Short communication

Impact of solvent on Co/SiO$_2$ activity and selectivity for the synthesis of n-butylamine from butyronitrile hydrogenation

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

Catalysis Science and Engineering Research Group (GICIC), INCAPE, UNL-CONICET, Santiago del Estero 2654, 3000 Santa Fe, Argentina

ABSTRACT

The impact of solvent on Co(9.8%)/SiO$_2$ activity and selectivity for the synthesis of n-butylamine from butyronitrile hydrogenation was investigated using methanol, benzene, toluene and cyclohexane as solvents. In non-polar solvents, the yield of n-butylamine increased from 60% to 79% following the order cyclohexane < toluene < benzene. Nevertheless, the highest n-butylamine yield (91%) was obtained in methanol, a protic solvent. The solvent effect on the catalyst performance was interpreted by considering: i) the solvent–catalyst interaction strength and ii) the solvent polarity and its ability for H-bond formation with n-butylamine.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The hydrogenation of nitriles is an important industrial process to produce primary amines that are valuable feedstock for obtaining many chemicals, pharmaceuticals and polymers [1]. The reaction is usually carried out over transition metal catalysts and forms secondary and tertiary amines as by-products. In order to obtain selectively primary amines, large amounts of ammonia have been often employed, which creates waste problems that make the process more difficult to implement on industrial scale [2]. Thus, there is a need for developing selective metal-supported catalysts and optimizing reaction conditions to efficiently hydrogenate nitriles to primary amines under mild operation conditions.

The general mechanism of nitrile hydrogenation and coupling to higher amines used by many authors is based on the pioneer work of Braun et al. [3], Sabatier and Senderens [4], and others [5,6]. This mechanism is shown in Scheme 1 for butyronitrile (BN) hydrogenation to n-butylamine (BA) and coupling reactions leading to dibutylamine (DBA) and tributylamine (TBA) [7,8]. Butyronitrile conversion in Scheme 1 proceeds via butylimine, a highly reactive aldimine that has never been detected among the reaction products in BN hydrogenation [9]. Thus, several authors have considered the participation of other intermediates such as carbenes and nitrenes [1,10–13]. The selective formation of primary amines from nitrile hydrogenation on metals would occur via nitrile intermediates [12,14–16]. There is a general agreement

that skeletal and supported Co and Ni catalysts are particularly suitable to yield primary amines [15,17–19].

The nitrile hydrogenation reaction has been mostly carried out in liquid phase using solvents, metal catalysts and batch reactors. Although the solvent nature may greatly influence the catalyst performance, very few papers on the impact of solvent on the catalyst activity and selectivity for nitrile hydrogenation have been published [1]. Rylander et al. [20] investigated the benzonitrile hydrogenation on Rh/C in ethanol, benzene and octane. Besson et al. [21] studied the hydrogenation of valeronitrile in different alcohols. In this work we investigate the liquid-phase BN hydrogenation on Co/SiO$_2$ in methanol (protic solvent), cyclohexane (non-polar naphthenic solvent), and toluene and benzene (non-polar aromatic solvents). We selected the Co/SiO$_2$ catalyst to carry out this study because in a previous paper we observed that cobalt was the most selective metal for obtaining n-butylamine from butyronitrile [19]. Optimal solvent selection needs a detailed knowledge on the relationship between the solvent nature and the gas–liquid–solid interactions taking place in slurry reactors. Precisely, we have discussed in recent works the influence that the interactions solvent–catalyst, solvent–reactant and reactant solvent–catalyst have on the activity and selectivity of metal-supported catalysts for hydrogenation reactions [22–24].

