

MCM-41 USED AS A SUPPORT OF Pd CATALYSTS FOR THE HYDRODECHLORINATION OF 1,2-DICHLOROETHANE

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Introduction

Catalytic hydrodechlorination of organic wastes containing a variety of detrimental compounds has recently attracted a considerable interest [1]. Several catalysts has been tested in fundamental studies and those catalysts containing a noble metal (mainly Pt and/or Pd), have shown to be very active to the hydrodechlorination reaction [2]. Supported Pd catalysts have been used under mild conditions in reactions in liquid phase. There are studies on Pd, which focus on developing stable catalysts using loading higher than 10%, thereby obtaining catalysts of low Pd dispersion [3-4].

There have not been done many efforts in using mesoporous materials such as MCM-41 as supports for this kind of reaction. Kawabata et al. [5] reported that on Pd/Al-MCM-41 catalyst the dechlorination proceeded by a heterogeneous mechanism catalyzed by Pd metal particles sized less than 10 nm on the surface catalyst. In the literature it has been reported that Ni supported on Al-MCM-41 showed an acceptable activity for the exhaustive hydrodechlorination of 1,2,4-trichlorobenzene. [6],

In the present paper we report the superior catalytic behavior of the Pd catalysts supported on MCM-41 in the hydrodechlorination of 1,2-dichloroethane (DCE) compared with that supported in a commercial silica.

Materials and Methods

MCM-41 was synthesized by using fumed silica, cethyltrimethylammonium chloride as a template and tetrabutylammonium hydroxide as the second organic agent. Pd supported catalysts were prepared by impregnation using a solution of PdCl₂ as precursor to obtain catalysts with 1 wt.% Pd content. Additional catalyst were prepared over a commercial SiO₂ (Ketjens, F2) by a similar procedure for comparison.

The materials were characterized by XRD, N₂ physisorption, UV-Vis DRS and TPR of H₂. The reaction of hydrodechlorination of 1,2-dichloroethane were carried out in a glass packed reactor at atmospheric pressure and 523 K. The partial pressure of DCE was 2.9 kPa. The reaction products were analyzed by GC. All reactions were run by a conversion change of less 20% in 4 h.

Results and Discussion

XRD patterns of MCM-41 at low diffraction angles show well-resolved diffractions corresponding to mesoporous MCM-41 type structure. The MCM prepared was found to have S_{BET} around 1000 m²/g and an average pore diameter centered around 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 of H₂ of the catalysts shown differences between the Pd/MCM41 and Pd/SiO₂. This differences can be related to the different species of metal over each support. In Pd /SiO₂ the higher reduction temperatures are observed indicating a strong interaction between metal and support.

In Table 1 it is shown the catalytic performance of supported catalysts for the hydrodechlorination of DCE. Regarding catalytic activity, as it can be seen Pd catalyst supported on MCM41 shows higher activity than that prepared over the commercial support. Taking into account that DCE hydrodechlorination over Pd/SiO₂ catalysts is a structure insensitive reaction [7], the change in activity can be related to the mesoporous structure, since in this kind of reactions coke deposition which appears on the pore wall, gives place to deactivation due to the fact that the access to the active sites is inhibited. In the catalytic reaction in both samples, ethylene and chloroethane were the main products, and only trace amounts of ethane were detected by GC. The selectivity towards ethylene is of approximately 86% and 70% for Pd/SiO₂ and Pd/MCM41 respectively. In the literature it has been reported that chloroethane is an intermediate product, which is produced from the reaction of DCE with hydrogen [8]. Chloroethane can be further hydrodechlorinated to ethane, but in this case it is not observed.

Table 1. Reaction rate (k) and selectivity (%S) in DCE hydrodechlorination reaction (T= 273 K, P_{DCE} = 2.9 kPa; atmospheric pressure, time of reaction: 240 min).

Catalysts	S _{BET}	k	Ethylene	Ethane	Chloroethane
	/m ² /g	mmols ⁻¹ kg ⁻¹	%S1	%S2	%S3
Pd/S	300	3.069	85.74	1.35	12.90
Pd/MS	954	4.410	70.05	0.00	29.91

The results are discussed in terms of the properties of the surface of the mesoporous supports and the role of a possible metal-support interaction on the hydrodechlorination activity and selectivity.

Significance

The work presents an approach to face up an environmental problem

References

1. L.E. Manzer Catal. Today, 13, 13 (1992).
2. F. Alonso, I.B. Beletskaya, M.Yus, Chem. Rev., 102, 4009 (2002).
3. L. Prati, M. Rossi, Applied Catalysis B, 23, 135 (1999).
4. V. Dal Santo, C. Dossi, S. Recchia, P.E. Colavita, G. Vlaic, R. Psaro, J. Mol. Catal. A, 182 (2002).
5. T. Kawabata, I. Atake, Y. Ohishi, T. Shishido, Y. Tian, K. Takachi, K. Takehira, Applied Catalysis B, 66, 151 (2006).
6. Y Cesteros, P. Salagre, F. Medina, J.E. Sueiras, Catal. Lett. 79, 83 (2002)