Ge K-edge and Pt-L_{2,3} spectra for the samples were collected in transmission mode at RT using a Si(111) single channel-cut crystal monochromator. Three ion chambers were used as detectors and were filled with air at ambient pressure. The energy calibration was obtained by simultaneous absorption measurements of metal foils positioned between the second and the third ionization chambers.

RESULTS AND DISCUSSION

As the amount of Ge is increased, a decreased in the overall activity of the catalyst is observed. Simultaneously, an in-

crease of the selectivity to isobutene is achieved, reaching values of 95 %, as a consequence of a penalization of the cracking reactions. This shows that this methodology leads to PtGe active and highly selective phases to olephines.

EXAFS results show that no Pt-Ge bimetallic phase is formed, contrary to what was previously observed in PtSn catalysts [3]. EXAFS results at the Pt L₃ edge show that Pt is found forming small metallic particles (Figure 1). As the quantity of Ge is increased, there is an increase in the Pt-Pt coordination number. This can be indicating that small quantities of Ge interact strongly with Pt, favoring the dispersion. As more Ge is added, it may segregate forming isolated phases.

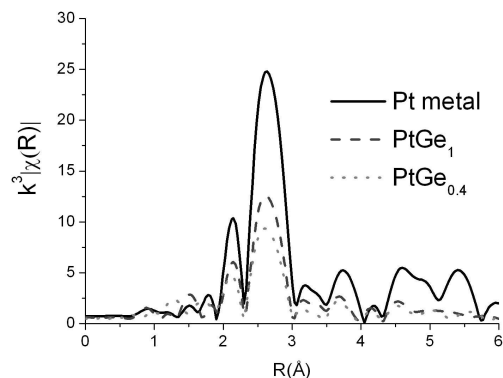


FIG. 1: Fourier Transforms of the Pt-L₃ edge EXAFS spectra.

This stronger interaction between Pt and Ge when smaller amounts of Ge are added is also evidenced in the Pt L₃ edge XANES spectra (Figure 2). It is observed that the increase of the white line intensity is bigger for PtGe_{0.4} indicating that there is a higher charge transfer per Pt atom to the Ge phase.

The most intriguing results are those obtained at the Ge K-edge as, contrary to what was expected, no metallic phase is observed. Both XANES (not shown here) and EXAFS (Figure 3) results show Ge forming and oxide phase which can no be responsible for the increase of the selectivity of the catalyst. It is suspected that only a small amount of Ge (less than 10 %) may be in metallic form and can not be detected by XAFS. Further experiments are required in order to clarify this apparent contradiction.

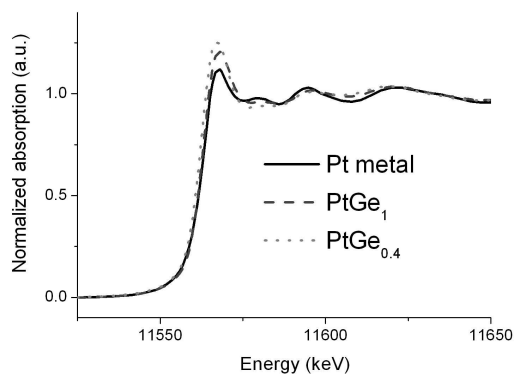


FIG. 2: XANES spectra at the Pt-L₃ edge.

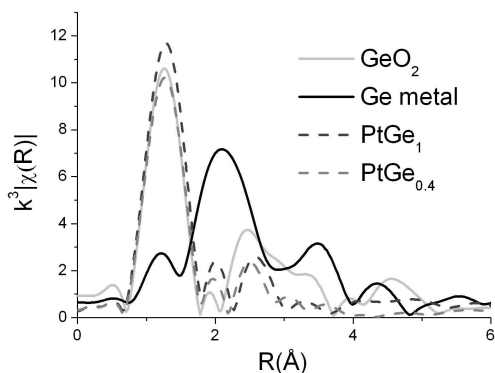


FIG. 3: Fourier Transforms of the Ge-K edge EXAFS spectra.

CONCLUSION

Highly selective PtGe catalysts were studied by XAFS. Results indicate that both metals form separated species with no evidence of the formation of alloys. However, Pt seems to be dispersed by small amounts of Ge and a stronger interaction between metals is found with the smaller amount of Ge. The existence of a metallic Ge phase, which could be responsible for the high selectivity to isobutene could not be detected.

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