2. Experimental section

Co(9.8%)/SiO$_2$ catalyst was prepared by impregnating Co(NO$_3$)$_2$·6H$_2$O (Aldrich 98%) on SiO$_2$ (Sigma-Aldrich G62, 300 m^2 g^{-1}) by incipient-wetness impregnation at 303 K. The impregnated sample was dried

* Corresponding author.
E-mail address: capesteg@fiq.unl.edu.ar (C.R. Apesteguía).
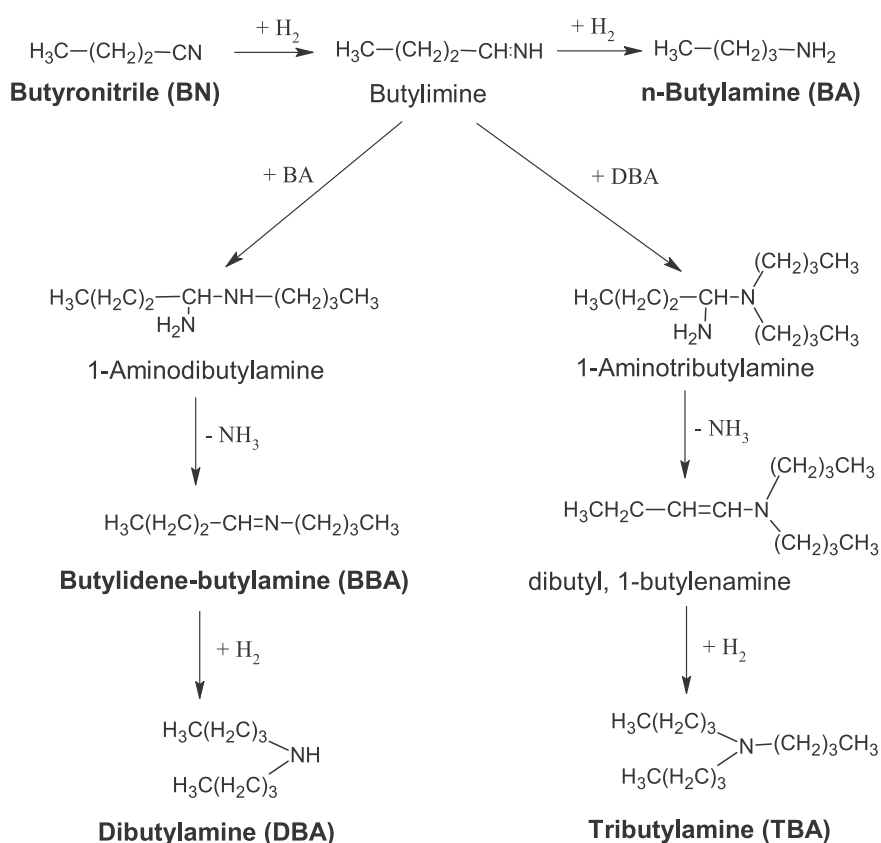
Scheme 1. Butyronitrile hydrogenation and coupling to amines based on von Braun's mechanism [3].

overnight at 373 K, then heated in air to 673 K and kept at this temperature for 2 h.

BET surface areas were measured by N_2 physisorption in a Micromeritics Accusorb 2100E sorptometer. Elemental compositions were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Powder X-ray diffraction (XRD) patterns were collected using a Shimadzu XD-D1 diffractometer. The temperature programmed reduction (TPR) experiments were performed in a Micromeritics AutoChem II 2920, using 5% H_2/Ar gaseous mixture.

The solvent-catalyst interactions were studied by temperature-programmed desorption (TPD) of the solvent preadsorbed at 298 K. Samples were reduced at 673 K in H_2(5%)/Ar, cooled down up to 298 K and finally exposed to a solvent-saturated He stream for 60 min. Then the weakly adsorbed solvent was removed by flushing with He at 298 K for 1 h. Temperature was then increased at 10 K/min and the gaseous effluent was analyzed by mass spectrometry in a Baltzers Omnistar unit.

