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# Hydrogenation of nitriles to primary amines on metal-supported catalysts: Highly selective conversion of butyronitrile to n-butylamine

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## ABSTRACT

The selective liquid-phase hydrogenation of butyronitrile to n-butylamine was studied in a batch reactor on Co(9.8%)/SiO<sub>2</sub>, Ni(10.5%)/SiO<sub>2</sub>, Cu(9.2%)/SiO<sub>2</sub>, Pt(0.27%)/SiO<sub>2</sub>, Pd(0.33%)/SiO<sub>2</sub>, and Ru(1.8%)/SiO<sub>2</sub> catalysts. At 373 K and 13 bar (H<sub>2</sub>), the initial butyronitrile conversion rate ( $r_{\rm BN}^0$ , mmol/hg) followed the order Ni > Co > Pt > Ru > Cu > Pd. Cu/SiO<sub>2</sub> and Pd/SiO<sub>2</sub> did not form n-butylamine and rapidly deactivated during the progress of the reaction. Pt/SiO<sub>2</sub> produced mainly dibutylamine and only minor amounts of n-butylamine and tributylamine. In contrast, Ru/SiO<sub>2</sub> formed preponderantly n-butylamine but also produced significant amounts of dibutylamine and butylidene–butylamine, an intermediate in the formation pathway of the secondary amine. The highest yield to n-butylamine was obtained on Ni/SiO<sub>2</sub> (84%). Co/SiO<sub>2</sub> was initially highly selective to n-butylamine but with the progress of the reaction the vection mixture diminished because it partially reacted with the solvent (ethanol) to form N-ethylbutylamine. In an attempt to reduce the formation of byproducts, Ni/SiO<sub>2</sub> and Co/SiO<sub>2</sub> catalysts were tested at lower temperatures and higher H<sub>2</sub> pressures. Butyronitrile was selectively converted to n-butylamine, similarly to the highest yields reported on Raney Co catalysts.

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## 1. Introduction

The hydrogenation of nitriles via homogenous or heterogenous 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 [1,2]. The reaction has been mostly carried out in liquid phase (except for acetonitrile hydrogenation), using metal catalysts and batch reactors. The pioneer work of Sabatier and Senderens [3], Von Braun et al. [4], and others [5,6] strongly contributed to gain insight on the reaction mechanism of nitrile hydrogenation and coupling to higher amines. In Fig. 1 we have depicted the reaction network of butyronitrile (BN) hydrogenation taking into account the currently accepted reaction pathways [7,8]. The hydrogenation of butyronitrile forms initially butylimine that is consecutively hydrogenated to the primary amine, n-butylamine (BA). Butylimine is a highly reactive aldimine intermediate that interacts with n-butylamine to form 1-aminodibutylamine. This later intermediate gives by deamination the secondary imine, butylidene-butylamine (BBA) that is finally hydrogenated to dibutylamine (DBA). Similarly, butylimine may react with dibutylamine giving 1-aminotributylamine that after consecutive deamination and hydrogenation leads to the formation of tributylamine (TBA).

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, in particular when high nitrile conversions are achieved. In order to eliminate the cost of product separation process, a high selectivity to a particular amine is usually wanted. However, the reaction selectivity depend on a number of parameters, in particular the nature of the metal component. Fundamental knowledge on the selectivity of nitrile hydrogenation toward different amines is still lacking. Unsupported Raney Co and Ni catalysts have been widely employed in liquid-phase [9–12] but supported-metal catalysts, specially using transition metals, have been lately studied in an attempt to overcome the difficulties of handling Raney catalysts [7,13-16]. In order to obtain selectively primary amines, the formation of secondary and tertiary amines has to be avoided. In previous work, large amounts of ammonia have been often employed to suppress the formation of higher amines by shifting equilibrium to the primary amine and the alkylimine, since ammonia is released in the condensation reaction of the intermediate with an amine group under formation of a dialkylimine (Fig. 1) [17-19]. However, the addition of ammonia creates a waste problem that makes the process more expensive, and less easy to implement on industrial scale. Thus, there is a need to develop stable and selective metal-supported

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Fig. 1. Reaction network of butyronitrile conversion reactions.

catalysts for hydrogenating nitriles to primary amines under mild operation conditions. Among the transition metals investigated, Ni, Co and Ru seem to exhibit the best chemoselectivity properties to primary amines while Rh would promote the formation of secondary amines and Pt and Pd that of tertiary amines [9,13]. Bimetallic and alloy catalysts, particularly based on Ni, have been investigated in an attempt of improving the selectivity to primary amines [16,17,20]. The effect of support acidity on catalyst selectivity has also been studied, but while some authors claimed that that acidity is detrimental for the formation of primary amines [21,22] other reported that acidity has no effect on selectivity [14]. Finally, very few papers dealing with the effect of solvent on the reaction selectivity have been published [23,24]. Bresson et al. [25] studied the hydrogenation of valeronitrile in different alcohols and reported that the selectivity to the primary amine increases with the alcohol polarity; in contrast, other authors observed that the selectivity is not dependent on the solvent polarity [7].

