Gas-phase hydrogenation of propionitrile on copper-lanthanide oxides

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ABSTRACT

The hydrogenation of propionitrile on copper-lanthanide oxide catalysts ($2Cu \cdot CeO_2$ and $4Cu \cdot Ln_2O_3$ ($Ln = La$, Pr, Nd)) was studied in the gas phase. The activity of the catalysts varies with the lanthanide in the order $2Cu \cdot CeO_2 > 4Cu \cdot Pr_2O_3 > 4Cu \cdot La_2O_3 \geq 4Cu \cdot Nd_2O_3$, while the activation energies varies in the opposite order, except for $2Cu \cdot CeO_2$. The main product was the primary amine, *n*-propylamine. The formation of the unstable imine $CH_3CH_2N=CHCH_3$ as a major product over $2Cu \cdot CeO_2$ seems to be consistent with the acidity of the catalyst. The catalysts were more selective than conventional copper impregnation catalysts, Cu (10 wt.%) on SiO_2, La_2O_3 or CeO_2, that produce significant quantities of the secondary amine.

1. Introduction

The catalytic hydrogenation of nitriles is one of the most important methods for preparing amines [1–3]. The reactions are usually accomplished in the presence of heterogeneous transition metal catalysts and the product distribution depends primarily on the catalyst nature: cobalt and nickel catalysts are preferred for the production of primary amines [4–13], copper and rhodium catalysts gives predominantly secondary amines [7,14–19], and platinum and palladium catalysts are quite selective for the production of tertiary amines [7,9,17–19].

The gas-phase hydrogenation of nitriles to produce amines [20–23] is an alternative to the classical liquid-phase reaction. The results obtained are different from those of the liquid-phase, namely what appear to be a better control of the selectivity by a suitable choice of the active phase and support [21,24–26].

The nature of the support seems to have a strong influence on the reaction selectivity, especially their acid–base properties. This fact leads to the proposition of a bifunctional mechanism, in which active sites for the hydrogenation are located on the metal, and strong basic sites appear to increase the selectivity to primary amines [26–29], while the acidic function of the support is responsible for the condensation reactions leading to secondary and tertiary amines [27,30].

However, this is a controversial subject in the literature and it is evident that a great deal of work is still to be done in order to fully understand the mechanism of the gas-phase hydrogenation of nitriles. For example, Volf and Pasek [12] noted that on supported nickel catalysts the support affects the activity of nickel without changing the catalysts selectivity. Others like Huang et al. [22] reported that the support acidity has no effect on the catalysts selectivity, corroborating this observation.

Nevertheless, the results obtained on the gas phase are clearly different from those obtained on the liquid-phase. Rode et al. [31] showed that supported platinum catalysts are highly selective for the formation of diethylamine, whereas on liquid-phase reactions the main product is triethylamine. Furthermore, the preparation method has a strong influence on the catalyst selectivity [20,32,33]. As an example, Arai and co-workers [32] reported that Pd-based catalysts supported on ZrO_2, CeO_2, MgO, SiO_2, Al_2O_3, ZnO, Ga_2O_3 and In_2O_3 were very selective for the gas-phase hydrogenation of acetonitrile to ethylamine and such enhanced selectivity was ascribed to the formation of Pd alloys PdZn, Ga_5Pd, $GaPd_5$, etc. and to the synergism between the two metals. Coq et al. [26] also reported an increase in the methylamine selectivity using Co/Ni/Mg/Al layered double hydroxides as catalytic precursors and attributed it to the formation of NiCo alloys. The lowest selectivity to by-products is reached in the presence of bimetallic NiCo catalysts where the synergism effect between Ni and Co appears to play a major role. Therefore, there is a great deal of interest in the search of new catalytic precursors.

In this context, we have recently reported that binary intermetallic compounds of lanthanide and copper $LnCu_2$ ($Ln = La$, Ce, Pr, Nd) are active and selective for the gas-phase hydrogenation of propionitrile into *n*-propylamine [34]. This result is clearly

different from those obtained in the liquid-phase with copper based catalysts that gives the secondary amines as major products.

Binary intermetallic compounds of lanthanide or actinide metals combined with d metals (namely Ni, Co, Mn, or Fe), which have drawn the attention of many researchers due to their catalytic properties [35–42], are attractive candidates for the gas-phase hydrogenation of nitriles. The intermetallic compounds were described as a new type of supported catalysts precursors, which can be more active and selective than those obtained by conventional routes [36,37,40–46]. The support (lanthanide oxide phase) sems to play an important role for their catalytic properties.

