

Selective Hydrodechlorination of 1,2-Dichloroethane over Pd-Pt Catalysts

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Introduction

An application of the dechlorination reaction in the presence of H₂ lies in the conversion of a chlorinated by-product into a useful compound, for example in the conversion of 1,2-dichloroethane into ethylene [1]. The subsequent hydrogenation to alkanes is not desirable due to the lower value of these compounds. VIII-B group metals have displayed good performance in the hydrodechlorination, however this reaction would lead to ethane. Bozelli et al. [1] have demonstrated the ability of bimetallic catalysts, composed of metals from Groups VIII and IB, to convert chlorinated alkanes into less-chlorinated or unchlorinated alkanes, due to the reduction in the hydrogenation capacity of these bimetallic systems. This new alternative is very attractive, because alkenes are raw materials for numerous of industrial reactions. These bimetallic catalysts display lower poisoning degree [2, 3] compared to monometallic catalysts, and the selectivity of the Pd/SiO₂ catalyst may be improved by the addition of a second metal, by a dilution effect and/or alloy formation [4].

Heinrichs et al. [3] reported an increase in the activity and selectivity to ethylene of Pd-Ag/SiO₂ catalysts during CClH₂ClCH₂ hydrodechlorination of 1,2-dichloroethane.

In the present paper we report the effect of Pt in the PdPt supported in SiO₂ and MCM-41 in the reaction of hydrodechlorination of 1,2-dichloroethane. PdPt catalysts have a molar relation Pd/Pt of 4. For comparison monometallic catalyst on the same support were evaluated. Monometallic and bimetallic catalysts were prepared by impregnation method.

Materials and Methods

MCM-41 was synthesized by using fumed silica, cetyltrimethylammonium chloride as a template and tetrabutylammonium hydroxide as the second organic agent. Pd and Pt supported catalysts were prepared by impregnation using a solution of H₂PtCl₆.3H₂O and PdCl₂ as precursor to obtain catalysts with a 1 wt% metallic content. A bimetallic catalyst Pd-Pt (molar relation Pd/Pt=4) was also prepared. The materials were characterized by XRD, N₂ physisorption, UV-Vis DRS, and TPR of H₂. The reaction of hydrodechlorination of 1,2-dichloroethane (DCA) were carried out in a glass packed reactor at atmospheric pressure and 523 K. The partial pressure of DCA was 2.9 kPa. The reaction products were analyzed by GC. All reactions were run by a conversion change of less 20% in a 4 h.

Results and Discussion

XRD patterns of MCM-41 at low diffraction angles show well-resolved diffractions corresponding to a mesoporous MCM-41 structure. The MCM prepared was found to have S_{BET} around 1000 m²/g and an average pore diameter centered on 3 nm. A slight reduction of the S_{BET} was observed due to the addition of the active components. The UV-Vis-DRS and TPR-H₂ profiles of the samples, shown differences between the MCM-supported and the SiO₂-

supported catalysts. These differences can be related to the different species of metal over each support and the possible interaction between both metals.

In Table 1 it is shown the catalytic performance of supported catalysts for the hydrodechlorination of DCA. Regarding catalytic activity, as it can be seen Pd catalyst shows higher activity in both supports similar as was shown in other work [5]. The bimetallic catalyst Pd-Pt presented low specific catalytic rate related with the monometallic catalysts.

In the catalytic reaction in all catalysts, ethylene and chloroethane were the main products, and only trace amounts of ethane were detected (Table 1). The selectivity towards ethylene is > 70% in all cases. The effect of the support is not evidenced in our reaction conditions. Pt catalysts present little differences in the selectivity behavior.

The results are discussed in terms of the role of the metal on the different supports and the possible interaction of Pd-Pt on the hydrodechlorination activity.

Table 1. Specific reaction rate (r) and selectivity (%S) in DCA hydrodechlorination reaction (T= 523 K; atmospheric pressure; reaction time = 240 min)

Metal	r (mol.s ⁻¹ g ⁻¹)	r (mol.s ⁻¹ g ⁻¹)	%S Ethylene	%S Ethane	%S Chloroethane
	MCM	SiO ₂	MCM - SiO ₂	MCM - SiO ₂	MCM - SiO ₂
Pd	5.11	3.05	70.0 - 85.7	0.0 - 1.3	30.0 - 13.0
Pt	1.74	0.56	77.0 - 74.7	3.2 - 6.2	19.8 - 19.0
Pd-Pt	0.75	1.38	75.6 - 87.1	0.0 - 1.7	24.4 - 11.2

Significance

The work presents an approach to face up an environmental problem.

References

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