Hydrogen Assisted Dechlorination of 1,2-dichloroethane over $PtCu/SiO_2$ and $PtCu/SiO_2/Si$ Catalysts: Influence of PtCu and PtSi Alloy Formation on Selectivity

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Reaction of hydrogen assisted dechlorination (HDCl) 1,2-dichloroethane (1,2-DCE) over conventional $PtCu/SiO_2$ and model $PtCu/SiO_2/Si$ catalysts prepared by spin-coating method [1] was studied by the set of physical surface and kinetic characterization techniques. The objective of this reaction is conversion of environmentally harmful 1,2-DCE into olefins, C_2H_4, with high selectivity.

$PtCu/SiO_2$ catalysts have showed a performance which is in an agreement with published data [2]: Pt/SiO_2 was unselective towards C_2H_4, in turn, all bimetallic catalyst showed non-zero selectivity towards C_2H_4. In general, there was correlation of selectivity with Cu/Pt ratio: the higher was the ratio the higher was selectivity towards ethylene. Variation of reduction temperature (220 or 500 ºC) during the pretreatment conditions was performed in order to control the degree of alloying between Pt and Cu. Selectivity response was inversely proportional to reduction temperature: increase of reduction temperature cause the decrease of selectivity towards C_2H_4. FTIR study of CO as a test molecule was implemented to address the influence of electronic ("ligand") and ensemble size effects upon alloying on selectivity of HDCl of 1,2-DCE reaction. It was found out that ensemble size effect is the prime factor which defines high selectivity.

Model $PtCu/SiO_2/Si$ catalysts with metal loading close to 6 at nm^{-2} showed very interesting behavior in comparison with conventional $PtCu/SiO_2$ catalysts. First, $Pt/SiO_2/Si$ reduced at 220 ºC showed non-zero (~35%) conversion towards C_2H_4(!), which was ascribed to partial HDCl of 1,2-DCE over Si. High dispersion of Pt can also impede to the passing of C_2H_4 hydrogenation reaction. Second, increase of pretreatment reduction temperature up to 500 ºC with the objective to decrease the dispersion of Pt led to very interesting result: selectivity towards C_2H_4 increased up to 70%. This behavior was ascribed to formation of Pt-Si alloy. And finally, increase of Cu content resulted in increase of selectivity. In turn, increase of reduction temperature led to 100% selectivity for $PtCu/SiO_2/Si$ catalyst with Cu/Pt ratio 1.

Mechanism of Pt-Cu and Pt-Si alloys formation, and influence of ensemble size effect on selectivity performance 1,2-DCE HDCl reaction will be discussed.

References:

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2. Vadlamannati, L.S., V.I. Kovalchuk, and J.L. d'Itrie, *Dechlorination of 1,2-dichloroethane catalyzed by Pt-Cu/C: unraveling the role of each metal.* Catalysis Letters, 1999. **58**(4): p. 173-178.