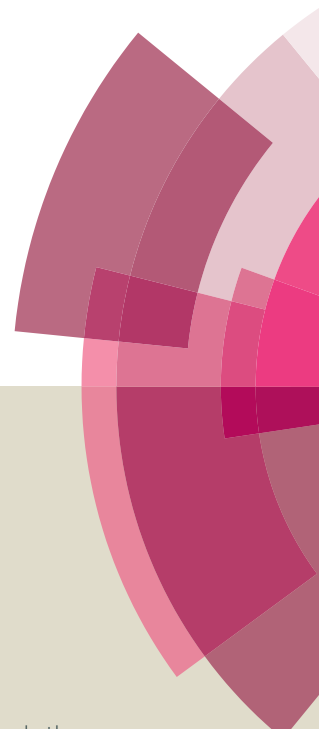


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Conversion of butyronitrile to butylamines on noble metals: Effect of solvent on catalyst activity and selectivity

D.J. Segobia, A.F. Trasarti and C.R. Apesteguía*

The liquid-phase hydrogenation of butyronitrile to butylamines was studied on Pt(0.27%)/SiO₂, Pd(0.33%)/SiO₂ and Ru(1.80%)/SiO₂ using n-butanol, toluene and cyclohexane as solvents. In n-butanol, Pt and Pd catalysts formed preponderantly dibutylamine and minor amounts of tributylamine while Ru/SiO₂ yielded mainly butylamine. Replacing n-butanol by toluene or cyclohexane caused significant changes in catalyst activity and selectivity. These changes were interpreted by relating the catalyst performance with the solvent-catalyst interaction strength that was investigated by temperature-programmed desorption of solvents and mass spectrometry. Pd/SiO₂ strongly deactivated with the progress of the reaction in all the solvents.

1. Introduction

The liquid-phase hydrogenation of nitriles is a common industrial process to produce the corresponding amines that are widely used as pharmaceutical and polymer intermediates, solvents, surfactants and speciality chemicals.^{1,2} Although saturated nitriles are initially hydrogenated to primary amines, consecutive condensation reactions usually produce also secondary and tertiary amines, in particular when high nitrile conversions are achieved. 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.^{3,4} There is a general agreement that on metal-supported catalysts the reaction selectivity depends mainly on the nature of the metal component.^{4,5,6} However, the influence of other parameters that may also determine the reaction selectivity such as operation conditions, the support acid/base properties and in particular the nature of solvent have been little investigated. A more detailed knowledge on the effect of these parameters on catalyst selectivity for nitrile hydrogenation is therefore needed.

The reaction mechanism of nitrile hydrogenation and coupling to higher amines analyzed by numerous authors is based on the pioneer work of Sabatier and Senderens,⁸ Braun *et al.*,⁹ and others.^{10,11} This mechanism is depicted in Scheme 1 for butyronitrile (BN) hydrogenation to n-butylamine (BA) and condensation/hydrogenation reactions leading to dibutylamine (DBA) and tributylamine (TBA).^{12,13} Based on the proposal of Von Braun *et al.*,⁹ Scheme 1 includes the initial hydrogenation of butyronitrile to butylimine that is consecutively hydrogenated to n-butylamine. 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 further hydrogenated to dibutylamine. Similarly, butylimine may react with dibutylamine giving 1-aminotributylamine that after consecutive deamination and hydrogenation leads to the formation of tributylamine.

Skeletal Co and Ni catalysts have been widely employed to selectively obtain primary amines by liquid-phase nitrile hydrogenation.¹⁴⁻¹⁶ Supported Co and Ni catalysts have been also studied in an attempt to overcome the difficulties of handling Raney catalysts.^{11,17-20} Recently, we reported that in ethanol Co/SiO₂ catalysts yield 97% n-butylamine from butyronitrile hydrogenation, similarly to the highest n-butylamine yields reported on Raney Co catalysts.⁷ In contrast, noble metals such as Pt, Pd and Rh promote the preferential formation of secondary and tertiary amines.^{5,6} The choice of suitable solvents is frequently 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.²¹⁻²³ Rylander *et al.*²⁴ investigated the benzonitrile hydrogenation on Rh/C in ethanol, benzene and octane and found that the nitrile conversion rate followed the order octane > benzene > ethanol. Besson *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.¹¹ In particular, butyronitrile hydrogenation has been studied using different solvents such as methanol, ethanol, ethyl acetate, and heptane, and also under solvent-free conditions.^{4,6,7,11,12}