Butyronitrile hydrogenation was studied at 13 bar (H_2) in a Parr 4843 reactor at 373 K, as in our previous studies [13,19]. The autoclave was loaded with 150 mL of solvent, 3 mL of butyronitrile, 1.0 g of catalyst, and 1 mL of n-dodecane as internal standard. Toluene, methanol, benzene and cyclohexane were used as solvents. Prior to catalytic tests, samples were reduced in H_2 at 673 K and loaded immediately to the reactor under inert atmosphere. Product concentrations were analyzed by gas chromatography using an Agilent 6850 GC chromatograph equipped with a flame ionization detector, a temperature programmer and a 50 m HP-1 capillary column. Selectivities (S_j, mol of product j/mol of butyronitrile reacted) were calculated as $S_j = C_j \nu_{BN}/(C_{BN}^0 - C_{BN})\nu_j$ where ν_{BN} and ν_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 $\eta_j = S_j X_{BN}$. We verified that the catalytic activity results obtained in this work were obtained under kinetically controlled regime. The quantitative criteria described by Ramachandran and Chaudhari [25] were used to analyze the significance of gas–liquid, liquid–solid and intraparticle mass transfer on the reaction kinetics.

3. Results

3.1. Catalyst characterization

The SiO_2 surface area (300 m²/g) did not change significantly after the metal impregnation and the consecutive oxidation/reduction steps used for obtaining Co/SiO_2 (290 m²/g). The calcined sample was characterized by XRD and TPR techniques. Co_3O_4 (ASTM 9-418) was identified from the XRD pattern in Fig. 1A. The Co_3O_4 particle size determined using the Debye–Scherrer equation was 12 nm. The TPR profile of Co/SiO_2 (Fig. 1B) exhibited two reduction peaks at 573 K and 623 K, which reflect the consecutive reduction $Co^{3+} \rightarrow Co^{2+} \rightarrow Co^0$ [26]. From these results, it is inferred that Co was totally in the metallic state after the standard reduction step used prior to catalytic tests (reduction in pure H_2 at 673 K).

3.2. Catalyst activity and selectivity

Fig. 2 presents the curves of BN conversion and yields as a function of time obtained for Co/SiO_2 in methanol, benzene, toluene and cyclohexane. From the X_{BN} vs time curves of Fig. 2 we determined the initial BN conversion rates per g of catalyst (r_{BN}^0, mmol/h g_{cat}) that are presented in Table 1. Data of selectivities (S_i) and X_{BN} at the end of the runs are also presented in Table 1.

In all the solvents, X_{BN} increased continuously on Co/SiO_2 with the progress of the reaction, reaching 100% at the end of the runs. The r_{BN}^0 values obtained in different solvents followed the order cyclohexane > toluene > methanol > benzene. Regarding catalyst
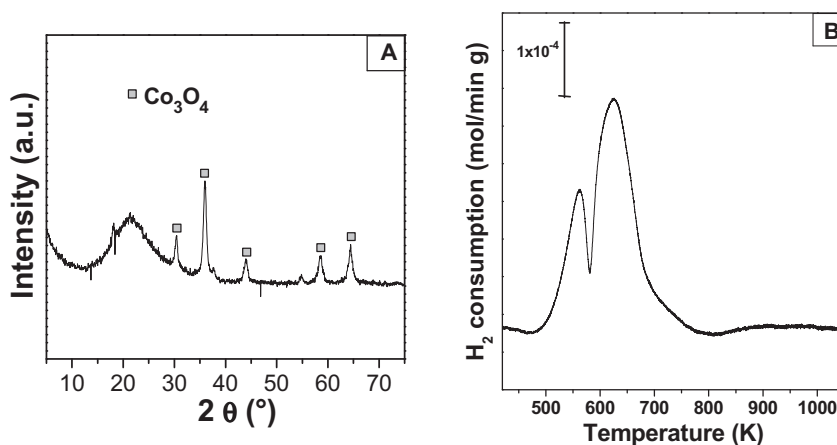
Fig. 1. Characterization of calcined Co/SiO$_2$ sample: (A) XRD pattern; (B) TPR profile.

