

Acetonitrile hydrogenation – Influence of Acido-Basic Properties of the Support on Selectivities

Camille La Fontaine, Lise Martial, Raluca Ionescu, Charles Kappenstein and Laurence Pirault-Roy*
LACCO, UMR 6503 CNRS-Univ. de Poitiers, 40 Av. du R. Pineau, 86022 Poitiers (France)
*laurence.pirault@univ-poitiers.fr

Introduction

Amines are widely used, directly or as reaction intermediates, for numerous industrial applications: solvents, polymers, pesticides, molecules for medical purposes (antibiotics, antiviral, antihistaminic...). Amines can be synthesized by several routes, including catalytic hydrogenation of nitriles. Although such processes are commonly used, f.i. for nylon precursors, catalytic mechanisms are not yet well established. Authors particularly disagree concerning the role of the support: some of them involve a bifunctional mechanism with condensation reactions occurring on support acid sites,¹ while others reject such hypotheses.^{2, 3} Our aim was to go further in the understanding of the catalytic pathway of nitriles hydrogenation by studying the influence of acido-basic properties of Al_2O_3 , TiO_2 and MgO supports on the selectivities of supported Pt or Rh catalysts.

Materials and Method

Catalysts (1 wt.-% Pt or Rh) were prepared by wet impregnation of Al_2O_3 ($97 \text{ m}^2 \cdot \text{g}^{-1}$), TiO_2 ($43 \text{ m}^2 \cdot \text{g}^{-1}$) or MgO ($36 \text{ m}^2 \cdot \text{g}^{-1}$) with aqueous solution of $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ or $\text{Rh}(\text{NO}_3)_3$ as precursors. After calcination and reduction, the metallic accessibilities were ca. 40 % for Pt catalysts and 20 % for Rh catalysts. The catalytic performances of the obtained samples were evaluated in the gas phase hydrogenation of acetonitrile carried out at 70°C , with a molar hydrogen / acetonitrile ratio of 7.5 and a GHSV of 7400 h^{-1} .

Results and Discussion

No important selectivity change was observed using Al_2O_3 or TiO_2 as supports: ethylamine and triethylamine were the main products over Pt, while a mixture of diethylamine and triethylamine was obtained over Rh (Figure 1). On the contrary, the use of MgO support increases considerably the formation of the primary amine; nevertheless, MgO support led to a lower catalytic activity compared to Al_2O_3 . Indeed, the selectivity towards ethylamine reached more than 75 % both over MgO supported Pt and Rh catalysts. Therefore, the nature of the support seems to be predominant to determine the selectivity of the reaction, whereas the nature of the metal displays only a second order effect. We can assume that the basic properties of MgO are responsible for inhibiting the condensation reactions, leading to this significant selectivity improvement for the formation of primary amines. Thus, a bifunctional mechanism seems to be involved in hydrogenation of acetonitrile, with condensation reactions occurring on acidic sites of the support.

Rh-based catalysts were more active than platinum-based samples. Moreover, intrinsic activities of the catalysts also depend on the support: the most active samples were the catalysts supported on Al_2O_3 .

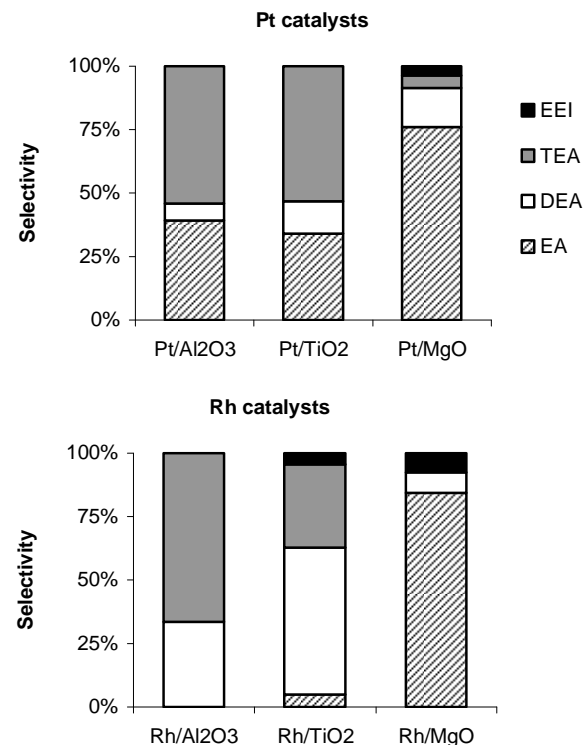


Figure 1. Selectivities (at 20 % conversion) of supported Pt and Rh catalysts in the gas phase acetonitrile hydrogenation (EA: ethylamine; DEA: diethylamine; TEA: triethylamine; EEI: N-ethyl-ethylamine).

References

1. Verhaak, M. J. F. M., van Dillen, A. J., and Geus, J. W., *Catal. Lett.* 26, 37 (1994).
2. Volf, J., and Pasek, J., *Studies in Surface Science and Catalysis* 27, 105 (1986).
3. Huang, Y., Adeeva, V., and Sachtler, W.M.H., *Appl. Catal. A, General* 196, 73 (2000).