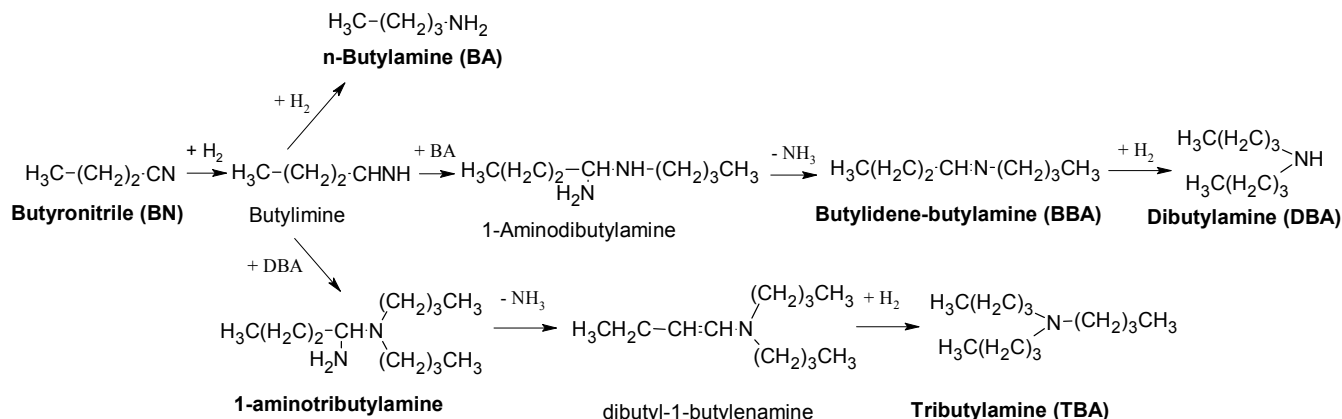
In this work, we have studied the liquid-phase hydrogenation of butyronitrile to amines on Ru/SiO₂, Pd/SiO₂ and Pt/SiO₂ catalysts in n-butanol (protic solvent), toluene (non-polar aromatic solvent) and cyclohexane (non-polar naphthenic solvent). The objective was to gain insight about the influence of the solvent on the noble metals performance for hydrogenating butyronitrile to amines. In recent

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works we have discussed the influence that the interactions solvent–catalyst, solvent–reactant and reactant–catalyst have on the activity and selectivity of metal-supported catalysts for liquid-phase hydrogenation reactions.^{26–28} Here, results will show that although the reaction selectivity depends mainly on the nature of the metal, the solvent–metal interaction strength may significantly change the metal activity/selectivity performance, in particular for Pt/SiO₂.

passed through a cold trap before entering the thermal conductivity detector.

The butyronitrile and solvent interactions with the catalysts were studied by temperature-programmed desorption (TPD) of butyronitrile or solvent preadsorbed at 298 K. Calcined samples (400 mg) were reduced at 673 K for 1 h in a 60 cm³/min flow of H₂(5%)/He and then cooled down up to 298 K. Afterwards, a He stream was



Scheme 1 Reaction network of butyronitrile conversion reactions according to von Braun's mechanism.⁹

2. Materials and Methods

2.1. Catalyst preparation

Silica-supported catalysts were prepared by supporting Pt, Pd, or Ru on a commercial SiO₂ powder (Sigma-Aldrich G62, 60–200 mesh, 300 m²/g) by incipient-wetness impregnation at 303 K. Metal nitrate solutions were used for impregnating Pt [Pt(NH₃)₄](NO₃)₂ Aldrich 99.99%] and Pd [Pd(NO₃)₂·H₂O Aldrich 98%] while Ru/SiO₂ was prepared by using RuCl₃·H₂O (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_{BET}) were measured by N₂ 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 $2\theta = 10\text{--}70^\circ$ using a Shimadzu XD-D1 diffractometer and Ni-filtered Cu K α radiation.

The metal dispersion (D_{M} , surface M atoms/total M atoms) of all the samples was determined by chemisorption of hydrogen. Volumetric adsorption experiments were performed at 298 K in a conventional vacuum unit. Catalysts were reduced in H₂ at 673 K for 2 h and then outgassed 2 h at 673 K prior to performing gas chemisorption experiments. Hydrogen uptake was determined using the double isotherm method as detailed in a previous work.²⁹ 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 temperature programmed reduction (TPR) experiments were performed in a Micromeritics AutoChem II 2920, using 5% H₂/Ar gaseous mixture at 60 cm³/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

bubbled through the solvent in order to saturate the gaseous stream with solvent vapor. Then, the reduced sample was exposed to this stream for 60 min following the effluent composition by mass spectrometry (MS) in a Baltzers Omnistar unit. Weakly adsorbed butyronitrile/solvent was removed by flushing with He (60 cm³/min) at 298 K for 1 h. Temperature was then increased at a rate of 10 K/min and the composition of the reactor effluent was measured by mass spectrometry.

2.3. Catalytic activity

The liquid-phase hydrogenation of butyronitrile (Aldrich, > 99%) was studied at 13 bar (H₂) in a Parr 4843 reactor at 403 K. The autoclave was loaded with 150 mL of solvent, 3 mL of butyronitrile, 1.0 g of catalyst, and 1 mL of n-dodecane (Aldrich > 99%) as internal standard. Toluene (Sigma-Aldrich, 99.8%), n-butanol (Cicarelli ACS) or cyclohexane (Sigma-Aldrich, 99.5%) were used as solvents. Prior to catalytic tests, samples were reduced ex-situ in hydrogen (60 mL/min) for 2 h at 673 K 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 H₂ pressure was then rapidly increased to 13 bar.

Product concentrations were followed during the reaction by ex-situ gas chromatography using an Agilent 6850 GC chromatograph equipped with flame ionization detector, temperature programmer and a 50 m HP-1 capillary column (50 m x 0.32 mm ID, 1.05 μm film). 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 450–650 min. The main reaction products detected were BA, DBA, TBA, and BBA. The batch reactor was assumed to be perfectly mixed. Interparticle and intraparticle diffusional limitations were verified as negligible. Conversion of butyronitrile was calculated as $X_{\text{BN}} = C_{\text{BN}} / (C_{\text{BN}}^0 - C_{\text{BN}})$, where C_{BN}^0 is the initial concentration of butyronitrile and C_{BN} is the concentration of butyri-

trile at reaction time t . Selectivities (S_j , mol of product j /mol of butyronitrile reacted) were calculated as $S_j = C_j v_{\text{BN}} / (C_{\text{BN}}^0 - C_{\text{BN}}) v_j$ where v_{BN} and v_j are the stoichiometric coefficients of butyronitrile and product j , respectively. Yields (η_j , mol of product j /mol of butyronitrile fed) were calculated as $\eta_j = S_j X_{\text{BN}}$.