In our laboratories we have used the binary intermetallic compounds $LnCu_2$ (Ln = La, Ce, Pr, Nd) [36], $ThCu_2$ and $AnNi_2$ (An = Cu, Ni) [37] as catalytic precursors and the oxidized products were described as heterobimetallic copper-lanthanide oxides, e.g. $3CuO·Ln_2CuO_4$ or $2CuO·ThO_2$. Such compounds exhibited selectivity for the 4-methylpentan-2-ol decomposition and the lanthanide-containing phase, CeO_2 or Ln_2CuO_4, seems to play a role in the formation of the CuO active sites [36]. Unpublished results show also that the copper-actinide oxides are active for the oxidative coupling of methane using carbon dioxide as reagent.

After reduction, these heterobimetallic oxides were described as supported copper catalysts on lanthanide oxides, $2Cu·CeO_2$ and $4Cu·Ln_2O_3$, which were active and selective for the mesityl oxide hydrogenation to 4-methylpentan-2-one (methylisobutylketone, MIKB) [47]. Their catalytic activity and selectivity were associated with the lanthanide-containing phase that seems to play an important role in the formation of the copper or nickel active sites.

On that account, we report here the results obtained for the gas-phase hydrogenation of propionitrile over $2Cu·CeO_2$ and $4Cu·Ln_2O_3$ (Ln = La, Pr, Nd). Samples were characterized by powder X-ray diffraction (XRD), temperature-programmed desorption of carbon dioxide (CO_2-TPD) and oxidative dehydrogenation–dehydration of 2-propanol.

2. Experimental

2.1. Catalysts preparation

The copper-lanthanide oxide catalysts ($2Cu·CeO_2$, $4Cu·Ln_2O_3$ (Ln = La, Pr, Nd)) were prepared from $LnCu_2$ (Ln = La, Ce, Pr, Nd), as described earlier [34,36,47]. Briefly, the intermetallic compounds were first oxidized under air (Air Liquide, $O_2:N_2 = 20:80$ (vol%), purity 99.995%, 17 cm^3 min^{-1}) at a heating rate of 10 °C min^{-1} up to 1000 °C, followed by reduction under pure hydrogen (Air Liquide, purity 99.99%, 17 cm^3 min^{-1}) at a heating rate of 10 °C min^{-1} up to 550 °C. The reduction products were characterized by XRD and the diffraction patterns indicate pure crystalline phase of Cu along with either CeO_2 or Ln_2O_3 (Ln = La, Pr, Nd). The characterization of the reduction end products by elemental analysis confirms the stoichiometries (Cu ≈ 40 wt.%) and the SEM/EDX measurements have shown that the catalysts surface are enriched with copper, except for $4Cu·La_2O_3$ (molar ratio between the d and f elements at the catalysts surface is equal to 1.5 for $4Cu·La_2O_3$ and higher in the case of $2Cu·CeO_2$, $4Cu·Pr_2O_3$ and $4Cu·Nd_2O_3$ (3.0, 4.0 and 4.0 ± 0.1, respectively)) [47]. The BET specific surface areas were determined on an Accusorb 2100E apparatus from Micromeritics using Kr or N_2 adsorption at −196 °C. The samples were pretreated under vacuum (10^{-3} mbar) at 523 °C for 15 h. Found (m^2/g): $4Cu·La_2O_3$, 2.9; $2Cu·CeO_2$, 6.5; $4Cu·Pr_2O_3$, 3.2; $4Cu·Nd_2O_3$, 2.4.

Impregnation supported copper catalysts, 10 wt.%, were obtained by the incipient wetness method using an aqueous solution of copper (II) acetate monohydrate on SiO_2, La_2O_3 or CeO_2. The reagents were used as supplied: $(CH_3COO)_2Cu·H_2O$ (Fluka, purity ≥99.0%), La_2O_3 and CeO_2 (Fluka, purity ≥99.0%), and SiO_2 (Degussa 200, purity 99.9%). After impregnation, water was removed and the residue was dried in an oven at 150 °C for 4 h and then treated with hydrogen at 750 °C (H_2, 50 cm^3/min). The copper content on each catalyst was determined at the Service Central d'Analyse du CNRS (Solaize, France) by inductively coupled plasma spectrometry (ICP). Found (wt.%): Cu, 9.2 ± 0.3; Si, 40.7 ± 1.2; calculated for 10% copper loading on SiO_2: Cu, 10; Si, 42.1. Found (wt.%): Cu, 8.3 ± 0.3; La, 68.1 ± 2.1; calculated for 10% copper loading on La_2O_3: Cu, 10; La, 76.7. Found (wt.%): Cu, 9.5 ± 0.3; Ce, 69.3 ± 2.1; calculated for 10% copper loading on CeO_2: Cu, 10; Ce, 73.3. BET specific areas (m^2/g): 196.0, 157.4, 110.0, 83.7 and 43.3 for SiO_2, 10% Cu/SiO_2, CeO_2, 10% Cu/CeO_2 and 10% Cu/La_2O_3 respectively. The XRD diffraction patterns after reduction show only the pure crystalline phase of metallic copper.