In this work, we have 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. Few papers have investigated the butyronitrile hydrogenation in liquid phase on metal-supported catalysts. Greenfield [6] used commercial catalysts consisting of a transition metal (Ni, Co, Pt, Pd, Rh, Ru) supported on different supports; best yields to n-butylamine (about 80%) were obtained on Co and Ni metals in methanol, at 398 K and 7 bar. Huang and Sachtler [13] supported Ru, Rh, Ni, Pd and Pt metals on a NaY zeolite to study the liquid-phase butyronitrile hydrogenation in heptane at 383 K and 24 bar. They reported that the highest yield to n-butylamine (about 60%) was obtained on Ru/NaY. P. Witte [7] investigated the reaction on Rh, Ru and Pd metals in ethanol and found that the best catalyst was a  $Rh/Al_2O_3$  catalyst that produced 93% of butylamine at 80% conversion, 323 K and 5 bar.

The objective of this work was twofold: (i) to select the best metal to selectively obtain n-butylamine from butyronitrile hydrogenation, without using ammonia or alkaline additives in the system; (ii) to find appropriate reaction operation conditions for enhancing the yield to n-butylamine. Results will show that  $Co/SiO_2$  is the most selective catalyst and converts almost completely butyronitrile to n-butylamine at 343 K and 25 bar (H<sub>2</sub>).

## 2. Experimental

#### 2.1. Catalyst preparation

Silica-supported catalysts were prepared by supporting Co, Ni, Cu, Pt, Pd, or Ru on a SiO<sub>2</sub> powder (Sigma–Aldrich G62, 60–200 mesh, 300 m<sup>2</sup>/g) by incipient-wetness impregnation at 303 K. Metal nitrate solutions (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O Aldrich 98%, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O Fluka 98%, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O Anedra 98% [Pt(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> Aldrich 99.99%, Pd(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O Aldrich 98%), were used for impregnating Co, Ni, Cu, Pt and Pd while Ru/SiO<sub>2</sub> was prepared by using RuCl<sub>3</sub>·H<sub>2</sub>O (Aldrich 99.98%). The impregnated samples were dried overnight at 373 K, then heated in air at 5 K/min to 673 K and kept at this temperature for 2 h.

## 2.2. Catalyst characterization

BET surface areas ( $S_g$ ) were measured by N<sub>2</sub> physisorption at its boiling point in a Micromeritics Accusorb 2100E sorptometer. Elemental compositions were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES), using a Perkin–Elmer Optima 2100 unit. Powder X-ray diffraction (XRD) patterns were collected in the range of  $2\theta = 10-70^{\circ}$  using a Shimadzu XD-D1 diffractometer and Ni-filtered Cu K $\alpha$  radiation. Oxide crystallite sizes were calculated using the Debye–Scherrer equation.

The metal dispersion ( $D_M$ , surface M atoms/total M atoms) of all the samples excepting Co/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> was determined by chemisorption of hydrogen. Volumetric adsorption experiments were performed at 298 K in a conventional vacuum unit. Catalysts were reduced in H<sub>2</sub> at 673K for 2h and then outgassed 2h at 673 K prior to performing gas chemisorption experiments. Hydrogen uptake was determined using the double isotherm method as detailed in a previous work [26]. A stoichiometric atomic ratio of  $H/M_s = 1$ , where  $M_s$  implies a metal atom on surface, were used to calculate the metal dispersion. The metallic copper dispersion was measured by titration with N<sub>2</sub>O at 363 K using a stoichiometry of  $(Cu^0)_s/N_2O = 2$ , where  $Cu_s$  implies copper atom on surface [27]. Pre-reduced samples were exposed to pulses of N<sub>2</sub>O in a flow of He. The number of chemisorbed oxygen atoms was calculated from the consumption of N<sub>2</sub>O measured by mass spectrometry in a Balzers Omnistar spectrometer.