3. Results and Discussion

3.1. Catalyst characterization

The metal loadings and the physical properties of metal/silica catalysts used in this work, together with the results of catalyst characterization by different techniques, are given in Table 1. The BET surface area of the silica support (300 m²/g) did not change significantly after the metal impregnation and the consecutive oxida-

Table 1 Physicochemical properties of the catalysts

Catalyst	S_{BET} (m ² /g)	Metal (%)	H ₂ uptake (l/mol metal)	D_{M} (%)	TPR T_{max} (K)
Ru/SiO ₂	280	1.80	0.18	2	470
Pt/SiO ₂	294	0.27	5.40	45	428
Pd/SiO ₂	303	0.33	2.47	22	393

tion/reduction steps used for obtaining metal/SiO₂ catalysts. The XRD diffractograms of calcined catalysts were presented in a previous paper.⁷ XRD patterns of Pt/SiO₂ and Pd/SiO₂ did not show the presence of crystalline metal oxides, probably because of the low metal contents. The XRD signal obtained for RuO₂ on Ru/SiO₂ was too weak for determining with exactitude the RuO₂ particle size.

The temperature maxima obtained for all the catalysts from the

3.2. Butyronitrile hydrogenation in butanol

Butyronitrile hydrogenation was initially carried out in butanol, a protic solvent of dipole moment $\mu = 1.66$ D. Fig. 1 presents the curves of BN conversion and yields as a function of time obtained for the catalysts used in this work. From the X_{BN} vs time curves of Fig. 1 we determined by polynomial regression and numerical differentiation the initial BN conversion rates per g of metal (r_{BN}^0 , mmol/h g_M) that are presented in Table 2. From r_{BN}^0 values and the metallic dispersions of Table 1 we determined the initial turnover frequencies (TOF, min⁻¹) and the values are included in Table 2. Data of selectivities (S_j) and X_{BN} at the end of the runs are also presented in Table 2.

The TOF values of Table 2 show that the initial intrinsic metal activity followed the order Ru > Pt > Pd. The butyronitrile conversion on Pd/SiO₂ was almost constant after 50 min reaction and thus X_{BN} reached only about 30% at the end of the 550-min run, which suggests a rapid in-situ catalyst deactivation. In contrast, X_{BN} increased continuously on Ru/SiO₂ and Pt/SiO₂ with the progress of the reaction, reaching 100% and 94%, respectively, at the end of the runs. Very few papers have quantitatively determined the activity of noble metals for the liquid-phase hydrogenation of butyronitrile. Huang and Sachtler studied the liquid-phase hydrogenation of butyronitrile at 383 K on 3% of Ru, Rh, Pd and Pt supported on NaY zeolite using heptane as solvent.¹⁹ They reported the following activity order: Rh > Pt > Pd > Ru. It is significant noting that the catalyst performance differences observed in Table 2 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.

Regarding catalyst selectivity, Pt/SiO₂ formed essentially DBA from the beginning of the reaction (Fig. 1). At the end of the run, the selectivity to DBA was 95% and only minor amounts of BA and

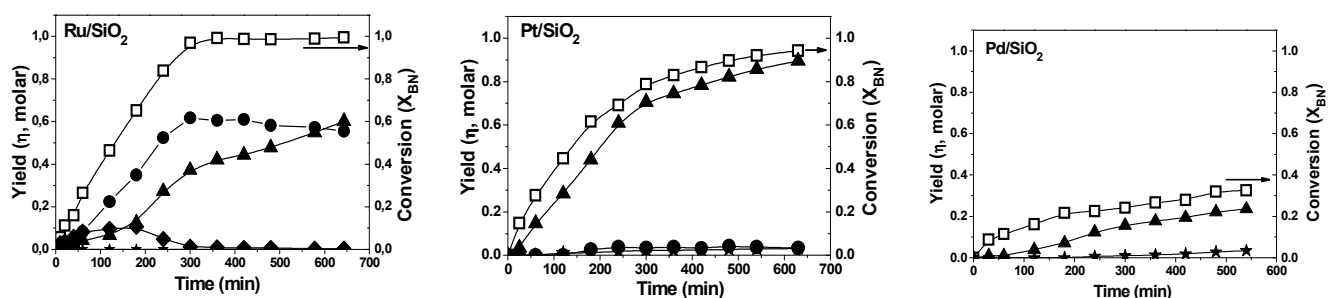


Fig. 1: Catalytic results: butyronitrile conversion (X_{BN}) and yields (η_j) in butanol. ● Butylamine (BA), ▲ Dibutylamine (DBA), ◆ Butylidene-butylamine (BBA), ★ Tributylamine (TBA) [$T = 403$ K, $P = 13$ bar, $W_{\text{cat}} = 1$ g].

TPR curves (not shown here) are presented in Table 1. Metal oxides were reduced between 393 K (Pd) and 470 K (Ru). From these results, it is inferred that on all the catalysts the metal fraction is totally in the metallic state after the standard reduction step used prior to catalytic tests (reduction in pure H₂ at 673 K).

