

Structure and Reactivity of Cluster-Derived PtFe/SiO₂ Catalysts

Attilio Siani,¹ Oleg S. Alexeev,¹ Burjor Captain,² Gwendoline Lafaye,³ Richard D. Adams,² and Michael D. Amiridis*¹

¹Department of Chemical Engineering and ²Department of Chemistry and Biochemistry
University of South Carolina, Columbia, SC 29208 (USA)

³Laboratoire de Catalyse en Chimie Organique,
UMR CNRS 6503 Université de Poitiers, Poitiers Cedex, F-86022 (France)

*amiridis@enr.sc.edu

Introduction

Research conducted with supported bimetallic catalysts for several years has led to the recognition that their catalytic properties often are better than the simple sum of the properties the two constituent metals. These properties can be dramatically affected by the size and composition of the metal nanoparticles in the bimetallic catalyst and their interactions with the support and between each other. The research interest in such materials continues to grow since various bimetallic combinations were found to be important for large-scale industrial applications [1-3]. The limited understanding of the nature of the bimetallic interactions contributes to difficulties in the preparation of stable, highly dispersed, and well-defined bimetallic structures by conventional catalyst preparation techniques. Organometallic chemistry provides opportunities to prepare supported bimetallic catalysts with maximized bimetallic interactions. The goal of this work was to prepare and characterize SiO₂-supported Pt-Fe catalysts starting from Pt₅Fe₂(COD)₂(CO)₁₂ and PtFe₂(COD)(CO)₈, precursors which already contain well-defined Pt-Fe bonds.

Materials and Methods

Supported catalysts were prepared by slurring of the Pt₅Fe₂(COD)₂(CO)₁₂ or PtFe₂(COD)(CO)₈ precursors in CH₂Cl₂ with the SiO₂ support in powder form for 24 h under nitrogen flow in the absence of light. The solvent was allowed to evaporate slowly during this period of time to ensure complete uptake of the precursor by the support. The amount of each precursor was chosen to yield samples containing 1 wt% Pt after ligand removal. The corresponding Fe content was 0.57 and 0.11 wt % for PtFe₂(COD)(CO)₈/SiO₂ and Pt₅Fe₂(COD)₂(CO)₁₂/SiO₂, respectively, as determined based on the stoichiometry of the clusters. Monometallic Pt/SiO₂ and bimetallic PtFe/SiO₂ samples were also prepared for comparison by conventional incipient wetness impregnation of the support with an aqueous solution of H₂PtCl₆ and a mixture of H₂PtCl₆ and Fe(NO₃)₃, respectively. EXAFS spectra were collected at beamline 2-3 at SSRL. FTIR spectra were recorded with a Nicolet Nexus 470 spectrometer equipped with a MCT-B detector cooled by liquid nitrogen. Spectra were recorded at a spectral resolution of 2 cm⁻¹, with 64 scans accumulated per spectrum.

Results and Discussion

EXAFS and IR spectroscopy were used to characterize the surface species formed following the interaction of Pt₅Fe₂(COD)₂(CO)₁₂ and PtFe₂(COD)(CO)₈ with SiO₂ and to monitor the decarbonylation process needed to activate these catalysts. The results indicate that both clusters can be deposited intact on the SiO₂ support. Both clusters remained weakly

bonded to the support and could be extracted from the surface back into a CH₂Cl₂ solution without any significant changes in their structure. Infrared data further indicate that subsequent heating in H₂ or He led to a gradual removal of the ligands, which was completed at approximately 350°C. The treatment in H₂ appeared to be more favorable than that in He. For example, when Pt₅Fe₂(COD)₂(CO)₁₂ was used as the precursor, the Pt atoms remained mostly bonded to Fe atoms after removal of the ligands in H₂, as evidenced by the first-shell Pt-Fe contributions with coordination numbers of 1.0 at a bond distance of 2.67 Å (measured at the Pt L₃ edge) and the first-shell Fe-Pt contributions with a coordination number of 2.3 at a distance of 2.67 Å (measured at the Fe K edge). Thus, the EXAFS results suggest that the Pt-Fe interactions were strong in this case and were largely maintained during decarbonylation under reducing conditions, although the geometry of the cluster frame was changed significantly, since the average Pt-Pt bond distance decreased from 2.77 to 2.74 Å, while the average Pt-Fe and Fe-Pt bond distances increased from 2.58 to 2.67 Å. In contrast, He treatment appears to lead to complete disintegration of the cluster frame. IR results further indicate that the original cluster can not be reconstructed by exposure of the decarbonylated species to CO, thus demonstrating the irreversible character of the structural changes taking place during removal of the ligands. The observed structural changes during removal of the ligands were also accompanied by an increase of the Pt-Pt first-shell coordination number from 3.2 to 6.0, indicating some aggregation of Pt. However, the values of the Pt-Pt first-shell coordination numbers observed in the fully decarbonylated samples indicate that the degree of aggregation was relatively low, which resulted in a formation of highly dispersed Pt-Fe bimetallic structures on the SiO₂ surface.

The cluster-derived samples were more active than conventionally prepared ones of the same nominal composition for the oxidation of CO. However, some deactivation was observed with time on stream, suggesting that the properties of the Pt-Fe sites can be altered by the reactants. Kinetic results show that the activity of cluster-derived samples for CO oxidation correlates well with the fraction of bimetallic interactions, the Pt/Fe ratio, and the strength of the CO adsorption. The cluster-derived samples were also more active than Pt/SiO₂ for the selective oxidation of CO in the presence of H₂, exhibiting a selectivity of approximately 92 % at temperatures up to 60°C. In this case the deactivation with time on stream was substantially lower, suggesting that the highly reducing reaction environment encountered in this case helps maintain the structure and properties of the active Pt-Fe bimetallic sites.

Significance

The characterization of PtFe/SiO₂ catalysts prepared from molecular bimetallic cluster precursors allowed us to gain a better understanding of the structure of the bimetallic species formed in this case, and their correlation with the rate of CO oxidation in the presence and absence of H₂. These results advance the current understanding of Pt-Fe bimetallic catalysts and lay a foundation for tailoring their catalytic properties in the future.

References

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