The temperature programmed reduction (TPR) experiments were performed in a Micromeritics AutoChem II 2920, using 5%  $H_2$ /Ar gaseous mixture at 60 cm<sup>3</sup>/min STP. The sample size was 150 mg. Samples were heated from 298 to 973 K at 10 K/min. Since water is formed during sample reduction, the gas exiting from the reactor was passed through a cold trap before entering the thermal conductivity detector.

#### 2.3. Catalytic activity

The liquid-phase hydrogenation of butyronitrile (Aldrich, >99%) was studied at 13 bar ( $H_2$ ) in a Parr 4843 reactor at 343 K and 373 K. The autoclave was loaded with 150 mL of solvent (ethanol, Cicarelli, ACS), 3 mL of butyronitrile, 1.0 g of catalyst, and 1 mL of n-dodecane (Aldrich, >99%) as internal standard. Prior to catalytic tests, samples were reduced ex situ in hydrogen (60 mL/min) for 2 h at 673 K (Co, Ni, Pt, Pd, Ru) or 543 K (Cu) and loaded immediately to the reactor at room temperature under inert atmosphere. The reaction system was stirred at 800 rpm and heated to the reaction temperature at 2 K/min; the H<sub>2</sub> pressure was then rapidly increased to 13 bar.

Product concentrations were followed during the reaction by ex situ gas chromatography using a Agilent 6850 GC chromatograph equipped with flame ionization detector, temperature programmer and a 50 m HP-1 capillary column (50 m  $\times$  0.32 mm ID, 1.05  $\mu$ m film). The product analysis was performed using n-dodecane as an external standard. Samples from the reaction system were taken by using a loop under pressure in order to avoid flashing. Data were collected every 15-40 min for 300-600 min. The main reaction products detected were BA, DBA, TBA, BBA, and N-ethylbutylamine (EBA). The batch reactor was assumed to be perfectly mixed. Interparticle and intraparticle diffusional limitations were verified as negligible. Conversion of butyronitrile was calculated as  $X_{BN} =$  $C_{\rm BN}/(C_{\rm BN}^0-C_{\rm BN})$ , where  $C_{\rm BN}^0$  is the initial concentration of butyronitrile and  $C_{BN}$  is the concentration of butyronitrile at reaction time *t*. Selectivities (S<sub>i</sub>, mol of product j/mol of butyronitrile reacted) were calculated as  $S_i = C_i v_{BN} / (C_{BN}^0 - C_{BN}) v_i$  where  $v_{BN}$  and  $v_i$  are the stoichiometric coefficients of butyronitrile and product *j*, respectively.



**Fig. 2.** X-ray diffractograms of the catalysts used in this work.  $\Box$  RuO<sub>2</sub>,  $\bullet$  CuO,  $\bigcirc$  NiO and  $\blacksquare$  C<sub>03</sub>O<sub>4</sub>.

Yields  $(\eta_j, \text{mol of product } j/\text{mol of butyronitrile fed})$  were calculated as  $\eta_i = S_i X_{BN}$ .

## 3. Results and discussion

## 3.1. Catalyst characterization

The hydrogenation of butyronitrile was studied on silicasupported metals containing about 10% of a non-noble metal (Ni, Co, or Cu) or between 0.27 and 1.80% of a noble metal (Pd, Pt, or Ru). The metal loadings and the physical properties of these catalysts, together with the results of catalyst characterization by different techniques, are given in Table 1. The BET surface area of the silica support  $(300 \text{ m}^2 \text{ g})$  did not change significantly after the metal impregnation and the consecutive oxidation/reduction steps used for obtaining metal/SiO<sub>2</sub> catalysts. XRD patterns of calcined samples are shown in Fig. 2. NiO (ASTM 4-835), CuO (ASTM 5-0661), Co<sub>3</sub>O<sub>4</sub> (ASTM 9-418) and RuO<sub>2</sub> (ASTM 21-1172) were identified on Ni/SiO<sub>2</sub>, Cu/SiO<sub>2</sub>, Co/SiO<sub>2</sub>, and Ru/SiO<sub>2</sub> catalysts, respectively. In contrast, the XRD diffractograms of silica-supported Pt and Pd catalysts did not show the presence of crystalline metal oxides, probably because of the low metal contents. The oxide particle sizes determined using the Debye-Scherrer equation were 18 nm (CuO), 12 nm (NiO) and 12 nm (Co<sub>3</sub>O<sub>4</sub>). The XRD signal obtained for RuO<sub>2</sub> on Ru/SiO<sub>2</sub> was too weak for determining with exactitude the RuO<sub>2</sub> particle size.