The accessible metallic fraction of reduced catalysts was characterized by hydrogen chemisorption and the obtained D_{M} values are shown in Table 1. The D_{Ru} value on Ru/SiO₂ catalyst was low, about 2%, probably because of the high Ru content. In contrast, the metallic dispersions on Pd/SiO₂ and Pt/SiO₂ that contain about 0.3% of metal were 22% (D_{Pd}) and 45% (D_{Pt}).

TBA were detected in the amines mixture; the carbon balance was practically 100% (Table 2). The selective conversion of BN to DBA observed here on Pt/SiO₂ is in agreement with results published by Huang and Sachtler.⁶ In contrast, H. Greenfield reported that on Pt/carbon the BN hydrogenation in methanol yields preponderantly TBA.¹¹

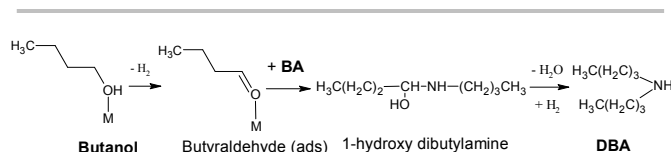
On Ru/SiO₂, BN was initially converted mainly to BA and BBA. The BA yield increased with the progress of the reaction reaching about 62% when the BN conversion was completed, after 300 min reaction (Fig. 1); then η_{BA} slowly diminished up to 55% at the end of the run. The presence of BBA among the reaction products is predicted in the reaction mechanism of Scheme 1 as the Schiff base leading by hydrogenation to the secondary amine. BBA is formed at the beginning of the reaction and then goes through a maximum as it

Table 2 Catalytic results for butyronitrile hydrogenation^a

Catalyst	Solvent	Initial activity		Conversion (X_{BN} , %) and Selectivities (%) at the end of reaction				
		r_{BN}^0 (mol/h g _M)	TOF (min ⁻¹)	X_{BN}	BA	DBA	TBA	Others
Ru/SiO ₂	Butanol	0.71	59.9	100	55	60	-	-
Ru/SiO ₂	Toluene	0.59	50.1	100	63	37	-	-
Ru/SiO ₂	Cyclohexane	1.37	115.6	100	46	53	-	1
Pt/SiO ₂	Butanol	4.63	33.4	94	2	95	3	-
Pt/SiO ₂	Toluene	9.22	66.6	94	-	74	21	5
Pt/SiO ₂	Cyclohexane	14.22	102.7	100	-	60	40	-
Pd/SiO ₂	Butanol	1.88	15.1	30	-	74	11	15
Pd/SiO ₂	Toluene	1.03	8.3	10	-	5	56	39
Pd/SiO ₂	Cyclohexane	0	-	0	-	-	-	-

^a Reaction conditions: T=403 K, P=13 bar (H₂), 800 rpm, $W_{\text{cat}} = 1$ g, $V_{\text{BN}} = 3$ mL

is consecutively hydrogenated to the secondary amine as depicted in Scheme 1. The local slopes of the η_i curves in Fig. 1 give the rate of

**Scheme 2** Formation of DBA via butanol/BA reductive amination

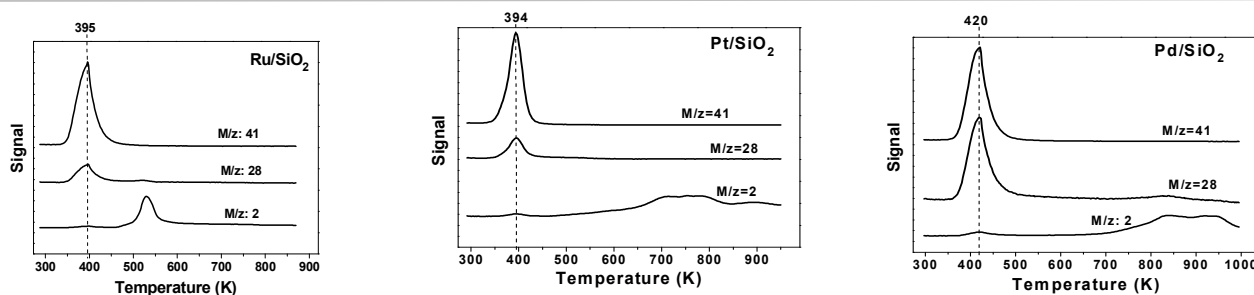
formation of each product at a specific BN conversion and reaction time. The DBA formation curve Ru/SiO₂ presents a zero initial slope indicating that DBA is a secondary product as postulated in the reaction network of Scheme 1. DBA yield increased continuously along the catalytic test; after complete BN conversion, the η_{DBA} increase was concomitant to η_{BA} drop. Formation of DBA from BA after total conversion of BN probably reflects the reaction of BA with adsorbed species formed from butanol/Ru interaction. Specifically, butanol dehydrogenated species would react with BA via a reductive amination mechanism, as proposed in Scheme 2.^{30,31} Similar reductive amination reaction was proposed to explain the formation of N-ethyl butylamine from BA on Co/SiO₂ when ethanol was used as solvent.⁷ At the end of the reaction Ru/SiO₂ yielded a mixture of BA (55%) and DBA (60%) (Table 2). Qualitatively, this product distribution is coincident with that reported on Ru/NaY at high BN conversion level in heptane.⁶ The carbon balance at the end of the run on Ru/SiO₂ was close to 115% which is consistent with additional formation of DBA from butanol according to Scheme 2.