2.2. Catalysts characterization

2.2.1. Temperature-programmed desorption of carbon dioxide (CO_2-TPD)

The CO_2-TPD was used to determine the basicity of the supports and catalysts. Prior to adsorption of CO_2, the catalysts (50 mg) were cleaned by passing a He stream (50 mL min^{-1}) at 250 °C for 30 min. The solids were then saturated with CO_2 (17 mL min^{-1}) at 50 °C for 1 h, followed by a pure He stream (50 mL min^{-1}) at the saturation temperature for 3 h. Once a stable line was obtained, the chemisorbed CO_2 was desorbed by heating from 50 °C up to 1000 °C at a rate of 10 °C min^{-1}. Desorption was monitored by a Shimadzu 9A gas chromatograph equipped with a thermal conductivity detector (TCD, $T_{column} = 105$ °C, $T_{detector} = 105$ °C, 150 mA). The amount of carbon dioxide desorbed was taken as a measure of the number of basic centers while the temperature range at which the carbon dioxide is desorbed is an indicator of the strength of the basic sites. The basic sites were classified as weak (T_m below 400 °C), medium strength (T_m between 400 and 600 °C) and strong basic sites (T_m over 600 °C) according to the different carbon dioxide maximum rate desorption temperatures, T_m [48,49].

2.2.2. Dehydrogenation/dehydration of 2-propanol

The oxidative dehydrogenation–dehydration of 2-propanol was used as a test reaction for effective acidity of catalysts. The catalytic activity tests were carried out in a U-shaped quartz reactor (plug-flow type) at 250 °C, with a glass frit and an inside volume of 15 cm^3, operating continuously at atmospheric pressure under a gaseous flow of 0.75 vol% of alcohol in air (N_2/O_2: 80/20 vol%, Air Liquide K, purity 99.9995%). Mass flow controllers were used to control air and He (Air Liquide N60, purity 99.9995%) flows. A thermocouple was placed near the catalytic bed for continuous monitoring of the sample temperature. The reaction was studied with an adequate gas hourly space velocity (GHSV) of 2000 mLi-PrOH/g h at $T = 250$ °C, $m = 50–100$ mg. The outlet gas composition was analyzed by on-line gas chromatography with a Carbopack C/0.1% SP-1000 packed column ($L = 2.0$ m, $f = 1/8$ in., 80–100 mesh) and a Shimadzu 9A instrument equipped with a flame ionization detector (FID). The reaction was performed under oxidative conditions to avoid catalyst deactivation, as the surface metal oxides can lose oxygen under reducing condition. None of the samples showed diffusion restrictions (Weisz–Prater criterion). The gaseous effluent was monitored every 60 min using a 6-port gas sampling valve with a 0.250 cm^3 loop. The reaction rate (r_i) has been calculated as the number of moles of 2-propanol converted per second and per m^2 of catalyst (mol s^{-1} m^{-2}).

2.3. Catalyst reactivity

2.3.1. Hydrogenation of propionitrile

The experimental procedure used for the gas-phase hydrogenation of propionitrile was identical to that used for the oxidative dehydrogenation–dehydration of 2-propanol with their own specificities: (i) the fixed bed U-shaped glass reactor operates continuously at atmospheric pressure under a gaseous flow of nitrile in hydrogen, (ii) low nitrile conversion to keep the reaction in the kinetic regime, (iii) the starting intermetallic compounds were treated *in situ* and (iv) unless otherwise stated, the reaction was studied with an adequate gas hourly space velocity (GHSV) of 1000 $mL_{Propionitrile}$/g h at $T = 200 °C$, $m = 10$–150 mg, partial pressure of propionitrile ($P_{Nitrile}$) = 0.01 bar and partial pressure of hydrogen (P_{H_2}) = 0.99 bar.