Sample characterization by TPR is presented in Fig. 3. Reduction of NiO and CuO on silica gave rise to single TPR peaks centered at 643 K and 543 K, respectively, corresponding to the direct reduction of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions to Ni<sup>0</sup> and Cu<sup>0</sup>. On Ni/SiO<sub>2</sub>, we found no reduction peak at higher temperatures that would reveal the presence of less reducible surface Ni silicates. The TPR profile of Co<sub>3</sub>O<sub>4</sub> on silica exhibited two reduction peaks at 573 K and 623 K, which reflect the consecutive reduction Co<sup>3+</sup>  $\rightarrow$  Co<sup>2+</sup>  $\rightarrow$  Co<sup>0</sup> [28,29]. Palladium and platinum oxides on silica were reduced at about 400 K. The temperature maxima obtained for all the catalysts from the TPR curves of Fig. 3 are shown in Table 1. Taking into account the above TPR results, it is inferred that on all the catalysts used in this work, the metal fraction is totally in the metallic state after the standard reduction step used prior to catalytic tests (reduction in pure H<sub>2</sub> at 543 K for Cu/SiO<sub>2</sub> and at 673 K for the rest of metal/SiO<sub>2</sub> samples).

The metallic fraction of reduced catalysts was characterized by hydrogen chemisorption, excepting Cu and Co catalysts (Table 1); it is known that the  $H_2$  chemisorption is not suitable for determining the metal dispersion of Cu(Co)-based catalysts. The adsorbed

Catalyst	Metal loading <sup>a</sup> (%)	$S_g(m^2/g)$	H <sub>2</sub> chemisorption(l STP/mol metal)	Metal dispersion $D_{M}$ (%)	Oxide particle size <sup>b</sup> (nm)	TPR, $T_{max}(K)$
Ru/SiO <sub>2</sub>	1.80	280	0.18	2	-	470
Pt/SiO <sub>2</sub>	0.27	294	5.40	45	-	428
Pd/SiO <sub>2</sub>	0.33	303	2.47	22	-	393
Cu/SiO <sub>2</sub>	9.20	285	-	1 <sup>c</sup>	18 (CuO)	543
Ni/SiO <sub>2</sub>	10.5	290	0.14	1	12 (NiO)	643
Co/SiO <sub>2</sub>	9.80	307	-	-	12 (Co <sub>3</sub> O <sub>4</sub> )	573, 623

 Table 1

 Characterization of the catalysts used in this work

<sup>a</sup> Determined by ICP-AES.

<sup>b</sup> Determined by XRD.

<sup>c</sup> Determined by N<sub>2</sub>O titration.

amount of irreversible H<sub>2</sub> was used to calculate the metal dispersion of Pt, Pd, Ru, and Ni samples, using a H:metal = 1 adsorption stoichiometry. The obtained  $D_{\rm M}$  values are presented in Table 1. The metallic dispersion of Ni<sup>0</sup> on Ni/SiO<sub>2</sub> was only about 1% and this result is consistent with the large NiO crystallite sizes determined from the X-ray diffraction pattern of Fig. 2 for the calcined sample. This low  $D_{\rm Ni}$  value is consequence of both the high Ni loading, and the preparation method used to impregnate Ni nitrates onto silica. The  $D_{\rm Ru}$  on Ru/SiO<sub>2</sub> catalyst was also low, about 2%. In contrast, the metallic dispersions on Pd/SiO<sub>2</sub> and Pt/SiO<sub>2</sub> that contain about 0.3% of metal were 22% ( $D_{\rm Pd}$ ) and 45% ( $D_{\rm Pt}$ ). The  $D_{\rm Cu}$  value determined by N<sub>2</sub>O titration on Cu/SiO<sub>2</sub> catalyst was 1%.

#### 3.2. Butyronitrile hydrogenation at 373 K

#### 3.2.1. Catalyst activity

Fig. 4 shows the evolution of BN conversion and yields as a function of time for all the catalysts used in this work. In order to quantitatively compare catalyst activity and selectivity we determined the initial BN conversion rate ( $r_{BN}^0$ , mmol/h g), and the values of  $X_{BN}$  and  $S_j$  at the end of the runs; data are presented in Table 2. The  $r_{BN}^0$  values were determined from the experimental curves of Fig. 4 by polynomial regression and numerical differentiation. We also determined the initial turnover frequencies (TOF, min<sup>-1</sup>) from  $r_{BN}^0$  values and the metallic dispersions of Table 1; results are shown in Table 2.