On Pd/SiO₂, BN produced essentially DBA and did not form BA (Fig. 1). Huang and Sachtler also observed that Pd-supported cata-

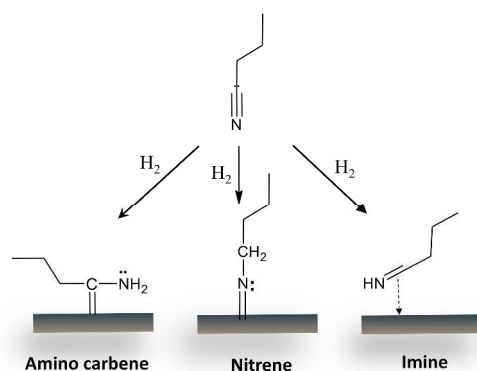
lysts form selectively DBA in the liquid-phase hydrogenation of butyronitrile.⁶ At the end of the run, the carbon balance was about 85% (Table 2; $S_{\text{Others}} = 15\%$) revealing that a part of the products formed during the reaction is retained on the catalyst surface and may explain the significant deactivation observed on Pd/SiO₂ in Fig. 1. Other authors have also reported that total conversion is not attained on Pd catalysts in BN hydrogenation.¹⁰ In order to explore if the observed Pd/SiO₂ deactivation is caused by a strong adsorption on the metal of the reactant or reaction intermediates, we investigated the BN/catalyst interaction by temperature-programmed desorption of BN preadsorbed at room temperature.

The obtained TPD curves are shown in Fig. 2; evolved gases were analyzed by mass spectrometry. Aliphatic nitriles RCN do not show molecular ion when R>3 but they undergo the McLafferty rearrangement producing $m/z=41$ CH₂C=NH⁺ ions.^{32,33} Fig. 2 shows that on the three catalysts the BN TPD run gave rise to a $m/z=41$ CH₂C=NH⁺ peak, a $m/z=28$ C₂ fragment peak, and the $m/z=2$ peak of hydrogen. The desorption temperatures (maxima) of $m/z=41$ and $m/z=28$ peaks on Ru and Pt were similar, about 395 K, whereas on Pd the temperature maximum shifted to 420 K. Besides, the C₂ fragment peak was clearly bigger on Pd than on Pt or Ru. All these results suggest a strong interaction between BN and Pd and give support to the interpretation that the Pd/SiO₂ deactivation observed in Fig. 1 during BN hydrogenation is caused by the strong adsorption of the reactant or reaction intermediates on the metal.

In summary, data in Fig. 1 and Table 2 show that Pt and Pd catalysts form preponderantly DBA while Ru/SiO₂ yields a mixture of similar amounts of BA and DBA. Previous reports on nitrile hydrogenation have noted that the selectivity of metal-supported catalysts for nitriles hydrogenation greatly depends on the metal nature. Authors have interpreted these results by considering that different reaction intermediates are formed from nitrile adsorption depending of the nature of the metal. Butylimine is the intermediate formed

**Fig 2** Temperature-programmed desorption (TPD) of BN preadsorbed at 298 K [He stream: 60 cm³/min, Heating rate: 10 K/min].

from BN in the reaction network depicted in Scheme 1. This aldimine formed by hydrogenation of the CN triple bond in the BN molecule, is highly reactive and has never been detected among the reaction products in BN hydrogenation, although a recent study of the butyronitrile adsorption on 5% Pt/Al₂O₃ using attenuated total reflection infrared spectroscopy indicated the presence of an adsorbed imine species upon BN adsorption, with the C=N group existing in a tilted configuration.³⁴ Several authors have discussed the formation of other intermediates such as carbenes and nitrenes that would result from the transfer of two hydrogen atoms to the nitrile C- or N-atom, respectively (Scheme 3).^{3,4,35} Differences in catalyst selectivity with the metal nature have been interpreted in terms of the formation of these different reactive intermediates and their adsorption strength on the metal surface. In general, it is accepted that the selective formation of primary amines from nitrile hydrogenation on metals occurs via nitrile intermediates whereas the preferential formation of secondary and tertiary amines takes place via carbene or aldimine intermediates.^{4,16,36,37} Our data show that Pd and Pt form preferentially DBA from BN; on both catalysts, the selectivity to DBA is 100% at the beginning of the reaction. On Pt/SiO₂, S_{DBA} remained very high up to the end of reaction (S_{DBA} = 95%). The DBA formation mechanism involves the nucleophilic addition of BA via the lone electron pair on the nitrogen atom at the unsaturated



Scheme 3 Reaction intermediates in BN hydrogenation on metals

carbon atom in the aldimine (or carbene) intermediate forming 1-amino-dialkylamine that by deamination and final hydrogenation yields DBA (Scheme 1). The strong inductive effect of butyl group would facilitate the nucleophilic attack of BA on the α -carbon of the unsaturated surface intermediate.⁵ Nevertheless, formation of BA was almost completely suppressed on Pt and Pd, thereby indicating that the condensation reaction leading to DBA is occurring between

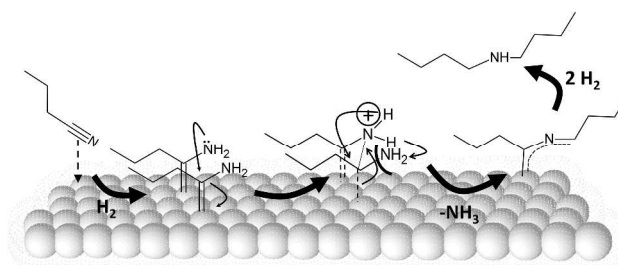


Fig. 3 Proposed reaction pathway for the formation of DBA from BN on Pt and Pd catalysts

adsorbed species, without desorption of BA to the liquid phase. In Fig. 3 we present a probable reaction pathway accounting for selective DBA formation on Pt and Pd. Postulation of this reaction mechanism is supported by the BN TPD results presented in Fig. 2 that show that BN and BN-derived intermediates are strongly adsorbed on the metals, in particular on Pd.