selectivity, Co/SiO$_2$ in toluene formed initially BA and BBA. According to the von Braun's mechanism [3], DBA is produced by hydrogenation of BBA which in turns would be formed by interaction between butylimine and BA. Consistently, Fig. 2 shows that BBA in toluene was formed at the beginning of the reaction and then went through a maximum as it was consecutively converted to DBA. The local slopes of the η$_i$ curves in Fig. 2 give the rate of formation of each product at a specific BN conversion and reaction time. The initial slope of DBA formation curve in toluene was zero, thereby confirming that DBA is a secondary product. At the end of reaction, Co/SiO$_2$ in toluene yielded a mixture of BA (70%) and DBA (29%), being the carbon balance 99% (Table 1). The Co/SiO$_2$ selectivity changed when toluene was replaced by other solvents. If we consider a methanol → benzene → toluene → cyclohexane sequence, data in Table 1 show that the selectivity to DBA increased at the expenses of BA formation.

Additional catalytic runs were performed on Co/SiO$_2$ in toluene to determine the reaction order in hydrogen. The reaction orders were obtained from Eq. (1) that represents the BN conversion rate:

$$r_{BN}^0 = k\left(P_{H_2}\right)^a \left(C_{BN}^0\right)^b. \tag{1}$$

The dependence of r_{BN}^0 upon P_{H_2} was studied at 373 K by varying P_{H_2} between 5 and 25 bar at $C_{BN}^0 = 0.22$ mol/L. From the logarithmic plot of r_{BN}^0 as a function of P_{H_2} (not shown here) we determined that reaction order a was about one. From this result, it could be expected that the catalyst hydrogenation activity will be higher in solvents providing the highest H$_2$ solubility. However, we do not observe here a direct correlation between catalyst activity and H$_2$ solubility. In fact, data in Table 2 show that the highest H$_2$ solubility occurs in methanol, in which we obtained the lowest initial BN conversion rate. Then, it is
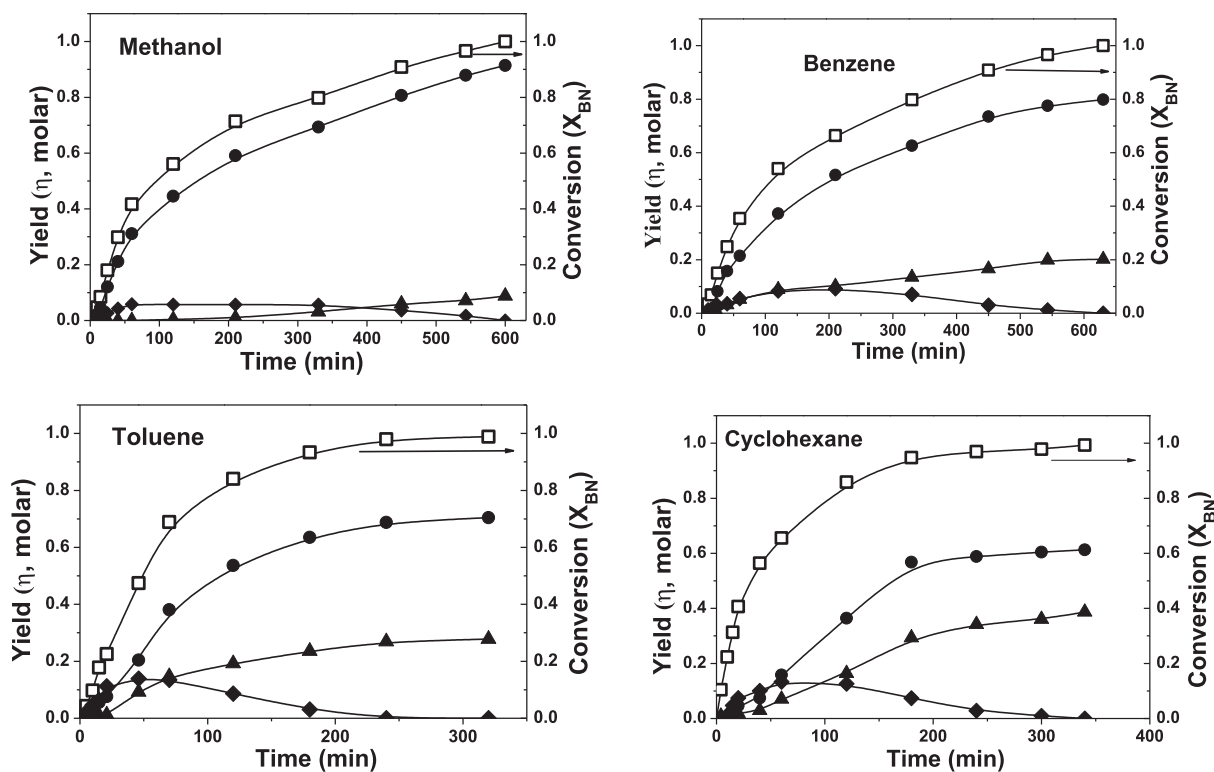