The  $r_{BN}^0$  values of Table 2 show that the catalyst activity followed the order: Ni > Co > Pt > Ru > Cu > Pd. If we considered the TOF values, then the activity order was: Ni > Ru > Pt > Pd > Cu. The butyronitrile conversion on Pd/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> was almost constant after 50 min reaction, suggesting a rapid in situ sample deactivation. Thus,  $X_{BN}$  on these catalysts was lower than 15% at the end



Fig. 3. TPR characterization of metal/SiO<sub>2</sub> catalysts. Heating rate: 10 K/min, W = 150 mg.

of the 300 min runs. On Pt/SiO<sub>2</sub> and Ru/SiO<sub>2</sub>,  $X_{BN}$  increased continuously during the progress of the reaction reaching 43 and 66%, respectively, at the end of the runs. Finally, Fig. 4 shows that buty-ronitrile was completely converted to different products on Co/SiO<sub>2</sub> and Ni/SiO<sub>2</sub> after about 150 min of reaction.

Results in Table 2 and Fig. 4 point out that all the silica-supported metals used in this work were active for converting butyronitrile to saturated amines in liquid-phase. Verhaak et al. [21] studied the gas-phase hydrogenation of acetonitirile on Ni-supported catalysts and proposed that the reaction occurs via a dual-function mechanism: the metal provides the hydrogenation function while the acid sites on the support would promote the condensation reactions leading to secondary or tertiary amines. The same gasphase reaction was investigated by other authors who reported that the activity and selectivity of Ni-supported catalysts were strongly influenced by the support acidity [30,31]. However, for the liquid-phase butyronitrile hydrogenation Huang et al. [14] did not observe any significant effect of support acidity on the selectivity of the reaction. Our results are consistent with this later observation. In fact, while we do not attempt here to investigate the effect of support on catalyst activity and selectivity, the significant differences observed in Table 2 for  $r_{BN}^0$  values cannot be explained by any bifunctional metal-support mechanism because all the metals are supported on an inert material. The results summarized in Table 2 on catalyst activity and selectivity would be essentially determined then by the chemical nature of the metals.

Very few papers have quantitatively determined the activity of metal-supported catalysts for the liquid-phase nitrile hydrogenation reaction in the absence of ammonia. Huang and Sachtler [17] studied the liquid phase hydrogenation of butyronitrile at 383 K on 3% of Ni, Ru, Rh, Pd and Pt suported on NaY zeolite using heptane as solvent. They reported the following activity order: Rh > Ni > Pt > Pd > Ru. Pašek et al. [32] studied the liquidphase hydrogenation of lauronitrile on Co, Ni and Cu powders and found that the ratio of initial reaction rates per unit of surface area of metals was Ni:Co:Cu = 20:10:1.

In this work, the highest values for the initial butyronitrile conversion rate in terms of catalyst weight  $(r_{BN}^0)$  were obtained on Ni/SiO<sub>2</sub> and Co/SiO<sub>2</sub>, followed by Pt/SiO<sub>2</sub> and Ru/SiO<sub>2</sub> (Table 2). Cu/SiO<sub>2</sub> and Pd/SiO<sub>2</sub> were the less active catalysts. Overall, we observe that this metal activity order is in agreement with the results reported by other authors that are summarized above. It is significant to note that the initial BN turnover conversion rate determined here on Ni/SiO<sub>2</sub> at 373 K (TOF = 35.6 min<sup>-1</sup>) compares favorably with that reported for Raney Ni at the same temperature (TOF = 8.4 min<sup>-1</sup>) [12].

#### 3.2.2. Catalyst selectivity

Regarding catalyst selectivity, Pd/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> did not form BA and produced essentially DBA (Fig. 4 and Table 2). Huang and Sachtler [13] have also reported that Pd/NaY catalysts form selectively DBA in the liquid-phase hydrogenation of butyronitrile. In the case of copper, Volk and Pasek [9] studied the liquid-phase

Catalyst	Initial activity		Reaction length (min)	Convers	ion (X <sub>BN</sub> ) an	d Selectiviti	es (S <sub>j</sub> , %) at t	he end of rea	ction			
	$r_{\rm BN}^0 ({\rm mmol/hg})$	TOF (min <sup>-1</sup> )		$X_{\rm BN}$	$S_{\rm BA}$	S <sub>DBA</sub>	S <sub>TBA</sub>	S <sub>BBA</sub>	S <sub>EBA</sub>	Sothers		
Ru/SiO <sub>2</sub>	5.8	27.2	550	66	65	18	-	17	-	-		
Pt/SiO <sub>2</sub>	7.9	21.1	430	43	7	68	5	-	-	20		
Pd/SiO <sub>2</sub>	2.5	6.1	300	11	_	54	_	-	-	46		
Cu/SiO <sub>2</sub>	3.9	4.5	300	13	-	46	-	-	-	54		
Ni/SiO <sub>2</sub>	38.2	35.6	300	100	84	16	-	-	-	-		
Co/SiO <sub>2</sub>	29.6	-	430	100	74	18	-	-	8	-		

Table 2Catalytic results for butyronitrile hydrogenation.

