Structure Property Relationships of Supported Pt/Ni Bimetallic Catalysts

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Introduction

Bimetallic catalysts are of great interest because they often display properties that differ from either of their parent metals [1]. Combined experimental and theoretical studies on the Ni/Pt(111) bimetallic system have shown that the location of Ni atoms in the Pt(111) surface greatly influences the electronic and chemical properties [2]. The bimetallic surface consisting of a monolayer of Ni on top of bulk Pt(111), designated Ni–Pt–Pt(111), binds hydrogen and alkenes much more strongly than either parent metal, resulting in decreased hydrogenation activity. In contrast the surface consisting of a monolayer of Ni atoms in the subsurface region designated as Pt–Ni–Pt(111), has been shown to weaken metal-hydrogen bonds in comparison to Ni–Pt–Pt(111) or either parent metal surface. The resulting abundance of weakly bound hydrogen and alkenes on the Pt–Ni–Pt(111) surface increases its activity for novel low temperature hydrogenation pathways [3, 4].

The objective of the current study is to extend previous investigations on single crystal surfaces to supported catalysts in an attempt to bridge the materials gap. A series of bimetallic catalysts was synthesized to study the effects of Pt:Ni metal atomic ratio and impregnation sequence. Using benzene hydrogenation as a probe reaction we show that the supported bimetallic catalysts outperform either monometallic catalyst. We also show that the enhanced activity of the bimetallic is a synergistic effect due to Pt-Ni interactions, since the monometallic Ni catalyst is completely inactive to benzene hydrogenation. The presence of bimetallic nanoparticles was confirmed using extended x-ray absorption fine structure (EXAFS).

Materials and Methods

In this work, Pt, Ni, and Pt-Ni bimetallic catalysts supported on γ-Al_2O_3 were synthesized via incipient wetness with $Pt(NH_3)_4(NO_3)_2$ and $Ni(NO_3)_2 \bullet 6H_2O$ precursors. The kinetics of benzene hydrogenation at 343 K on the reduced monometallic and bimetallic catalysts was measured in a stainless steel batch reactor using Fourier transform infrared (FTIR) spectroscopy to monitor the gas-phase concentrations of reactants and products. Pt L_{III} edge EXAFS measurements were collected and analysis of the first coordination shell was performed to detect bimetallic interactions. Catalyst particle size distribution and surface area were characterized using high angle annular dark field (HAADF) microscopy and CO chemisorption, respectively. Catalysts were reduced *in-situ* at 723 K for reactor, EXAFS, and chemisorption studies, while microscopy was performed on spent catalysts.

Results and Discussion

Table 1 summarizes the compositions of the catalysts, rate constants for benzene hydrogenation, and the results of EXAFS analysis. The rate constants for benzene hydrogenation were obtained by performing a first order fit to the disappearance of benzene. Inspecting these rate constants reveals that the 1.5 wt% Ni/γ-Al_2O_3 catalyst is completely inactive to this reaction. The Pt/γ-Al_2O_3 catalyst does show activity to benzene hydrogenation; however the bimetallic catalysts are more active, as evidenced by the rate constants in Table 1. The activity of the bimetallic catalysts increase with increased Ni loadings. The EXAFS analysis also shows that as Ni loading increases, so do the coordination numbers (CN) for the Pt-Ni bimetallic interaction. Combining the EXAFS results with the hydrogenation results shows that the activity of the catalysts correlates to the extent of bimetallic nanoparticle formation.

Table 1. Summary of catalyst loading, rate constants, and first shell EXAFS analysis

	Metal Loading (wt%)		Atomic Ratio Pt:Ni	k_{-C6H6} (min^{-1})	Pt L_{III} EXAFS	
	Pt	Ni			Shell	CN
Ni/γ–Al_2O_3	---	1.5	---	~ 0	---	---
Pt/γ–Al_2O_3	1.7	---	---	2.5×10^{-3}	Pt-Pt	5.8 ± 0.6
Pt/Ni/γ–Al_2O_3	1.7	0.5	1:1	4.2×10^{-3}	Pt-Pt	6.6 ± 0.8
					Pt-Ni	2.0 ± 0.7
Pt/Ni/γ–Al_2O_3	1.7	1.5	1:3	4.1×10^{-3}	Pt-Pt	4.6 ± 0.7
					Pt-Ni	2.6 ± 0.6
Pt/Ni/γ–Al_2O_3	1.7	5.0	1:10	6.0×10^{-3}	Pt-Pt	5.4 ± 0.8
					Pt-Ni	3.2 ± 0.5

Significance

In this work we demonstrate that supported Pt/Ni bimetallic catalysts are better benzene hydrogenation catalysts than either parent metal catalysts. This suggests that the low temperature hydrogenation pathways that are observed on the Pt–Ni–Pt(111) surface may also be present on the supported catalysts. Observing these similarities between single crystal surfaces and supported catalysts is an important step in bridging the materials gap, and shows that model surfaces can be used as predictive tools in the rational design of novel catalysts.

References

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