Ru/SiO₂ formed initially BA and then DBA via BBA (Fig. 1), in agreement with the reaction network shown in Scheme 1. Similarly, Huang and Sachtler reported the preferential formation of BA from BN on Ru-based catalysts and proposed that BN is adsorbed onto the metal via nitrene intermediates.³⁸ They observed that the mobility of Ru=N bonded species is minimal because the Ru=N bond is very strong. Thus, condensation steps yielding secondary and tertiary amines would be not favored via “immobile” nitrene intermediates because the formation of higher amines requires mobility of adsorbed groups to react with each other. Similarly, Chojcecki *et al.* explain the selective formation of BA from BN on Raney Co catalysts by speculating that strong binding via the nitrogen atom may stimulate fast hydrogenation of the carbon atom in the nitrile group, which prevents secondary condensation reactions.³⁹ Other authors have also noted that the nucleophilic attack of BA to the nitrene intermediate to yield DBA is unlikely because the nitrene intermediate does not contain saturated α -carbon.³⁶

3.3 Butyronitrile hydrogenation in toluene

Butyronitrile hydrogenation was also performed in toluene, a non-polar solvent of dipole moment $\mu = 0.37$ D. The obtained curves of BN conversion and yields as a function of time on stream are shown in Fig. 4; kinetic data determined from these curves are presented in Table 2. On Pt/SiO₂, the activity for BN conversion in toluene duplicated the value obtained in butanol. Regarding product distribution, Pt/SiO₂ formed preponderantly DBA but also yielded significant amounts of TBA (21%). Pd/SiO₂ suffered stronger deactivation in toluene than in n-butanol and reached only 10% at the end of the run.

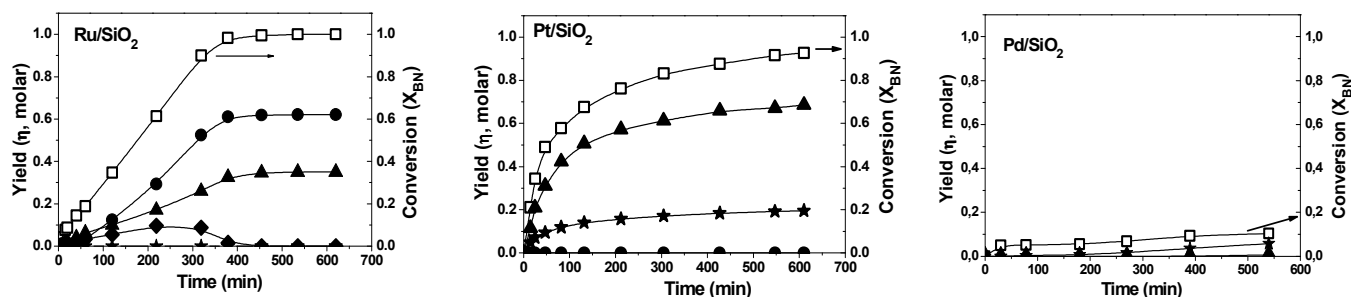


Fig. 4: Catalytic results: butyronitrile conversion (X_{BN}) and yields (η_i) in toluene. ● Butylamine (BA), ▲ Dibutylamine (DBA), ◆ Butylidene-butylamine (BBA), ★ Tributylamine (TBA) [T = 403 K, P = 13 bar, $W_{cat} = 1$ g].

Consistently, the carbon balance on Pd/SiO₂ was only 61% suggesting that BN and BN-derived compounds remain strongly adsorbed on the metal and block surface active sites. This catalyst yielded essentially TBA. The initial activity of Ru/SiO₂ in toluene was slightly lower than in butanol but converted totally the reactant after 400 min reaction. It is significant noting that Ru/SiO₂ did not produce DBA after X_{BN} reached 100%, thereby supporting the assumption that the formation of DBA observed in butanol after complete BN conversion was due to a solvent-derived reaction with BA as depicted in Scheme 2. Ru/SiO₂ yielded 63% BA and 37% DBA at the end of the run.

3.4 Butyronitrile hydrogenation in cyclohexane

Finally, the butyronitrile hydrogenation reaction was studied in cyclohexane, a non-polar solvent of dipole moment $\mu = 0$ D. The BN conversion was negligible on Pd/SiO₂ which showed that this sample is inactive in cyclohexane for hydrogenating BN. The catalytic results obtained for Ru/SiO₂ and Pt/SiO₂ are presented in Fig 5 and Table 2. Pt/SiO₂ converted completely the reactant in cyclohexane