The outlet gas composition was analyzed on-line by gas chromatography using a Gas Chrom Q column ($L = 2.0$ m, $f = 1/8$ in., 80–100 mesh; liquid phase AT223 + KOH (28 + 4, w/w%)) and an Intersmat 120 DFB instrument equipped with a flame ionization detector (FID). GC–MS (Hewlett Packard 5971, 70 eV, electronic impact, column 25 m, Ø = 0.2 mm, Gaz Chrom Q (80–100 mesh) coated at 10% with Carbowax 20 M (film of 1.3 mm)) was used to identify all the collected reaction products.

The reaction rate (r_i) has been calculated as the number of moles of nitrile converted per second and per m^2 of catalyst (mol s^{-1} m^{-2}). The extent of deactivation is defined as the fraction of the initial activity loss at steady state. Apparent activation energies (E_a) were obtained by plotting $\ln r_i$ against $1/T$ (K^{-1}), using the equation of Arrhenius.

3. Results and discussion

3.1. Activity and stability of catalysts

Fig. 1 shows that the activity of the copper-lanthanide oxides (2Cu·CeO$_2$ and 4Cu·Ln$_2$O$_3$ (Ln = La, Pr, Nd)) for the gas-phase hydrogenation of propionitrile decreases significantly with time on stream. In all cases, the loss of activity was higher than 80% and the primary amine (n-propylamine) the only product observed under our experimental conditions.

This deactivation can be related either to the formation of coke or to modifications on the catalysts surface, namely due to particle sintering [22]. Nevertheless, other contributions such as poisoning attributed to amines strongly adsorbed on the catalysts that cover the active sites and/or formation of an overlayer must not be discarded [20–22,33].

The catalytic activity varies with the lanthanide in the order 2Cu·**CeO$_2$** > 4Cu·**Pr$_2$O$_3$** > 4Cu·**La$_2$O$_3$** ≥ 4Cu·**Nd$_2$O$_3$**, while the activa-
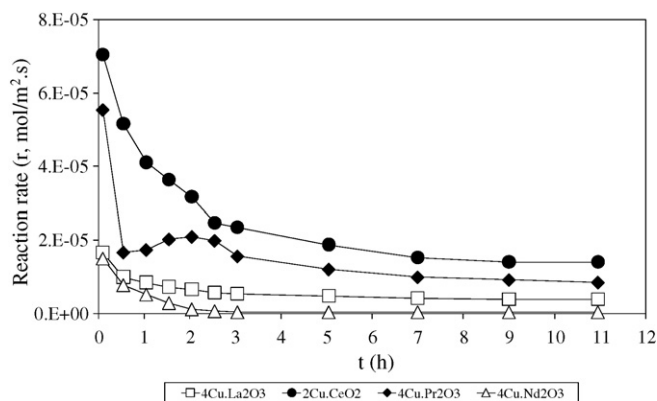

Fig. 1. Conversion of propionitrile over the copper-lanthanide oxides as a function of time on stream at 175 °C.
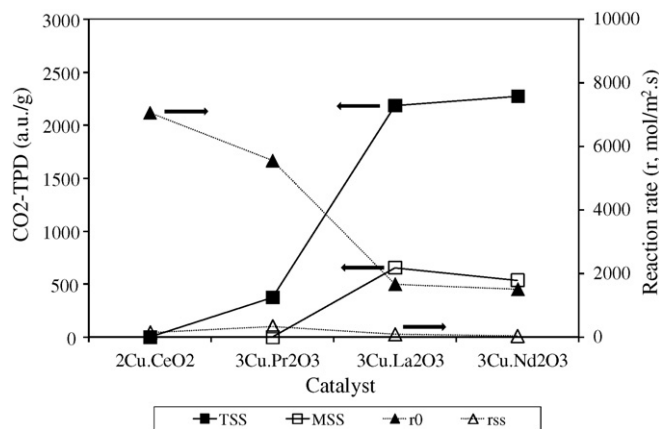

Fig. 2. Effect of the catalysts basicity in the propionitrile reaction rate to n-propylamine.

tion energies varies in the opposite order, except for 2Cu·CeO$_2$ (Table 1). These kinetic data could indicate that different catalytic species are present which exclude the predominant role of the Cu phase; the lanthanide phases, Ln$_2$O$_3$ and CeO$_2$ appear to contribute to the catalytic behavior of copper-lanthanide oxides [36].

