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# Application of supported lanthanum catalysts in the hydrogenation of nitriles

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## Abstract

Nickel and lanthanum on MgO or MgO–Al<sub>2</sub>O<sub>3</sub> catalysts were prepared and characterized. The applicability of the catalysts was studied in the liquid-phase hydrogenation of benzonitrile. A La/MgO catalyst showed surprisingly high activity and selectivity. The scope of the reaction was extended to other nitriles (benzyl cyanide, cinnamitrile, adiponitrile) over this La/MgO catalyst.

**Keywords** Heterogeneous catalysis · Hydrogenation · Lanthanum · Magnesium oxide · Nitriles

**JEL Classification codes** O33 Technological change · Choices and consequences · Diffusion processes

## Introduction

Heterogeneous catalysis is a widely researched field in organic chemistry. About 85–90% of all chemical manufacturing processes require the use of a catalyst. Among these reactions about 80–85% applies heterogeneous catalysis [1]. Therefore, the elaboration of new heterogeneous catalytic methods is of great importance in synthetic organic chemistry.

Primary amines represent an important group of intermediates and are widely used in the pharmaceutical and herbicide industry. There are various methods for

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their synthesis, such as the alkylation of ammonia and the reductive amination of oxo compounds. However, a frequently used preparation method in the pharmaceutical industry is the heterogeneous catalytic hydrogenation of nitriles [2].

Benzylamine is an important intermediate for the synthesis of several drugs [3], dyes or synthetic resins [2]. Another application is as a corrosion inhibitor [4]. In the asymmetric hydrogenation of  $\alpha,\beta$ -unsaturated carboxylic acids over cinchonidine-modified 5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, benzylamine is used as an additive to enhance the enantioselectivity [5].

It is well-known, that during the conversion of nitriles into primary amines secondary and tertiary amines can be formed in side reactions decreasing the selectivity of the reaction [6–10]. The amount of the secondary and tertiary amines in the reaction mixture can be minimized by the removal of the primary amine [11–16] or by the addition of excess ammonia [17–20]. Usually a Raney® nickel [17, 19, 20] or rhodium catalyst [18] is required to achieve high primary amine selectivity. However, more and more methods have been elaborated for the selective hydrogenation of benzonitriles using nickel [21–23] ruthenium [24–26] and palladium [27–31] catalysts.

Although lanthanum was used in the heterogeneous catalytic hydrogenation of olefinic double bonds [32], p-chloronitrobenzene [33], dimethyl oxalate [34], anthraquinone [35] or carbon oxides [36], its role has been limited to act as a part of a support (Pd/Mg-La mixed oxide [32]) or as a promoter of NiB [33, 35] and Ni [36], as well as Cu [34]. In addition, only few methods are mentioned in the literature, where lanthanum is used in the hydrogenation of nitriles to amines, but it was also applied as a promoter of nickel only [37, 38]. Accordingly, to our best knowledge, there are no examples concerning the hydrogenation activity of lanthanum itself.

Our research group has efficiently used various supported heterogeneous catalysts in organic reactions [39, 40]. For example, a nickel on magnesium-lanthanum mixed oxide catalyst has recently been applied in the Kumada reaction [41]. A Pd/MgLa mixed oxide or a Pd/MgAl mixed oxide catalyst was used in the catalytic transfer hydrogenation of cinnamic acid derivatives and hydrogenolysis of aromatic halides in ionic liquids [42].

In continuation of our interest, various metal oxide (MgO) and mixed oxide (MgO–Al<sub>2</sub>O<sub>3</sub>) supported base metal (Ni and La) catalysts were prepared. The catalysts were characterized by BET, ICP-OES, SEM and EDS technique. The activity of the catalysts was tested in the heterogeneous catalytic hydrogenation of benzonitrile.

## Experimental

### Materials

The catalyst precursors (magnesium ethoxide, aluminium-tri-*sec*-butoxide), as well as Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and oxalic acid (99%) were purchased from Merck KGaA, Darmstadt, Germany.

Benzonitrile (99%), benzyl cyanide (99%), cinnamionitrile (98%) and adiponitrile (99%) were supplied from Merck-Schuchardt (Hohenbrunn, Germany). Methanol (p.a.) and ethanol (p.a.) were also purchased from Merck KGaA (Darmstadt, Germany).

