

## Selective Hydrogenation of Nitriles to Primary Amines on Metal-supported Catalysts

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### Introduction

The hydrogenation of nitriles via homogeneous or heterogeneous catalysis is an important route to produce the corresponding amines that are widely used in industry as intermediates for fungicides, pesticides, pharmaceuticals, and other chemicals. Although saturated nitriles are initially hydrogenated to primary amines, the condensation reactions between the highly reactive imine intermediate and amines usually produce also secondary and tertiary amines. Figure 1 shows the reaction network of butyronitrile (BN) hydrogenation according to currently accepted reaction pathways. Unsupported Raney Co and Ni catalysts have been widely employed in liquid-phase but supported-metal catalysts, specially using transition metals, have been lately studied in an attempt to overcome the difficulties of handling Raney catalysts. In this work, we have

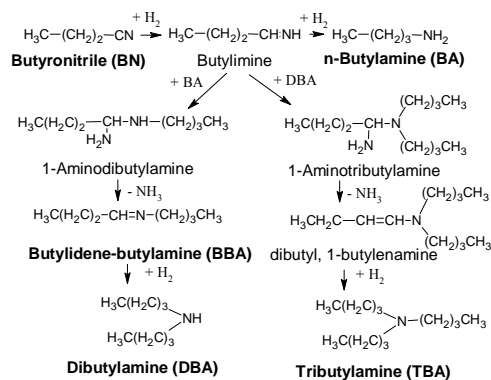


Figure 1: Reaction network

studied the liquid-phase hydrogenation of butyronitrile to n-butylamine on Ni, Co, Ru, Cu, Pd, and Pt metals supported on an inert single oxide (silica), using ethanol as solvent and without the presence of any additive such as ammonia in the reactor.

### Materials and Methods

Silica-supported catalysts were prepared by supporting Co, Ni, Cu, Pt, Pd, or Ru on a commercial SiO<sub>2</sub> (Sigma-Aldrich G62) by incipient-wetness impregnation at 303 K. Catalysts were characterized by a variety of physical and spectroscopic techniques. The metal dispersion ( $D_M$ ) was determined by H<sub>2</sub> chemisorption or by titration with N<sub>2</sub>O. The main reaction products were n-butylamine (BA), dibutylamine (DBA), tributylamine (TBA), butylidene-butylamine (BBA), and N-ethylbutylamine (EBA).

### Results and Discussion

The initial reaction rate ( $r_{BN}^0$ , mmol/h g), and BN conversion ( $X_{BN}$ ) and selectivities ( $S_i$ ) at the

end of the runs at 373 K and 13 bar are presented in Table 1. The  $r_{BN}^0$  values show that the catalyst activity followed the order: Ni > Co > Pt > Ru > Cu > Pd. Pd/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> did not form BA and produced essentially DBA, while Pt/SiO<sub>2</sub> formed mainly DBA and minor amounts of BA and TBA. Ru/SiO<sub>2</sub> formed preponderantly BA but also produced significant amounts of DBA and BBA. The highest selectivity to BA was obtained on Ni/SiO<sub>2</sub> ( $S_{BA}$ =84%).

Table 1. Catalytic results for butyronitrile hydrogenation (373 K, 13 bar)

Catalyst	% Metal	$D_M$ (%)	$r_{BN}^0$ (mmol/h g)	Conversion ( $X_{BN}$ , %) and Selectivities ( $S_i$ , %) at the end of reaction						
				$X_{BN}$	$S_{BA}$	$S_{DBA}$	$S_{TBA}$	$S_{BBA}$	$S_{EBA}$	$S_{Others}$
Ru/SiO <sub>2</sub>	1.80	2	5.8	66	65	18	-	17	-	-
Pt/SiO <sub>2</sub>	0.27	45	7.9	43	7	68	5	-	-	20
Pd/SiO <sub>2</sub>	0.33	22	2.5	11	-	54	-	-	-	46
Cu/SiO <sub>2</sub>	9.20	1	3.9	13	-	46	-	-	-	54
Ni/SiO <sub>2</sub>	10.5	1	38.2	100	84	16	-	-	-	-
Co/SiO <sub>2</sub>	9.80	-	29.6	100	74	18	-	-	8	-

Co/SiO<sub>2</sub> was also highly selective to BA giving 83 % BA after 90 min of reaction; then, the BA concentration diminished because it reacted with the solvent (ethanol) to form EBA.

In an attempt to improve the BA yields we carried out additional catalytic tests changing the reaction conditions. Specifically, we evaluated the Ni/SiO<sub>2</sub> and Co/SiO<sub>2</sub> activity and selectivity for BN hydrogenation at a low temperature (343 K) and higher H<sub>2</sub> pressure (25 bar). Results are given in Table 2.

Table 2. Butyronitrile hydrogenation at 343 K

Catalyst	$P_{H_2}$ (bar)	$r_{BN}^0$ (mmol/h g)	Values at the end of the runs		
			$X_{BN}$	$S_{BA}$	$S_{DBA}$
Ni/SiO <sub>2</sub>	13	15.2	100	78	22
Ni/SiO <sub>2</sub>	25	26.4	100	76	24
Co/SiO <sub>2</sub>	13	10.8	100	93	7
Co/SiO <sub>2</sub>	25	19.5	100	97	3

ethanol/butylamine reductive amination reaction did not take place at 343 K. The initial BN conversion rate on Ni/SiO<sub>2</sub> and Co/SiO<sub>2</sub> clearly increased when  $P_{H_2}$  was increased from 13 bar to 25 bar, showing that the reaction was order one with respect to H<sub>2</sub>. Regarding the effect of H<sub>2</sub> pressure on catalyst selectivity, Table 2 shows that on Ni/SiO<sub>2</sub> the selectivity to BA slightly diminished when  $P_{H_2}$  was increased from 13 bar to 25 bar, probably because the order in H<sub>2</sub> for hydrogenating butylimine to BA on Ni is lower in comparison with the order for BN hydrogenation to butylimine (Figure 1). On the contrary, the selectivity (and the yield) to BA on Co/SiO<sub>2</sub> at the end of reaction increased with  $P_{H_2}$ , from 93 % at 13 bar to 97 % at 25 bar, suggesting a positive effect of the H<sub>2</sub> pressure on BA selectivity.

### Significance

Co/SiO<sub>2</sub> yields 97% n-butylamine from butyronitrile at 343 K and  $P_{H_2}$  = 25 bar, similarly to the highest n-butylamine yields reported on Raney Co catalysts.