Acid–base properties of metal oxides play a key role in catalysis and can be characterized by different methods, e.g. test-reactions or probe molecules adsorption. In this work, we have measured the total number of basic sites, its density and strength distribution on the copper-lanthanide oxides by temperature-programmed desorption using carbon dioxide as a molecular probe for basic sites (CO$_2$-TPD) [49,50] and we have used the 2-propanol (IPA) oxidative dehydrogenation/dehydration for the characterization of the catalysts surface redox properties [51,52]. For comparison, the results obtained with Ln$_2$O$_3$ (Ln = La, Pr, Nd), CeO$_2$, ThO$_2$ and MoO$_3$ are also reported. ThO$_2$ and MoO$_3$ are well known basic and acid oxides, respectively.

According to the total basic site density measured by CO$_2$-TPD (Table 2), the catalysts can be ranked as follows: 4Cu·Nd$_2$O$_3$ = 4Cu·La$_2$O$_3$ > 4Cu·Pr$_2$O$_3$ ≫ 2Cu·CeO$_2$. The metal oxides that presented an acidic character were CeO$_2$, 2Cu·CeO$_2$ and MoO$_3$, whereas ThO$_2$ has a basic surface in agreement with the literature [51,53,54]. Therefore, the acid–base properties of 2Cu·CeO$_2$ are significantly different from those of the other copper-lanthanide metal oxide tested is this work that have basic properties.

The basicity (total number of basic sites) of copper-lanthanide metal oxides clearly leads to the increase in the activity of the catalysts (Fig. 2). The total number of weak and medium strength sites (T_m below 600 °C) seems to have also a good correlation with the increase in the reaction rate (the number of strong basic sites is always very low, except for 4Cu·La$_2$O$_3$). On the other hand, the decrease in total basic site density correlates with the increase in the reaction rate but did not modify the catalysts selectivity towards the primary amine.

Using IPA test reaction, the catalysts can be classified by their propensity towards the dehydration or the dehydrogenation activity to propene (PPE) or acetone (ACE), respectively. From a mechanistic point of view, the acid site catalyzes the dehydration of 2-propanol, whereas both acid and basic sites catalyze the dehydrogenation through a concerted mechanism [52]. For a number of catalysts, good correlations were found between the acidity measured by the adsorption of ammonia and the 2-propanol dehydration rate measured and the basicity measured by adsorption of CO$_2$ and the ratio of the 2-propanol dehydrogenation to the dehydration rate [51].

In this work, the main products were ACE and PPE, and the formation of other products such as diisopropyl ether (DIPE) was

Table 1
Activity and selectivity of the copper-lanthanide oxides for the gas-phase hydrogenation of propionitrile at 250 °C.

Catalysts	2Cu·**Ce**O_2	4Cu·**Pr**$_2O_3$	4Cu·**La**$_2O_3$	4Cu·**Nd**$_2O_3$
r_o[a], 10^{-8} (mol m^{-2} s^{-1})	7051 (45971)	5547 (17917)	1659 (4762)	1502 (3576)
r_{ss}[a], 10^{-8} (mol m^{-2} s^{-1})	1410 (9190)	853 (2754)	392 (1124	39 (94)
E_a[b] (kJ mol^{-1})	100	51	77	107

[a] Reaction rate at start of run (r_o) and at steady state (r_{ss}); between parentheses the values in mol g$_{Cu}^{-1}$ s^{-1}.

[b] Determined between 150 and 250 °C.

Table 2
CO_2-TPD distribution and strength of basic sites over the copper-lanthanide oxides.

Catalysts	CO_2-TPD[a] (a.u./g)			
	Total	WSS	MSS	SSS
2Cu·CeO_2	0	0	0	0
CeO_2	0	0	0	0
4Cu·Pr$_2O_3$	371	371	0	0
Pr$_2O_3$	3328	2363	587	378
4Cu·La$_2O_3$	2183	1438	654	91
La$_2O_3$	9470	5081	1403	2986
4Cu·Nd$_2O_3$	2270	1734	536	0
Nd$_2O_3$	9397	6487	2771	139
CuO	5939	0	0	5939
ThO_2	322	0	322	0
MoO_3	0	0	0	0

[a] SSS, Strong strength sites (600–1000 °C); MSS, medium strength sites (400–600 °C); WSS, weak strength sites (<400 °C).

never detected. This study confirms that the main property of the copper-lanthanide oxides surface is their basicity, except for 2Cu·CeO_2. 4Cu·Ln$_2O_3$ (Ln = La, Pr, Nd) exhibited a high selectivity to acetone (>96%), whereas 2Cu·CeO_2 exhibited a significant selectivity to propene (25%).