T = 373 K, P = 13 bar (H<sub>2</sub>), 800 rpm, solvent: ethanol (150 mL),  $W_{cat} = 1$  g,  $V_{BN} = 3$  mL.

hydrogenation of stearonitrile on Cu-supported catalysts and observed the selective formation of the secondary amine. This result that shows that the condensation rate on Cu catalysts is higher than hydrogenation (Fig. 1) would reflect the low activity of copper with respect to hydrogenation of the C=C bond [9]. Nevertheless, the final BN conversion on Pd/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> was only 11% and 13%, respectively, suggesting that both catalysts are deactivated during the progress of the reaction. Results in Table 2 show that the  $S_{\text{Others}}$  values at the end of the runs were 46% (Pd/SiO<sub>2</sub>) and 54% (Cu/SiO<sub>2</sub>) revealing that the carbon balance on both samples was only about 50%. These results indicate that a part of the products formed during the reaction is retained on the catalyst surface and may explain the significant deactivation observed for these catalysts in Fig. 4. Other authors [6] have also observed that total conversion is not attained on Pd catalysts in BN hydrogenation, probably due to a strong adsorption on the metal of secondary amine intermediates.

Pt/SiO<sub>2</sub> formed mainly DBA and minor amounts of BA and TBA (Fig. 4 and Table 2). At the end of the run,  $X_{BN}$  was 43% and DBA represented 85% molar of the amines mixture. The slow increase of  $X_{BN}$  with the progress of the reaction probably reflects a partial deactivation of the catalyst caused by the strong adsorption of reaction products; the carbon balance was, in effect, only 80%. The selective conversion of BN to DBA observed here on Pt/SiO<sub>2</sub> is in agreement with results published by Huang and Sachtler [13]; in contrast,

Greenfield [6] reported that on Pt/carbon the BN hydrogenation in methanol yields mainly the tertiary amine.

The carbon balance for Ru/SiO<sub>2</sub>, Ni/SiO<sub>2</sub> and Co/SiO<sub>2</sub> was about 100%. Ru/SiO<sub>2</sub> formed preponderantly the primary amine (S<sub>BA</sub> = 65%) but also produced significant amounts of dibutylamine  $(S_{DBA} = 18\%)$  and butylidene-butylamine  $(S_{BBA} = 17\%)$  at  $X_{BN} = 66\%$ (Table 2). This product distribution is coincident with that reported on Ru/NaY at similar BN conversion in heptane [13]. The presence of BBA among the reaction products is predicted in the reaction mechanism of Fig. 1 as the Schiff base leading by hydrogenation to the secondary amine. Fig. 4 shows that the BBA yield curve does not exhibit a maximum on Ru/SiO<sub>2</sub>, which probably reflects the low activity of Ru for hydrogenating BBA to DBA (Fig. 1). In contrast, we did not detect butylimine that according to Fig. 1 is formed by hydrogenation of the CN triple bond in the BN molecule. This aldimine is highly reactive and has never been detected among the reaction products in BN hydrogenation. Thus, several authors have discussed the formation of other intermediates such as carbenes and nitrenes that would result from the BN reaction with two hydrogen atoms [33,34]. Nevertheless, a recent study of the butyronitrile adsorption on 5% Pt/Al<sub>2</sub>O<sub>3</sub> using attenuated total reflection (ATR) infrared spectroscopy indicated the presence of an adsorbed imine species upon BN adsorption, with the C=N group existing in a tilted configuration [8]. This imine-type intermediate showed transient behavior



**Fig. 4.** Catalytic results: butyronitrile conversion ( $X_{BN}$ ) and yields ( $\eta_i$ ).  $\bullet$  Butylamine (BA),  $\blacktriangle$  dibutylamine (DBA),  $\blacklozenge$  butylidene–butylamine (BBA), $\star$  tributilamine (TBA),  $\blacksquare$  N-ethylbutylamine (EBA) [T = 373 K, P = 13 bar, solvent: ethanol,  $W_{cat} = 1$  g].