Fig. 2. Effect of solvent on Co/SiO$_2$ activity and selectivity. Butyronitrile conversion (X$_{BN}$) and yields (η$_i$): ● Butylamine (BA), ▲ Dibutylamine (DBA), ♦ Butylidene-butylamine (BBA). [T = 373 K, P = 13 bar, W$_{cat}$ = 1 g].

Table 1
Catalytic results.

Solvent	Initial rate	Reaction time	Conversion (X_{BN}, %) and selectivities (%) at the end of reaction				
	r_{BN}^0 (mmol/h g_{cat})	(min)	X_{BN}	BA	DBA	TBA	Others
Methanol	15.1	600	100	91	9	–	–
Benzene	12.4	630	100	79	20	–	1
Toluene	22.1	320	100	70	29	–	1
Cyclohexane	43.7	340	100	60	39	–	1

T = 373 K, P = 13 bar (H_2), 800 rpm, W_{cat} = 1 g, V_{BN} = 3 mL.

clear that other solvent effects such as solvent–catalyst and solvent–re-actant interactions have to be taken into account in order to interpret the observed changes in Co/SiO$_2$ activity and selectivity.

3.3. Solvent–catalyst interactions

In order to obtain insight on the solvent–catalyst interaction strength, we investigated the temperature-programmed desorption of the solvents on Co/SiO$_2$ by analyzing the evolved products by mass spectrometry. Fig. 3 presents the solvent TPD profiles obtained on Co/SiO$_2$. The TPD of cyclohexane shows the evolution of $m/z = 56$ signal (the most intense signal in the cyclohexane fragmentation mass spectrum) and $m/z = 28$ and 44 signals accounting for possible fragmentation of the cyclohexane molecule. No signals of evolved compounds were detected thereby revealing that the interaction between cyclohexane and Co is negligible.

The desorption of toluene, followed by the $m/z = 92$ signal corresponding to the molecular ion, occurred as a small peak at 365 K. Desorption of several C$_2$ and C$_4$ fragments ($m/z = 26, 28, 43$ and 44 signals) associated with toluene decomposition into lighter hydrocarbons took place at 404 K. Evolution of C$_2$ and C$_4$ fragments was also observed at higher temperatures, between 573 and 620 K. These results showed that toluene adsorbs irreversibly on Co and decomposes at low and middle temperatures.

The TPD of benzene was followed by recording the $m/z = 78$ signal that corresponds to the molecular ion, and other signals representing fragments formed from benzene decomposition. Fig. 3 shows that no benzene desorption ($m/z = 78$) was observed while significant evolutions for H$_2$, C$_1$ and C$_2$ species ($m/z = 2, 16, 28$) were detected at temperatures higher than 500 K. These high-temperature evolutions reflect the decomposition of strongly chemisorbed benzene over Co.

Finally, Fig. 3 shows that the desorption temperature maximum of the peaks corresponding to two of the most abundant methanol ions ($m/z = 31, 32$) appeared at 381 K. Two additional broad bands corresponding to high temperature H$_2$ were detected at about 570 K and 880 K respectively, which were accompanied by C$_2$ and C$_3$ hydrocarbon fragment evolutions ($m/z = 28, 44$). These evolutions indicate the presence of surface cobalt sites on which methanol adsorbs very strongly and decomposes at high temperatures.