The acidity of 2Cu·CeO_2 is significantly higher than that of 4Cu·Pr$_2O_3$ and the acidity of 4Cu·La$_2O_3$ and 4Cu·Nd$_2O_3$ is lower than that of 4Cu·Pr$_2O_3$, which is reflected in the reaction rate of the gas-phase hydrogenation of propionitrile (Fig. 3). We have also studied the catalytic decomposition of 2-propanol over pure lanthanide oxides and the values obtained for the dehydrogenation (>99% over Ln$_2O_3$) and dehydration products (100% over CeO_2) confirms that in the case of the copper–cerium oxide catalyst the acidity can be ascribed to the support.

Therefore, the importance of the catalyst basicity as a precondition for a good selectivity seems to be a fact, whereas in the case of the cerium compound the presence of an important acidic function on the support and the existence of a synergism effect between copper active phase and the cerium oxide support could play a major role in the catalysts activity and selectivity (see below).
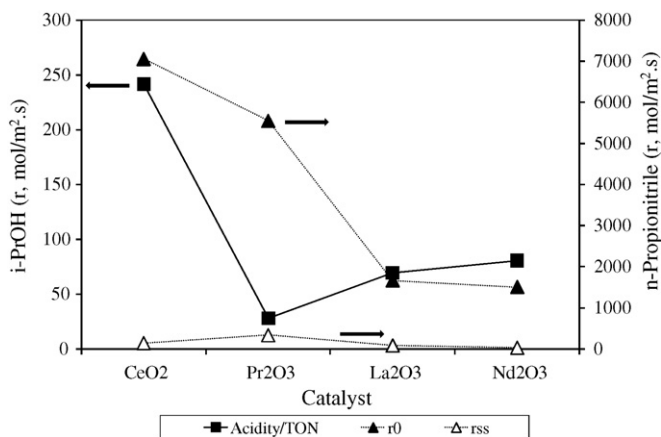
3.2. Reaction conditions

The reaction rate of the gas-phase hydrogenation of propionitrile over the copper-lanthanide oxide catalysts increases with the temperature, residence time (τ) and hydrogen partial pressure (P_{H_2}). However, the selectivity was not affected by these variables and the propionitrile is selectively hydrogenated to *n*-propylamine. This result is clearly different from that reported for the liquid-phase hydrogenation of nitriles using copper based catalysts and agree with the results previously reported for the gas-phase hydrogenation of propionitrile on LnCu$_2$ (Ln = La, Ce, Pr, Nd) [34].

We have found that the hydrogenation of propionitrile over the copper-lanthanide oxides is a pseudo-first-order with respect to hydrogen and a pseudo-zero-order with respect to propionitrile, in agreement with the literature [34,55]. The independence of the reaction rate from nitrile concentration is in line with previous hydrogenation reactions, for which zero order with respect to nitrile has been reported [25,55]. This fact suggests that the active sites of the copper-lanthanide oxide catalysts were fully saturated with nitrile, which could contribute to the primary amine selectivity. Previous studies have also demonstrated that high hydrogen pressures increases the reaction rates and can lead to a decrease in the condensation reactions and therefore to a decrease in the formation of secondary and tertiary amines [28].

Nevertheless, in this work the selectivity in the gas-phase hydrogenation of propionitrile over the copper-lanthanide oxide catalysts was not controlled by P_{H_2}. In contrast, the increase in $P_{Nitrile}$ decreased the selectivity to *n*-propylamine; the selectivity decreases with decreasing H$_2$/nitrile molar ratios. Fig. 4 presents a plot of the selectivity *vs.* H$_2$/nitrile molar ratio (for clarity purposes we have omitted *n*-propylamine).

The results obtained over 4Cu·Ln$_2O_3$ (Ln = La, Pr, Nd) show that the decrease in the H$_2$/nitrile ratio increases the dipropylamine selectivity. *n*-Propylamine is highly selectively (>90%) formed for a hydrogen partial pressure (H$_2$/nitrile ratio ≥50), which corroborate the hydrogen partial pressure effects. The decrease in the H$_2$/nitrile ratio is always accompanied by the increase in the

