

Characterization and catalytic evaluation of dendrimer-derived Pt-Cu/SiO₂ catalysts

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Introduction

A comparative study of dendrimer-derived (DD) and conventionally-derived (CD) monometallic Pt and Cu catalysts and bimetallic Pt-Cu catalysts with Pt/Cu atomic ratio of 1:1 (Pt₂₀Cu₂₀) and 1:3 (Pt₁₀Cu₃₀), all supported on SiO₂, showed different features in particle size and distribution, FTIR of CO adsorption and catalytic performance for hydrodechlorination of 1,2-dichloroethane (DCE). FTIR analyses using ¹²CO/¹³CO isotope dilution were conducted to investigate the band shifts caused by dipole coupling interactions, possible electron transfer between Cu and Pt sites, and Cu-Pt surface heterogeneities. Metal dispersion was determined from H₂ chemisorption and scanning transmission electron microscope (STEM) measurements. Metal surface compositions were determined by EDX and XPS analysis. Catalysts were also evaluated for the hydrodechlorination of DCE to determine the effects of composition and preparation methodology on reactivity and selectivity patterns to different products.

Materials and Methods

Mesoporous SiO₂ support was obtained from Engelhard Corporation and used as received. The metal salts used as Pt and Cu precursors were H₂PtCl₆·6H₂O (99.9%) and CuCl₂ (99%), both from Alfa. The reactant 1,2-dichloroethane (99.8%) and PAMAM G4OH dendrimer (10 wt% in methanol) were purchased from Aldrich. The synthesis of DD monometallic Pt nanocomposites has been described elsewhere [1], and a co-complexation method was used for the synthesis of the DD bimetallic composites. The metal-complexed dendrimers were deposited on SiO₂ using standard wet impregnation methods. Corresponding CD samples using the same metal salt precursors (in absence of dendrimer) were also prepared using standard wet impregnation methods for comparison with the DD analogs. All samples were calcined in 10% O₂ (balance He) at 350°C for 1 h to decompose dendrimers and to remove the organic residues from the support, and subsequently reduced in flowing H₂ for 1 h at 350°C to obtain the final catalysts. STEM measurements were carried out using a Hitachi HD2000 and *in situ* FTIR spectra were recorded using a Nicolet 4700 spectrometer equipped with a liquid N₂-cooled MCT/A detector. The effluent from the hydrodechlorination reaction was analyzed using an in-line GC equipped with both TC and FI detectors. Products were separated using a 30m long Poraplot Q capillary column.

Results and Discussion

STEM analysis suggests that the G4OH dendrimer exerts significant control over particle formation and particle size stability on the catalyst support (Table 1). EDX analysis confirms the formation of both Pt-enriched and Cu-enriched sites in the bimetallic catalysts which favor the formation of different products during the hydrodechlorination of DCE. Differences in IR spectra can be related to the differences in metal oxidation state, particle sizes, and relative Pt/Cu compositions of the catalysts. Addition of Cu to Pt lowers the stretching frequency for linearly adsorbed CO (Figure 1). However, no obvious electronic

modification of the active Pt sites by Cu in the Pt-Cu bimetallic catalysts can be inferred from the FTIR ¹³CO isotope studies. Two different mechanisms for hydrodechlorination of DCE reaction are proposed for Pt-enriched and Cu-enriched sites, respectively.

Table 1. Average particle size for SiO₂-supported, Pt-containing catalysts. Pt₄₀* refers to 40 Pt atoms for each dendrimer molecule while other compositions refer to number of Pt and Cu atoms per dendrimer molecule. The data summarize the results of the average particle size for both DD and CD catalysts based on STEM measurements. The DD catalysts have smaller particles and more narrow size distributions than their CD analogues.

Mean size (nm)	Pt ₄₀ *		Pt ₂₀ Cu ₂₀		Pt ₁₀ Cu ₃₀	
	DD	CD	DD	CD	DD	CD
	1.5±0.5	3.0±2.3	2.2±0.8	2.6±1.6	1.6±0.6	2.7±1.6

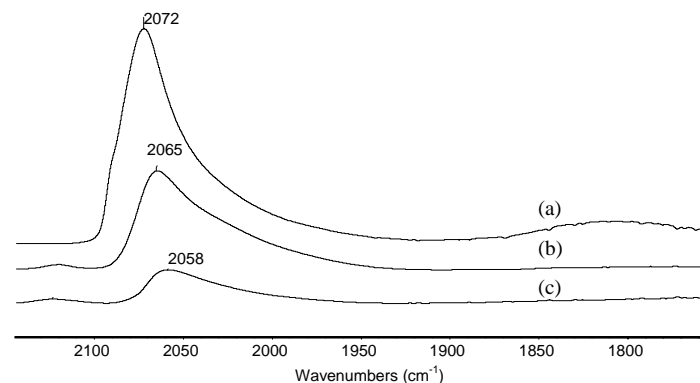


Figure 1. FTIR CO adsorption on a) Pt₄₀-DD catalyst, b) Pt₂₀Cu₂₀-DD catalyst, c) Pt₁₀Cu₃₀-DD catalyst. This figure shows the difference in FTIR spectra of the adsorbed CO on DD catalysts. The addition of Cu in Pt-Cu catalysts weakens the dipole coupling interactions between the adsorbed CO species on Pt ensembles.

Significance

Chlorinated hydrocarbon by-products from industrial processes can cause severe environmental pollution [2]. The results of this study show that optimal effects of bimetallic Pt-Cu catalysts on the reactivity and selectivity for hydrodechlorination of DCE can be achieved if intimate contact between the Cu and Pt components exists.

References

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