In summary, the TPD results of Fig. 3 indicate that the solvent–catalyst interaction strength in non-polar solvents follows the order benzene > toluene > cyclohexane.

Table 2
H$_2$ solubility and polarity parameters of BN, BA and the solvents used in this work.

Compounds	ε	μ (Debye)	α	β	$C_{H_2}^*$ [a] (mol/L)
Methanol	32.7	1.7	0.98	0.66	1.21×10^{-1}
Benzene	2.28	0	0	0.10	5.45×10^{-2}
Toluene	2.38	0.37	0	0.11	5.37×10^{-2}
Cyclohexane	2.02	0	0	0	5.63×10^{-2}
BN	20.3	3.5	0	0.40	–
BA	4.92	1.3	0	0.72	–

[a] H$_2$ solubility at 373 K and 13 bar obtained from bibliography [27,28].

4. Discussion

Results of Fig. 2 and Table 1 show that the Co/SiO$_2$ activity and selectivity greatly depend on the solvent nature. By analyzing the results obtained in non-polar solvents it is inferred that r_{BN}^0 decreases while S$_{BA}$ increases in the sequence cyclohexane → toluene → benzene. These changes in catalyst activity and selectivity may be interpreted by taking into account that according to solvent TPD experiments the solvent–metal interaction strength on Co/SiO$_2$ follows the order benzene > toluene > cyclohexane. The reaction mechanism of Scheme 1 predicts that formation of DBA requires the readsorption of BA on the Co surface to react with butylimine and produce the secondary amine. The selective formation of BA would be favored therefore when a strong solvent–Co interaction takes place and hampers the readsorption of BA on the metal surface. This assumption explains why S$_{BA}$ increases when cyclohexane is replaced by toluene or benzene following the solvent–Co interaction strength trend. Moreover, the fact that Co/SiO$_2$ exhibits the highest activity in cyclohexane probably reflects also the very weak cyclohexane–Co interaction, because this solvent will not block any surface active sites for BN adsorption and conversion.

The BA yield obtained in methanol was higher than in non-polar solvents. This result cannot be explained in terms of a stronger methanol–metal interaction strength because our solvent TPD results showed that the methanol adsorption on Co is weaker than that of benzene, for example. In an attempt of interpreting the highest BA selectivity observed in methanol, we analyzed the possible interactions occurring in the liquid phase between the solvent and BA. In Table 2 we present the values of classical polarity parameters (dipole moment μ and dielectric constant ε) and hydrogen-bond-donation (α) and hydrogen-bond-acceptance (β) properties for the solvents used in this work. The values corresponding to BN and BA are also included in Table 2. Non-polar solvents exhibit low μ and ε values and they have no capability to act as H bond donor (α = 0). Methanol is a protic H-bond donor (β = 0.98) solvent that exhibits high values for polarity parameters ε and μ. In contrast, BA is an H-bond acceptor molecule of β = 0.72. Thus, a strong interaction is expected to exist between BA and protic methanol causing the BA solvation in the liquid phase. The BA molecules would be then surrounded by alcohol molecules that will hinder the BA adsorption on Co and, as a consequence, also the formation of DBA that occurs by surface condensation between BA and butylimine. The solvation of BA in methanol, i.e. a solvent–reactant interaction, would explain then the high selectivity to BA that Co/SiO$_2$ exhibits in this alcohol.