Fig. 3. Effect of the catalysts acidity in the propionitrile reaction rate to *n*-propylamine.
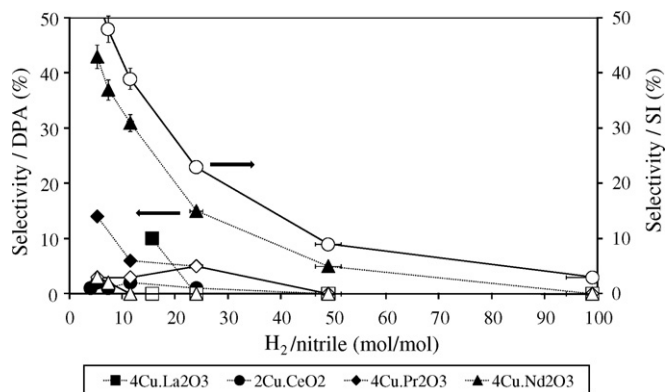
Fig. 4. Effect of the H$_2$/nitrile molar ratio in the reaction selectivity over the copper-lanthanide oxide catalysts at 200 °C ($P_{Nitrile}$ = 0.01–0.16 bar, on a gaseous flow of pure hydrogen at atmospheric pressure). Legend: DPA, dipropylamine (bold symbols); SI, secondary imine (CH$_3$CH$_2$N=CHCH$_3$) (open symbols).

Table 3
Activity and selectivity of the impregnation supported copper catalysts for the gas-phase hydrogenation of propionitrile at 250 °C.

Catalysts	10% Cu/La$_2$O$_3$	10% Cu/SiO$_2$	10% Cu/CeO$_2$
r_o[a], 10^{-8} (mol m^{-2} s^{-1})	955 (41337)	281 (44262)	94 (402)
r_{ss}[a], 10^{-8} (mol m^{-2} s^{-1})	105 (4547)	14 (2213)	4 (294)
E_a[b] (kJ mol^{-1})	69	75	94
Selectivity (%)			
n-Propylamine	75	35	85
Dipropylamine	25	65	15

[a] Reaction rate at start of run (r_o) and at steady state (r_{ss}); between parentheses the values in (mol g$_{Cu}$$^{-1}$ s^{-1}).

[b] Determined between 150 and 250 °C.

dipropylamine selectivity and a minor production of the secondary imine (CH$_3$CH$_2$N=CHCH$_3$, <5%). Earlier studies have confirmed that low space velocities and high H$_2$/acetonitrile ratios increase the acetonitrile conversion and limit the yield of higher amines [21,28].

Over 2Cu·CeO$_2$ the behavior is different and the decrease in the primary amine selectivity was not followed by an increase in the secondary amine selectivity but by a significant increase in the secondary imine selectivity. To the best of our knowledge, it is the first time that a stable formation of an intermediate such as a secondary imine is reported is the gas phase. On the other hand, the increase in the hydrogen pressure is reported as a way to eliminate catalysts deactivation [22], which was not the case on our materials.

3.3. Catalysts preparation method

The performance of metallic catalysts depends on the preparation method and, as a result, on the metal distribution and degree of reduction. In this work, the results of copper catalysts (10 wt.%) loaded on La$_2$O$_3$ and SiO$_2$ were significantly different from those of the copper-lanthanide oxides, namely a lower selectivity to *n*-propylamine (Table 3).

The effects of other reaction conditions such as temperature, gas hourly space velocity (GHSV) and the H$_2$/nitrile molar ratio on the reaction rate were considerably different from those obtained on the copper-lanthanide oxides. For example, at a low partial pressure of nitrile ($P_{Nitrile}$ = 0.01 bar in a gaseous flow of pure hydrogen, the decrease in the H$_2$/nitrile molar ratio decreases the rate of formation of the primary amine that was selectively formed over 4Cu·Ln$_2$O$_3$ and 2Cu·CeO$_2$ (Fig. 5).

Therefore, the products were substantially influenced by the reaction conditions and by the catalysts preparation method and in the case of the copper-lanthanide oxides the selectivity is clearly

Fig. 5. Effect of the H$_2$/nitrile molar ratio and WHSV in the reaction selectivity to *n*-propylamine (PA) over the impregnation supported copper catalysts at 200 °C ($P_{Nitrile}$ = 0.01–0.16 bar, on a gaseous flow of pure hydrogen at atmospheric pressure). Legend: H$_2$/nitrile (bold symbols); WHSV (open symbols).

improved. To understand these results we must take in account: (i) the nitrile hydrogenation mechanism [6,30], (ii) the nature of the catalysts surface (active sites) and (iii) the bond strength between reagent, intermediates and products and the active metal sites.

