

Performances of Noble Metal Catalysts in Acetonitrile Hydrogenation

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Introduction

Amines are involved directly or as reaction intermediates for many industrial applications: solvents, polymers, pesticides, molecules for medical purposes (antibiotics, antiviral, antihistaminic...). The existing production processes are complex and generally not selective towards the desired amine, requesting an additional separation step. The interest of catalytic hydrogenation of nitriles consists in decreasing the number of steps during the syntheses and mostly in affording better selectivities. To achieve such objectives, heterogeneous catalysts based on noble metals have been chosen due to their good performances in similar reactions, such as hydrogenation of carbonyl derivatives [1]. The aim of our work was to study the catalytic properties of monometallic M / Al₂O₃ catalysts (M = Pt, Pd, Rh) in the gas phase hydrogenation of acetonitrile in order to investigate the metal influence and the effect of the particle size.

Materials and Methods

1 wt% M / Al₂O₃ catalysts were obtained by wet impregnation of alumina (Oxid C from Degussa, 100 m².g⁻¹) with Pt(NH₃)₂(NO₂)₂, Rh(NO₃)₃ and Pd(acac)₂. After calcination and reduction, the obtained samples were characterized by different techniques (H₂ chemisorption, TEM). Finally, their catalytic performances were evaluated in gas phase hydrogenation of acetonitrile carried out at 50°C, with a molar hydrogen / acetonitrile ratio of 7.5 and a GHSV of 7200 h⁻¹. The reaction temperature was chosen pretty low to decrease the initial activity of some of the samples, so that selectivities of all samples could be compared at a reasonable and identical conversion reached during the first minutes of the catalytic tests.

Results and Discussion

The study was first focused on the activity of the prepared catalysts in acetonitrile hydrogenation. Pd appeared as the least interesting metal from those evaluated during this study: the activity in our operating conditions was rather low and these samples allowed to produce only triethylamine which was not the desired product. Compared to Pd samples, catalysts based on Rh or Pt exhibited a higher activity. However, Pt and Rh catalysts were also affected by deactivation, especially Rh samples. Indeed, although the activity was initially particularly interesting on Rh catalysts, it decreased considerably during the first twenty minutes on stream (see Figure 1a). On the contrary, the deactivation observed over Pt catalysts was less pronounced.

Concerning the selectivities, we compared Pt and Rh catalysts at 40% conversion (see Figure 1b). Rh catalysts produced a mixture of diethylamine and triethylamine, whereas Pt catalysts were the most interesting since they led to the formation of ethylamine (the desired product). Nevertheless, studies are in progress to enhance the selectivity towards this primary amine as triethylamine is still produced in important amount.

Further work will be focused on the optimization of these noble metal catalysts by adding other elements via organometallic grafting. Indeed, controlled surface reactions lead to very specific interactions between metals [2, 3] that could improve stabilities and selectivities.

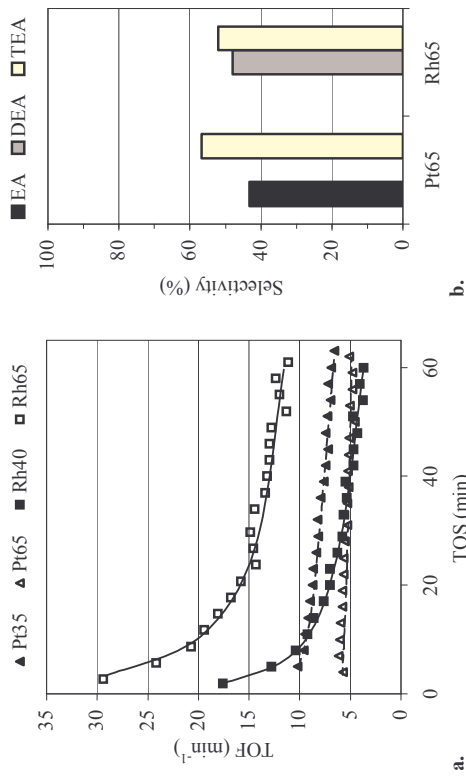


Figure 1. Catalytic behaviour of Pt and Rh catalysts in gas phase acetonitrile hydrogenation (each sample is named from the symbol of the element followed by the value of the metallic accessibility determined by H₂ chemisorption).

a. TOF of the catalysts as a function of time on stream.
b. Selectivities of two of the catalysts at 40% conversion.

Significance

Although amines are commonly used for many industrial applications, their production involves multi-steps processes. Moreover, bad selectivities towards primary amines (most required amines) and separation steps due to monophasic systems lead to high production cost. So, catalytic hydrogenation of nitriles appears to be an interesting alternative to decrease the number of steps and to selectively produce the desired amine. Especially, the use of heterogeneous catalysts based on noble metals is promising since interesting results have been obtained for activities and selectivities.

References

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