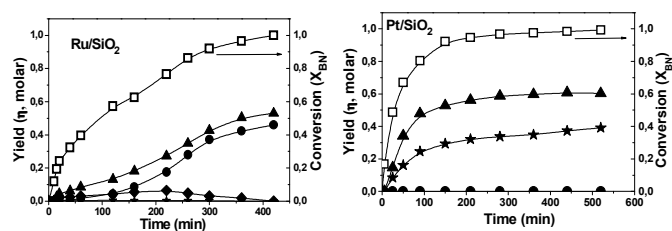


Fig 5 Butyronitrile conversion (X_{BN}) and yields (η_i) in cyclohexane; ● Butylamine (BA), ▲ Dibutylamine (DBA), ◆ Butylidene-butylamine (BBA), ★ Tributylamine (TBA)

and was more active than in toluene or n-butanol; for example, the r_{BN}^0 value obtained in cyclohexane was three times higher than that determined in n-butanol. Regarding product distribution, Pt/SiO₂ formed exclusively a mixture of DBA (60%) and TBA (40%) at the end of the run. It is significant noting that the selectivity to TBA was clearly higher than those obtained in toluene (21%) and n-butanol (3%). Ru/SiO₂ was also more active in cyclohexane than in toluene or n-butanol. However, a significant induction period for the formation of initial products BA, DBA, and BBA was observed (Fig 5). In fact, the sum of the initial formation rates of these three products was 0.16 mol/h g_M, which is significantly lower than the initial BN conversion rate ($r_{BN}^0 = 1.37$ mol/h g_M). This result suggests that in cyclohexane a significant part of the BN initially converted on Ru/SiO₂ remains adsorbed on the metal surface before reacting and desorbing to the liquid phase. With regard to product distribution, Ru/SiO₂ formed more DBA (53%) than BA (46%) at the end of the run, thereby contrasting with the corresponding values obtained in toluene (63% BA; 37% DBA).

In summary, our results above show that the activity and selectivity of noble metal-supported catalysts for butyronitrile hydrogenation to saturated amines depend essentially on the nature of the metal but the solvent nature also plays a crucial role to determine the final catalyst performance. If we consider a sequence n-butanol → toluene → cyclohexane, the main effects of solvent on catalyst activity/selectivity for each individual catalyst may be summarized as follows: i) Pt/SiO₂: the BN conversion rate and the selectivity to TBA increase; ii) Pd/SiO₂: the activity decreases and is null in cy-

clohexane; iii) Ru/SiO₂: the selectivity changes by forming increasing amounts of DBA. In an attempt of interpreting these observed effects of solvent on catalyst performance we performed additional studies addressing the solvent-metal interaction strength. Specifically, we investigated the temperature-programmed desorption of the solvents on our catalysts by analyzing the evolved products by mass spectrometry.

3.5 Solvent-metal interaction and catalyst activity and selectivity

Taking into account that Pd/SiO₂ showed very low (or null) activity for BN hydrogenation, we performed the solvent TPD experiments only on Pt/SiO₂ and Ru/SiO₂ catalysts. The results obtained for TPD of butanol and toluene on Pt and Ru catalysts are presented in Fig 6 and 7, respectively. Regarding the TPD of cyclohexane, no signals of evolved compounds were detected on both catalysts, thereby showing that cyclohexane was completely eliminated from the catalyst by the pretreatment with He at 298 K. This result revealed that the interaction between cyclohexane and Pt or Ru is negligible. Fig 6A shows the n-butanol TPD curves on Pt/SiO₂. The desorption temperature maximum of the peaks corresponding to the most abundant n-butanol ions ($M/z = 41, 27, 28, 43$) appeared at 422 K. Desorption of H₂ and C₂⁺ and C₃⁺ fragmentation ions with peak maxima at about 840 K were also observed. The TPD of toluene on Pt/SiO₂ (Fig 6B) showed that toluene desorbed at 378 K (we represented in Fig 6B only the most important signals of toluene at $M/z = 91$ and 92). Desorption of several fragments formed from a toluene-derived species took also place at 400 K. Results in Fig 6A and 6B show that n-butanol desorbed from Pt at higher temperatures than toluene, thereby indicating a stronger interaction n-butanol-metal. Thus, from solvent TPD experiments it can be inferred that the

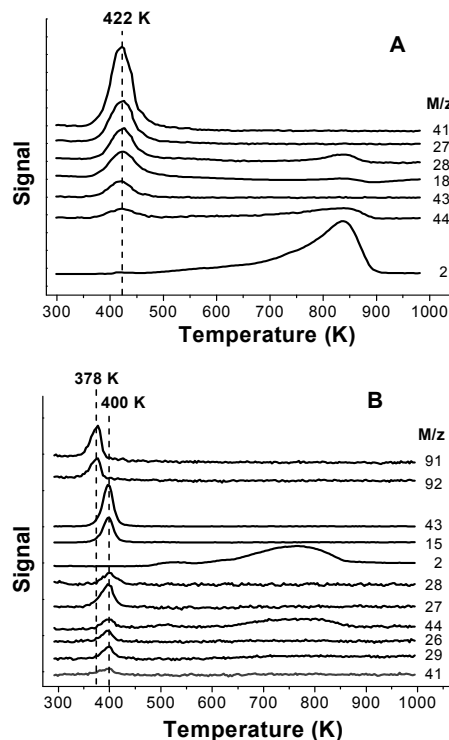


Fig 6 TPD profiles of butanol (A) and toluene (B) preadsorbed at 298 K on Pt/SiO₂.

solvent-metal interaction strength on Pt/SiO₂ follows the order n-butanol > toluene > cyclohexane. This result may explain the observed effect of solvent on Pt/SiO₂ activity and selectivity. In fact, the selective formation of DBA on Pt/SiO₂ in n-butanol probably reflects the fact that the strong interaction of butanol with Pt hinders the readsorption of DBA to react with butylimine and form TBA (Fig 3). Formation of TBA would be favored then by replacing butanol by solvents having a weaker interaction with Pt, which is exactly what we observed here. This interpretation also explains that Pt/SiO₂ in cyclohexane exhibited the highest BN conversion rate (cyclohexane does not block surface active sites) and significant induction periods for the formation of products (products remain longer adsorbed on the metal surface because there is no competition with the solvent for surface metal sites).

