

Synthesis of Amines from Nitriles on Metal-supported Catalysts: Impact of Solvent on Catalyst Activity and Selectivity

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Introduction

The catalytic hydrogenation of nitriles is an important route to produce the corresponding amines that are widely used in industry as pharmaceutical and polymer intermediates, solvents, surfactants and speciality chemicals. Although saturated nitriles are initially hydrogenated to primary amines (BA), consecutive condensation reactions usually produce also secondary (DBA) and tertiary amines (TBA). Frequently, a high selectivity to a particular amine is wanted in order to eliminate the cost of product separation process. Thus, increasingly research efforts have been devoted to gain fundamental knowledge on the selectivity of nitrile hydrogenation toward different amines. There is a general agreement that on metal-supported catalysts the reaction selectivity depends mainly on the nature of the metal component [1], but the choice of suitable solvents is also critical to obtain high catalytic activity and selectivity. However, very few papers dealing with the effect of solvent on the reaction activity and selectivity for nitrile hydrogenation towards amines have been published. Optimal solvent selection needs a detailed knowledge on the relationship between the chemical nature of the solvents and the gas-liquid-solid interactions taking place in slurry reactors. Precisely, in recent works, we have discussed the influence that the interactions solvent-catalyst, solvent-reactant and reactant-solvent-catalyst have on the activity and selectivity of metal-supported catalysts for liquid-phase hydrogenation reactions [2]. Here we study the liquid-phase hydrogenation of butyronitrile (BN) to amines on Ru/SiO₂, Pd/SiO₂ and Pt/SiO₂ catalysts in n-butanol (BOL, protic solvent), toluene (TOL, non-polar aromatic solvent) and cyclohexane (CYH, non-polar naphthenic solvent).

Materials and Methods

Pt(0.27%)/SiO₂, Pd(0.33%)/SiO₂, and Ru(1.8%)/SiO₂ catalysts were prepared by incipient-wetness impregnation. The solvent-catalyst interaction strength was investigated by temperature-programmed desorption (TPD) of solvents and mass spectrometry. BN hydrogenation was studied at 13 bar in a batch reactor at 403 K. The main reaction products detected were BA, DBA, TBA, and butylidene-butyamine (BBA).

Results and Discussion

As an example, Figure 1 shows the curves of BN conversion (X_{BN}) and yields as a function of time obtained on Ru/SiO₂ in toluene. Data of the initial BN conversion rates per g of metal (r_{BN}^0 , mol/h g_M) and of selectivities and X_{BN} at the end of the runs are presented in Table 1. The catalyst activity and selectivity for BN hydrogenation depended mainly on the nature of metal, probably because the metal determines the type of reaction intermediate involved (imine, carbene or nitrene). In n-butanol, Pt and Pd yielded essentially DBA while Ru

formed a mixture of BA and DBA. Nevertheless, the solvent nature also played a crucial role

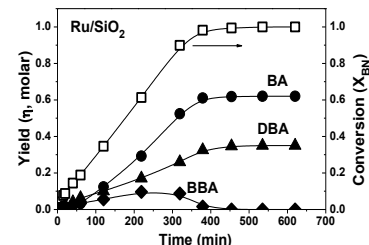


Figure 1: BN hydrogenation in TOL

because the strong interaction butanol/Pt hampers the readsorption of DBA and the consecutive formation of TBA. Production of TBA on Pt/SiO₂ was favored when butanol was replaced by

Table 1. Catalytic results

Catalyst	Solvent	Initial activity	Conversion and selectivities (%)				
		r_{BN}^0	X_{BN}	BA	DBA	TBA	Others
Ru/SiO ₂	BOL	0.71	100	55	60	-	-
Ru/SiO ₂	TOL	0.59	100	63	37	-	-
Ru/SiO ₂	CYH	1.37	100	46	53	-	1
Pt/SiO ₂	BOL	4.63	94	2	95	3	-
Pt/SiO ₂	TOL	9.22	94	-	74	21	5
Pt/SiO ₂	CYH	14.22	100	-	60	40	-
Pd/SiO ₂	BOL	1.88	30	-	74	11	15
Pd/SiO ₂	TOL	1.03	10	-	5	56	39
Pd/SiO ₂	CYH	0	0	-	-	-	-

and adsorbed BA is easier to proceed when no competition with the solvent for metal active sites takes place. Pd/SiO₂ strongly deactivated in all the solvents, probably because of the strong adsorption of BN and amine intermediates on the metal surface. The Pd/SiO₂ activity decay increased when using solvents that do not interact with the metal such as cyclohexane.

Significance

The solvent nature plays a crucial role in controlling the activity and selectivity of metal-supported catalysts for the butyronitrile conversion to butylamines

References

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