Copper-lanthanide oxides are better described as copper catalysts supported on rare earth metal oxides that have a very strong basic character [36]. Consequently, one possible reason for the selective formation of the primary amine lies on the lack of acid sites, which are known to catalyze condensation reactions that could lead to secondary or tertiary amines [21,25]. A weaker interaction between *n*-propylamine and the catalysts surface also explain the higher selectivity to the primary amine [28]. Verhaak et al. have demonstrated that basic supports favor the formation of primary amines [30].

The nature of the metal is probably the parameter that has the major influence on the activity and selectivity of the catalysts. Nevertheless, the support can affect the catalysts behavior and the precise nature of the elementary processes at the surface among adsorbed species is still a point of controversy in the literature and most of the intermediates of the nitrile hydrogenation mechanism have not been confirmed with the exception of the Schiff bases (secondary imines, enamines) [6,56] that were only reported on supported metal catalysts where secondary reactions to higher amines can continue on the support acid sites by condensation between amine and protonated imine to yield a protonated aminal. The secondary imine formed after NH$_3$ release is in turn hydrogenated on the metal sites to secondary amine (bifunctional mechanism) [57–59]. However, this mechanistic model seems to fail when applied to some catalytic systems where all the reaction steps leading to higher amines seemed to take place only on the metal sites [20,56].

Recently, Sachtler and co-workers [22,56,60,61] have studied the absorption and hydrogenation of nitriles on supported transition metals and proposed a new model for the nitrile hydrogenation mechanism. Their key finding was that higher amines are formed in the chemisorbed layer on the metal by a nucleophilic attack from the carbon of a solution phase formed by the nitrile and an adsorbed intermediate (M = NR, where M is the metal surface) and that the hydrogen is donated by the nitrile molecule and not from adsorbed hydrogen.

In this work, both the copper and support sites are basic (except for the cerium compound) and the hydrogen partial pressure study shows that the availability of hydrogen (at a low nitrile partial pressure) does not play a significant role in catalysts selectivity, whereas the data from the nitrile partial pressure study confirm the formation of the secondary amine or the secondary imine intermediate at high nitrile partial pressure (low H$_2$/nitrile ratio).

Therefore, the model that seems more consistent to explain the catalytic behavior of the copper-lanthanide oxides is that of Sachtler where high nitrile concentration could increase the formation of higher amines by the reaction on the overlayer involving the amine meanwhile formed and an unsaturated surface intermediate. Moreover, the stability of the partially hydrogenated reaction intermediate (CH$_3$CH$_2$N=CHCH$_3$) over 2Cu·CeO$_2$ can be also explained
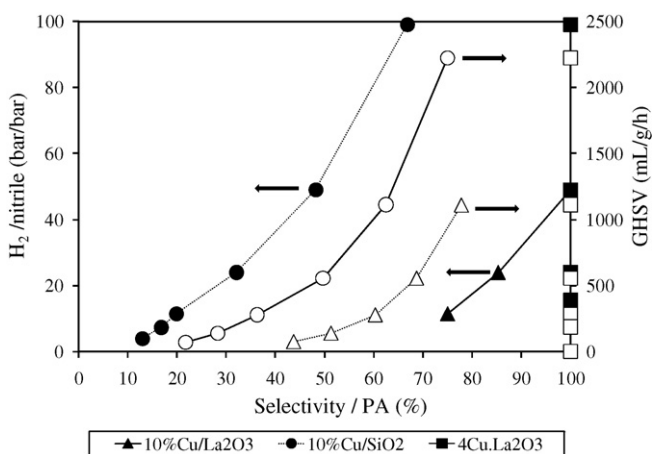
by a higher adsorption strength of the C=N bond on the catalyst surface due to the acidity of the support that blocks the active sites and slow down the hydrogenation to the secondary amine [62]. Nevertheless, further work is needed to elucidate the mechanism operating in the gas-phase hydrogenation of propionitrile over this type of catalysts, including the precise nature of the active copper sites.

4. Conclusions

The work covering copper-based catalysts shows that the formation of primary amines is normally accompanied by a significant formation of secondary amines. This study shows that the supported copper-lanthanide oxides are active and very selective for the gas phase propionitrile hydrogenation to *n*-propylamine. The results obtained are consistent with the copper-lanthanide oxides basicity that seems to play a key role in the behavior of this new type of supported copper catalysts. One possible reason for the selective formation of the primary amine lies on the lack of acid sites, which are known to catalyze condensation reactions that could lead to secondary or tertiary amines. The model that seems more consistent to explain the catalytic behavior of the copper-lanthanide oxides is that of Sachtler.

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