## Catalyst preparation

### Preparation of MgO with sol–gel method

For the preparation of MgO, magnesium ethoxide (15.4 g, 0.1346 mol) in ethanol (134 mL) was stirred at reflux for 15 min. Next, oxalic acid (1.0 g) dissolved in water (5 mL) was added to the reaction mixture to obtain a pH of 5. The mixture was stirred at reflux for 2.5 h. Then, water (162 mL) was added and the mixture was stirred at reflux for another 15 min. Then it was dried at 80 °C overnight and continued to dry at 120 °C for 8 h. Finally, the dried mixture was calcined under air with the following temperature profile: at 5 °C/min to 250 °C, 250 °C hold for 1 h, at 5 °C/min to 500–550 °C, 550 °C hold for 3 h, then cooling at 10 °C/min to 30 °C.

### Preparation of the MgO–Al<sub>2</sub>O<sub>3</sub> mixed oxide with sol–gel method

For the preparation of MgO–Al<sub>2</sub>O<sub>3</sub>, magnesium ethoxide (15.4 g, 0.1346 mol) in ethanol (134 mL) was stirred at reflux for 15 min. Next, oxalic acid (1.0 g) dissolved in water (5 mL) was added to the reaction mixture to obtain a pH of 5. The mixture was stirred at reflux for 2.5 h. Then, aluminium-tri-*sec*-butoxide (0.08978 mol) and water (162 mL) were added, and the mixture was stirred at reflux for another 15 min. Then, it was dried at 80 °C overnight and continued to dry at 120 °C for 8 h. Finally, the dried mixture was calcined under air with the following temperature profile: 5 °C/min to 250 °C, 250 °C hold for 1 h, 5 °C/min to 500–550 °C, 550 °C hold for 3 h, then cooling 10 °C/min to 30 °C.

### Preparation of the monometallic catalysts with wet impregnation

To prepare the monometallic catalysts 1.0 g of powdered MgO or MgO–Al<sub>2</sub>O<sub>3</sub> and 1.0 mmol of the corresponding metal precursor [Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O] was stirred in 30 mL of deionized water at room temperature for 12 h. Then it was dried at 120 °C for 24 h and calcined with the following temperature profile: 5 °C/min to 500 °C, 500 °C hold for 2 h, then cooling 10 °C/min to 30 °C. Then the catalyst was reduced with a 60 mL/min H<sub>2</sub> flow using the following temperature profile: 5 °C/min to 700 °C, 700 °C hold for 4 h, then cooling 10 °C/min to 30 °C.

## Preparation of the bimetallic catalyst with successive impregnation

For the preparation of the bimetallic catalyst the previously prepared La/MgO–Al<sub>2</sub>O<sub>3</sub> catalyst was stirred with Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as described above. The thermal treatments were also the same as mentioned afore.

## Typical procedure for the hydrogenation reactions

The hydrogenation reactions were carried out in a 250 mL stainless steel autoclave (Technoclave, Budapest, Hungary) equipped with a magnetic stirrer (stirring speed: 1100 rpm), and electric heating system, at 10 bar and 100–130 °C. The reactor containing nitrile (2.0 g), supported Ni or La catalyst (0.2 g) and methanol (50 mL) was flushed with nitrogen and hydrogen, then charged with hydrogen to the specified pressure and heated up to the given temperature. After finishing the hydrogen uptake, the catalyst was filtered off and the filtrate was evaporated under vacuum. The products were isolated in 96–99% and analysed by GC–MS.

The MS data of the starting materials and the products are the following: BN (see Figs. 4, 5, 6 and 7 for the abbreviations) *m/z* (rel%) 103 (100), 76 (38), 50 (18); BA *m/z* (rel%) 106 (100), 91 (12), 79 (40), 51 (38), 30 (85); DBA *m/z* (rel%) 196 (10), 120 (11), 106 (57), 91 (100), 65 (17), 51 (8); BC *m/z* (rel%) 117 (100), 90 (39), 77 (10), 63 (13), 51 (19); PEA 121 (23), 103 (11), 91 (100), 77 (20), 65 (90), 51 (72); BPEA *m/z* (rel%) 134 (100), 105 (60), 91 (11), 77 (11), 65 (11), 42 (11); CN *m/z* (rel%) 129 (100), 102 (44), 76 (13), 63 (10), 51 (17); PPN *m/z* (rel%) 131 (30), 91 (100), 77 (4), 65 (10), 51 (6); BPPA *m/z* (rel%) 253 (18), 148 (100), 117 (16), 105 (7), 91 (99), 77 (10), 65 (12), 56 (11); AN *m/z* (rel%) 107 (2), 80 (4), 68 (90), 54 (100); ICN *m/z* (rel%) 109 (19), 100 (95), 86 (28), 73 (78), 68 (76), 54 (100); BACN *m/z* (rel%) 207 (1), 165 (12), 151 (16), 123 (100), 96 (43) 84 (36), 70 (25), 56 (60). These analytical results are in accordance with the literature data [43].