5. Conclusions

The Co/SiO$_2$ activity and selectivity for the liquid-phase synthesis of n-butylamine from butyronitrile hydrogenation greatly depend on the solvent nature. In protic alcohols such as methanol, the solvent–butylamine interaction in the liquid phase controls the selectivity to n-butylamine. Methanol is an H-bond donor solvent that strongly interacts with H-bond acceptor n-butylamine and causes its solvation in the liquid phase. The n-butylamine molecules are then surrounded by alcohol molecules that hinder the n-butylamine adsorption on Co and, as a consequence, impede the formation of dibutylamine via surface
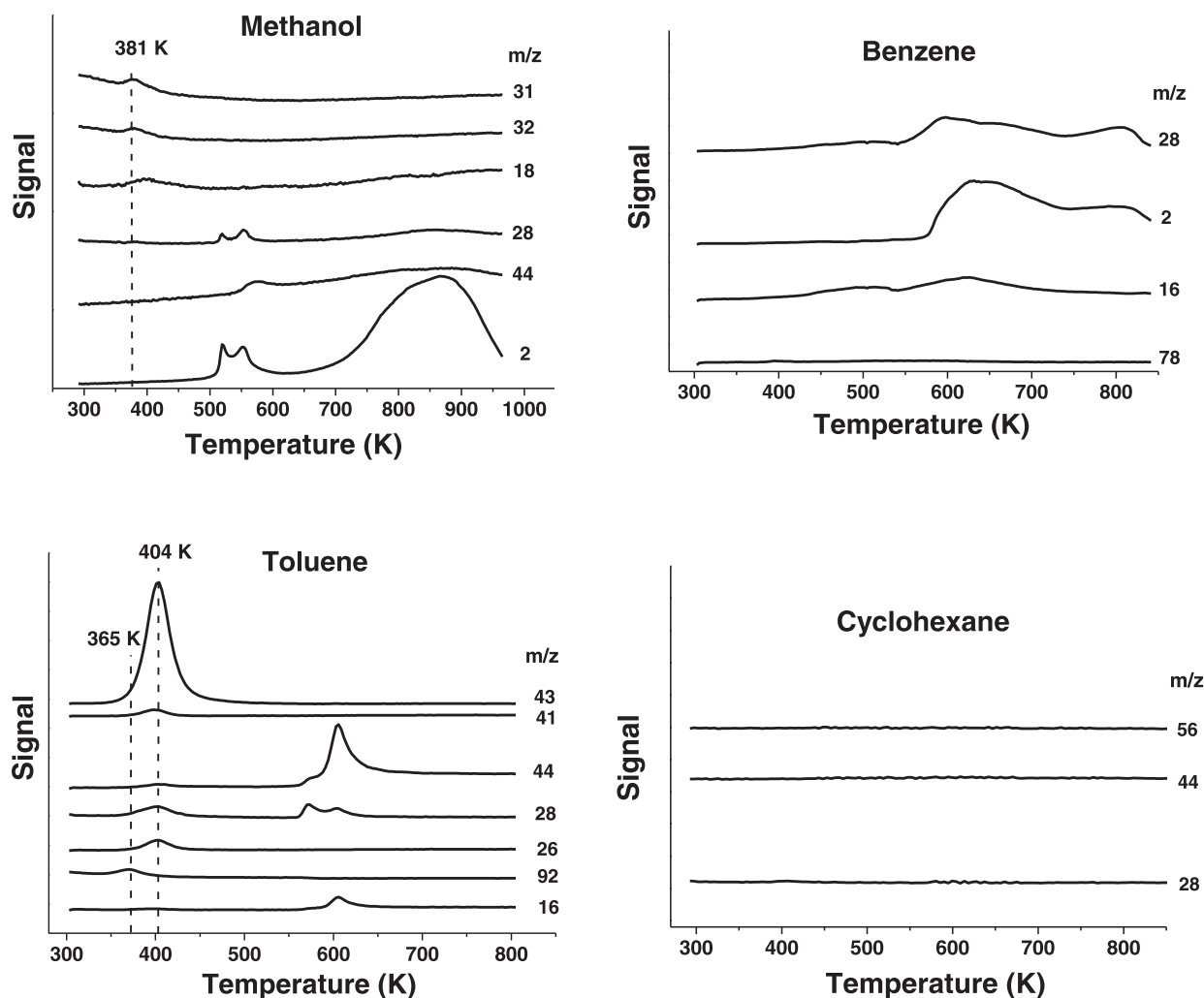
Fig. 3. TPD profiles of solvents preadsorbed at 298 K on Co/SiO₂.

condensation between n-butylamine and nitrene intermediates. When non-polar solvents such as cyclohexane, toluene or benzene are used, the solvent–catalyst interaction strength determines the selectivity to n-butylamine: the stronger the solvent–catalyst interaction the higher the n-butylamine yield. This is because a strong solvent–Co interaction hinders the readsorption of n-butylamine over the metal surface and, as a consequence, also decreases its condensation rate to dibutylamine.