Fig. 5. Formation of N-ethylbutylamine via cobalt-catalyzed ethanol/n-butylamine reductive amination.

in the presence of solution phase hydrogen, suggesting that it can be converted into amine products that adsorb on the catalyst surface.

The highest selectivity to BA was obtained on Ni/SiO<sub>2</sub> ( $S_{BA} = 84\%$ ) that produced DBA as the only byproduct at  $X_{BN} = 100\%$  (Table 2). BBA is formed at the beginning of the reaction and then goes through a maximum because is consecutively hydrogenated to the secondary amine as depicted in Fig. 1. In agreement with our results, Greenfield [6] reported that the BN hydrogenation on Ni/kieselguhr in methanol at 398 K yields 81% BA and 19% DBA. In contrast, according to Huang and Sachtler [13] the liquid-phase BN hydrogenation on Ni/NaY in heptane yields 23.5% BA and 61.2% DBA at 383 K.

Co/SiO<sub>2</sub> was also highly selective to BA giving 83% BA after 90 min of reaction; however, with the progress of the reaction the BA concentration in the reaction mixture diminished concomitantly with the formation of a new secondary amine, Nethylbutylamine (EBA) (Fig. 4). Thus at the end of the 420 min catalytic run the selectivities on Co/SiO2 were 74% BA, 18% DBA and 8% EBA at  $X_{BN} = 100\%$  (Table 2). As in the case of Ni/SiO<sub>2</sub>, the BBA intermediate yield curve exhibited a maximum at about 50 min reaction because BBA is rapidly converted then to DBA. The observed formation of N-ethylbutylamine at the expenses of BA probably reflects the reaction of BA with adsorbed species formed from the solvent/metal interaction. Specifically, ethanol dehydrogenated species would react with BA via a reductive amination mechanism [35,36], as proposed in Fig. 5. The liquid-phase nitrile hydrogenation to amines has been widely studied on Raney Co and cobalt borides [11,37,38,15], but very few papers have investigated this reaction on Co-supported catalysts. For butyronitrile hydrogenation, it has been reported that 60% Co on kieselgur in methanol yields 79% BA and 21% DBA [6].

In summary, our results show that Ni/SiO<sub>2</sub> and Co/SiO<sub>2</sub> were the most active and selective catalysts for producing BA from BN hydrogenation. Ni/SiO<sub>2</sub> was more active than Co/SiO<sub>2</sub>, probably because of the relatively stronger adsorption of the reactants and butylimine intermediate [15,39]. The maximum BA yield,  $\eta_{BA}$  = 84%, was obtained on Ni/SiO<sub>2</sub>. On Raney Ni and Co, BA yields of 66% and 98%, respectively, have been reported in octane at 373 K and  $P_{H_2}$  = 30 bar [12]. In an attempt to improve the BA yields obtained on our metal-supported catalysts we decided to carry 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). By lowering the temperature, we expected to decrease the importance of the secondary reactions observed on Co/SiO<sub>2</sub> with participation of the solvent. By increasing the H<sub>2</sub> pressure, the relative hydrogenation/condensation rates involved in the synthesis of BA and higher amines may change. Nevertheless, the effect of H<sub>2</sub> pressure on the reaction network depicted in Fig. 1 is complex and difficult to predict because, among other factors, the selectivity to the primary amine depends on the metal nature, as it is proved in this work.

#### 3.3. Butyronitrile hydrogenation at 343 K

The catalytic results obtained on Ni/SiO<sub>2</sub> and Co/SiO<sub>2</sub> at 343 K and 13 bar are presented in Fig. 6 and Table 3. BN was completely converted on both catalysts after 200 min (Ni/SiO<sub>2</sub>) and 450 min (Co/SiO<sub>2</sub>) of reaction. Consistently, the initial BN conversion rate was higher on Ni/SiO<sub>2</sub> as compared with Co/SiO<sub>2</sub> (Table 3), thereby confirming that Ni is more active than Co for butyronitrile hydrogenation. The selectivity to BA on Ni/SiO<sub>2</sub> at the end of reaction was 78%, slightly lower than the  $S_{BA}$  value determined at 373 K (84%). In contrast, the value of BA selectivity on Co/SiO<sub>2</sub> (93%) clearly increased as compared with that obtained at 373 K (75%). Nethylbutylamine was not detected among the products on Co/SiO<sub>2</sub> indicating that the ethanol/butylamine reductive amination reaction did not take place at 343 K.

