The role of Pt and Rh nanoparticles in the hydrogenation of unsaturated nitriles

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Introduction

The chemoselective hydrogenation of unsaturated carbonyl or nitrile compounds is basic process in the synthesis of important fine chemicals. The unsaturated amines are most valuable products in the reaction of nitriles, however, the selective hydrogenation of –CN group in the presence of C=C bond is a difficult task. These reactions can be achieved over supported noble metals, however, there are several factors affected on the activity and selectivity. These are the metal, support, size and shape of the particles, preparation, activation, etc. Pt, Rh nanoparticles supported on MCM-41 or SBA-15 mesoporous materials could be active and selective in the hydrogenation of unsaturated nitriles. Pt and Rh nanoparticles can be prepared by alcohol reduction of the proper salt in the presence of PVP [poly(vinyl-pyrrolidone)].

In this work we prepared different Pt and Rh catalysts supported on SBA-15 and MCM-41 mesoporous structures and tested them in the hydrogenation of light α,β-unsaturated nitriles (acrylonitrile: AN, methacrylonitrile: MAN and crotonitrile: CN).

Experimental

For synthesis of Pt nanoparticles PVP was sonicated in ethylene glycol (EG), and K_2PtCl_4 was dissolved in distilled water was dropped into the PVP solution slowly. In the synthesis of Rh nanoparticles $RhCl_3$ was dissolved in water and it was added to a stirred solution of PVP in EG at 190 °C.

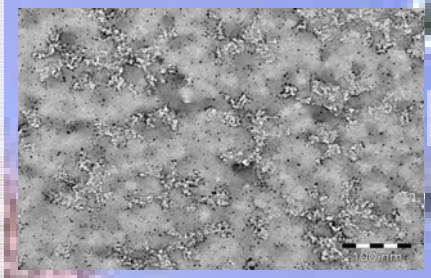
For preparation of supported catalysts, calculated amount (0.1, 1.0 or 2.0 w/w%) of Pt, Rh or Pt-Rh (bimetallic) nanoparticle solution was mixed in ethanol and pure siliceous SBA-15 or MCM-41 was added and the suspension was sonicated.

The nanoparticles were characterized by TEM and the supported samples were analyzed by XRD, TEM and nitrogen adsorption.

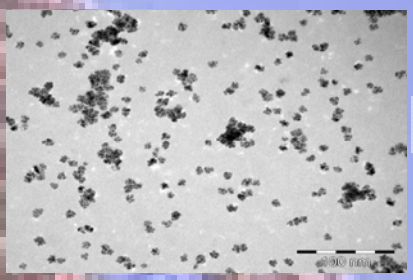
Acrylonitrile hydrogenation was monitored using a reaction cell that permitted IR measurements of the gas phase as well as the catalyst surface that was pressed in a wafer and inserted in the reactor. IR spectroscopy is an excellent tool for analyzing different unsaturated nitriles.

The hydrogenation of nitriles was carried out in the temperature range of 20-50 °C in a laboratory batch reactor with flowing hydrogen at atmospheric pressure using acetone as solvent. For each experiment 1 cm^3 reactant (AN, MAN or CN) and 100 mg catalyst were added into 50 cm^3 solvent, and the reaction was followed by five hours. The GC analysis was carried out using a *Shimadzu GC2010* equipment with a *Supelco* SPB-PUFA column.

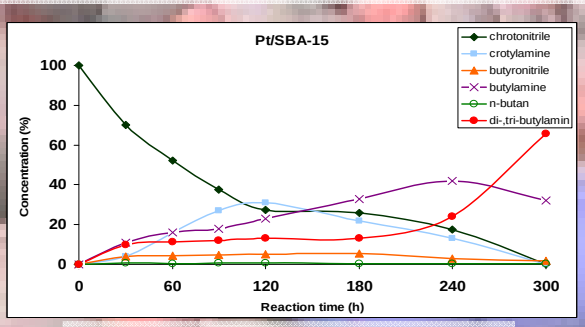
Characteristics of the catalysts



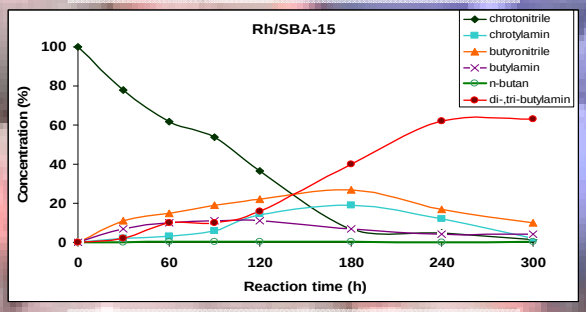
TEM image of Pt nanoparticles



TEM image of Rh nanoparticles



The kinetic curves of crotonitrile hydrogenation on Pt/SBA-15



The kinetic curves of crotonitrile hydrogenation on Rh/SBA-15

Results and discussion

The particles are dominantly cubic, while the particle size distribution is quite uniform. We found that the average particle size of Pt nanocrystals is 3-4 nm, while the average size of the discrete Rh particles is about 7-8 nm. In the hydrogenation of AN in the presence of Pt/SBA-15 the formation of allylamine as intermediate and propylamine (PA) could be detected. Unexpectedly amount of propionitrile could be observed, while it would be the main product of hydrogenation of C=C bond. However, all of the components mentioned reacted further to form di- and tri-PA.

Over Rh/SBA15 formation of propionitrile was observed indicating the activity of this catalyst in the hydrogenation of C=C bond.

In the hydrogenation of MAN over Pt/SBA-15, the formation of methallylamine (max. selectivity 20 % at 1 h reaction time) and isobutylamine (25 % at 4 h) was higher than the similar products in the reaction of AN. Formation of higher amines also took place with total hydrogenation into isobutene. Over Rh/SBA-15 both butyronitrile (max. 27 % at 3 h) and isobutylamine (~ 20 % at 4 h) formed.

The conversion of CN is close to 100 % at 5 h. The selectivities have similar features but higher values for the valuable products than that of AN or MAN.

Conclusions

The nanoparticles containing Pt/SBA-15 and Rh/SBA-15 catalyst are active in the hydrogenation of light unsaturated nitriles, the reactions are different over the catalysts system, which is a proper starting point to the optimization for production the desired compounds.

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