References

[1] C. De Bellefon, P. Fouilloux, Catal. Rev. Sci. Eng. 36 (1994) 459–506.
[2] P. Kukula, M. Studer, H.U. Blaser, Adv. Synth. Catal. 346 (2004) 1487–1493.
[3] J. Von Braun, G. Blessing, F. Zobel, Ber. Dtsch. Chem. Ges. 36 (1923) 1988–2001.
[4] P. Sabatier, J.B. Senderens, C. R. 140 (1905) 482–483.
[5] R. Juday, H.J. Adkins, Am. Chem. Soc. 77 (1955) 4559.
[6] H. Greenfield, Ind. Eng. Chem. Prod. Res. Dev. 6 (1967) 142–144.
[7] P.T. Witte, Collect. Czechoslov. Chem. Commun. 72 (2007) 468–474.
[8] I. Ortiz-Hernandez, C.T. Williams, Langmuir 23 (2007) 3172–3178.
[9] Y. Huang, W.M.H. Sachtler, Appl. Catal. A Gen. 182 (1999) 365–378.
[10] Y. Huang, W.M.H. Sachtler, J. Catal. 190 (2000) 69–74.
[11] P. Schärringer, T.E. Müller, J.A. Lercher, J. Catal. 253 (2008) 167–179.
[12] J. Krupka, J. Pasek, Curr. Org. Chem. 16 (2012) 988–1004.
[13] D.J. Segobia, A.F. Trasarti, C.R. Apesteguía, Catal. Sci. Technol. 4 (2014) 4075–4083.
[14] B. Coq, D. Tichit, S. Ribet, J. Catal. 189 (2000) 117–128.
[15] P. Scharringer, T.E. Muller, A. Jentys, J.A. Lercher, J. Catal. 263 (2009) 34–41.
[16] C. Poupin, R. Maache, L. Pirault-Roy, R. Brahmi, C.T. Williams, Appl. Catal. A Gen. 475 (2014) 363–370.
[17] A. Chojecki, M. Veprek-Heijman, T.E. Müller, P. Schärringer, S. Veprek, J.A. Lercher, J. Catal. 245 (2007) 237–248.
[18] Y. Huang, W.M.H. Sachtler, J. Catal. 188 (1999) 215–225.
[19] D.J. Segobia, A.F. Trasarti, C.R. Apesteguía, Appl. Catal. A Gen. 445–446 (2012) 69–75.
[20] P.N. Rylander, L. Hasbrouck, Engelhard Ind. Tech. Bull. 11 (1970) 19–24.
[21] M. Besson, J.M. Bonnier, M. Joucla, Bull. Soc. Chim. Fr. 127 (1990) 5–12.
[22] N.M. Bertero, C.R. Apesteguía, A.J. Marchi, Appl. Catal. A Gen. 349 (2008) 100–109.
[23] N.M. Bertero, A.F. Trasarti, C.R. Apesteguía, A.J. Marchi, Appl. Catal. A Gen. 394 (2011) 228–238.
[24] N.M. Bertero, A.F. Trasarti, C.R. Apesteguía, A.J. Marchi, Appl. Catal. A Gen. 475 (2014) 282–291.
[25] P.A. Ramachandran, R.V. Chaudhari, Three phase catalytic reactors, Gordon and Breach, New York, 1983.
[26] A.J. Marchi, J.I. Di Cosimo, C.R. Apesteguia, Catal. Today 15 (1992) 383–394.
[27] E. Brunner, J. Chem. Eng. Data 30 (1985) 269–273.
[28] J. Park, R.L. Robinson Jr., K.A.M. Gasem, J. Chem. Eng. Data 41 (1996) 70–73.