In an attempt to increase further the yield to butylamine, the H<sub>2</sub> pressure was increased to 25 bar. Results obtained on Ni/SiO<sub>2</sub> and Co/SiO<sub>2</sub> at 343 K are shown in Fig. 7 and Table 3. The initial Ni/SiO<sub>2</sub> activity for butyronitrile conversion clearly increased when  $P_{\rm H_2}$  was increased from 13 bar to 25 bar (Table 3). The  $r_{\rm BN}^0$ value also increased on Co/SiO<sub>2</sub>, from 10.8 mmol/hg at 13 bar to 19.5 mmol/hg at 25 bar. These data in Table 3 shows that on both catalysts the butyronitrile hydrogenation rate is approximately order one with respect to H<sub>2</sub>. This result is consistent with previous studies on the nitrile hydrogenation kinetics on Raney Ni and Co reporting that the nitrile conversion rate increases with the hydrogen pressure [40]. Regarding the effect of H<sub>2</sub> pressure on catalyst selectivity, Table 3 shows that on Ni/SiO2 the selectivity to BA slightly diminished when  $P_{\rm H_2}$  was increased from 13 bar to 25 bar. Similarly, Volf and Pasek [9] studied the liquid-phase BN hydrogenation on Ni/Al<sub>2</sub>O<sub>3</sub> and observed that  $S_{BA}$  diminishes when  $P_{H_2}$ is increased. They stated that this phenomenon might be explained by considering that 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 (Fig. 1). On the contrary, the selectivity (and the



#### Table 3

	Catalytic results f	or butyronitrile	hydrogenation on	Ni/SiO <sub>2</sub> and	$Co/SiO_2$ at 343 K.
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Catalyst	$P_{\rm H_2}$ (bar)	Initial activity $r_{\rm BN}^0 ({\rm mmol/hg})$	Reaction length (min)	Conversion (X <sub>BN</sub> ) and selectiv %) at the end of reaction		vities (S <sub>j</sub> ,
				X <sub>BN</sub>	S <sub>BA</sub>	S <sub>DBA</sub>
Ni/SiO <sub>2</sub>	13	15.2	450	100	78	22
Ni/SiO <sub>2</sub>	25	26.4	400	100	76	24
Co/SiO <sub>2</sub>	13	10.8	520	100	93	7
Co/SiO <sub>2</sub>	25	19.5	500	100	97	3

Solvent: ethanol (150 mL),  $W_{cat} = 1$  g,  $V_{BN} = 3$  mL.



Fig. 7. Butyronitrile hydrogenation on Co/SiO<sub>2</sub> (A) and Ni/SiO<sub>2</sub> (B) at 343 K and 25 bar.  $\Box$  BN,  $\blacklozenge$  BA,  $\blacklozenge$  DBA,  $\blacklozenge$  BBA. [Solvent: ethanol (150 mL), W<sub>cat</sub>: 1 g, V<sub>BN</sub> = 3 mL].

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.

#### 4. Conclusions

The activity and selectivity of Pt, Pd, Ru, Cu, Co and Ni metals supported on silica for the liquid-phase hydrogenation of buty-ronitrile in ethanol at 373 K depend essentially on the metal nature. The initial butyronitrile conversion rate ( $r_{BN}^0$ , mmol/hg) follows the order Ni > Co > Pt > Ru > Cu > Pd. Pd/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> produce essentially dibuytilamine but are rapidly deactivated during the reaction because a part of the products remains strongly adsorbed on the catalyst surface. Pt/SiO<sub>2</sub> is also selective for the formation of the secondary amine and presents initially a good activity; however, the butyronitrile conversion increases slowly with reaction time because of the in situ catalyst deactivation. On Ru/SiO<sub>2</sub>, Ni/SiO<sub>2</sub> and Co/SiO<sub>2</sub> the main reaction product is the primary amine, n-butylamine.

At 373 K and 13 bar ( $H_2$ ), the n-butylamine yield on Ni/SiO<sub>2</sub> was 84% that is higher than those reported at the same temperature using Raney Ni catalysts. Under these reaction conditions, Co/SiO<sub>2</sub> is initially highly selective to n-butylamine but with the progress of the reaction this primary amine reacts with the solvent (ethanol) to form N-ethylbutylamine.

The n-butylamine selectivity on Co/SiO<sub>2</sub> was greatly improved by lowering the temperature and increasing the hydrogen pressure. Thus, at 343 K and  $P_{H_2} = 25$  bar Co/SiO<sub>2</sub> yielded 97% n-butylamine, similarly to the highest n-butylamine yields reported on Raney Co catalysts.

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