The n-butanol TPD curves obtained on Ru/SiO₂ are given in Fig 7A and show that n-butanol desorbed at 396 K. On the other hand, the M/z=29 signal probably represents a molecular ion formed from butyraldehyde desorbing at the same temperature. The presence of butyraldehyde on the metal surface would reflect the dissociative adsorption of n-butanol via O-H bond scission that forms simultaneously atomic hydrogen. This assumption is supported by the evolution of the H₂ signal (M/z=2) in Fig 7A that shows a small peak

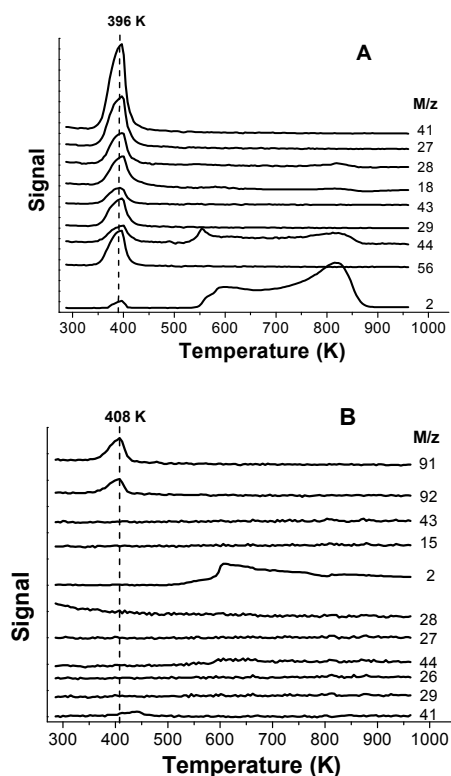


Fig 7 TPD profiles of butanol (A) and toluene (B) preadsorbed at 298 K on Ru/SiO₂

appearing at 396 K. Besides, formation of butyraldehyde gave support to the proposal that during BN hydrogenation in butanol on Ru/SiO₂ the production of DBA occurs also via the reductive amination of butyraldehyde with BA as depicted in Scheme 2. The fact that a part of n-butanol adsorbs dissociatively on Ru furnishing surface hydrogen species that may participate in the BN hydrogenation reaction pathways, led us to perform an additional catalytic test on Ru/SiO₂ using a hydrogen-free atmosphere. We observed that

Ru/SiO₂ was inactive under these operation conditions showing that the surface hydrogen species generated from n-butanol decomposition on the metal were not active enough for converting BN to any significant extent. Fig 7B shows the toluene TPD profiles obtained on Ru/SiO₂. Toluene desorbed at 408 K and no fragments formed from other toluene-derived species were detected, in contrast with the results obtained for toluene TPD on Pt (Fig 6B). Differences in solvent/metal interaction strength may also explain the observed Ru/SiO₂ activity and selectivity changes when toluene was replaced by cyclohexane. As in the case of Pt/SiO₂, the Ru catalyst is more active in cyclohexane for BN hydrogenation because this solvent practically does not interact with the metal and does not block therefore surface active sites. Regarding catalyst selectivity, Ru/SiO₂ would form more DBA in cyclohexane than in toluene because the reaction between butylimine and adsorbed BA is easier to proceed when no competition with the solvent for metal active sites takes place.

4. Conclusions

The activity and selectivity of Ru/SiO₂, Pt/SiO₂ and Pd/SiO₂ catalysts for the liquid-phase hydrogenation of butyronitrile depend mainly on the nature of metal, probably because the metal determines the type of reaction intermediate involved (imine, carbene, nitrene). In n-butanol, Pt and Pd yield essentially dibutylamine while Ru forms a mixture of butylamine and dibutylamine. Nevertheless, the solvent nature also plays a crucial role in controlling the catalyst performance. In fact, by considering a sequence n-butanol → toluene → cyclohexane the following changes occur: i) Pt/SiO₂: the butyronitrile conversion rate and the selectivity to tributylamine increase; ii) Pd/SiO₂: the activity decreases and is null in cyclohexane; iii) Ru/SiO₂: the selectivity changes by forming increasing amounts of DBA. These effects of solvent on catalyst activity/selectivity may be explained by considering the solvent-metal interaction strength that follows the order n-butanol > toluene > cyclohexane. Pt/SiO₂ is highly selective towards dibutylamine in n-butanol probably because the strong interaction butanol/Pt hampers the readsorption of dibutylamine and the consecutive formation of tributylamine. Production of tributylamine on Pt/SiO₂ is favored when butanol is replaced by solvents having a weaker interaction with Pt such as toluene and cyclohexane. Consistently, Pt/SiO₂ exhibits the highest activity in cyclohexane because this solvent does not block surface active sites. Regarding the Ru/SiO₂ selectivity, this catalyst would form more dibutylamine in cyclohexane than in toluene because the reaction between butylimine and adsorbed butylamine 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 butyronitrile and amine intermediates on the metal surface. The Pd/SiO₂ activity decay increases when using solvents that do not interact with the metal such as cyclohexane.

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The solvent nature plays a crucial role in controlling the activity and selectivity of Ru/SiO₂, Pt/SiO₂ and Pd/SiO₂ catalysts for the liquid-phase hydrogenation of butyronitrile to butylamines