GC–MS analyses were performed by an Agilent 7890A GC-system (7683 autosampler and 7683B injector) connected to an Agilent 5975C mass spectrometer using a Restek Rxi®-5Sil MS capillary column (15 m × 0.25 mm ID, 0.25 μm film). The temperature program was the following: 45 °C (1 min) to 300 °C at 50 °C/min, hold 1 min for BN, BC and AN, as well as 70 °C (1 min) to 300 °C at 33 °C/min, hold 2 min for CN.

## Catalyst characterization

Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was carried out on a Perkin-Elmer Optima 2000DV to determine the metal content on the support.

The specific surface area of the catalysts was measured by nitrogen adsorption and desorption at –196 °C with BET (Brunauer–Emmett–Teller) surface analyser

(Micromeritics Model TRISTAR 3000) using BET-BJH (Barrett-Joyner-Halenda) method after drying each material in anaerobic chamber for 12 h.

The structure and morphology of the catalysts were investigated with a JEOL JSM-5500LV scanning electron microscope. Samples for SEM analysis were placed on a copper grid coated with carbon film then coated with gold nano-layer prior to analysis. Electron beam energy of 20 kV was used in every case.

The elemental analysis was carried out with energy dispersive spectroscopy/energy dispersive X-ray analysis (EDS/EDAX with Si(Li) detector) coupled with JEOL JSM-5500LV SEM applying 20 kV accelerating voltage and sampling time of 60 s. The element composition of the samples was calculated from five parallel measurements.

## Results and discussion

### Catalyst characterization

An ICP-OES analysis of the catalysts was carried out to determine the real metal content. The metal content on the surface of the catalysts was also examined by EDS measurements. Based on the ICP-OES data, it can be concluded that the metal contents of the catalysts are in accordance with the theoretical values. The EDS results show that the metallic particles can unambiguously be detected on the surface of the catalysts (Table 1).

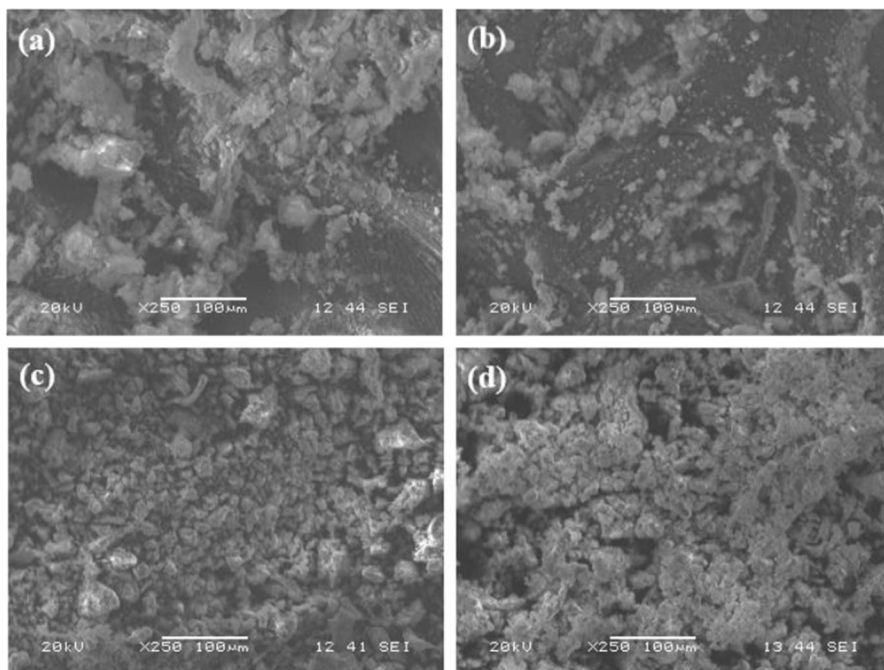
Fig. 1 shows the SEM images of the prepared catalysts. In case of the MgO-supported materials higher aggregation of the particles can be seen. The MgO–Al<sub>2</sub>O<sub>3</sub>-supported materials have a less compact structure. This more porous structure may result the higher specific surface area observed (Table 1).

In Fig. 2, the particle size distributions of the different catalysts are shown. In all cases most of the particles are between 1 and 30  $\mu\text{m}$ . The average particle size is around 18–19  $\mu\text{m}$ , except for the La/MgO, where the average particle size is 12  $\mu\text{m}$ . Generally, the particles are between 1 and 50  $\mu\text{m}$ , but a few particles with a particle size of up to 85  $\mu\text{m}$  can be observed.

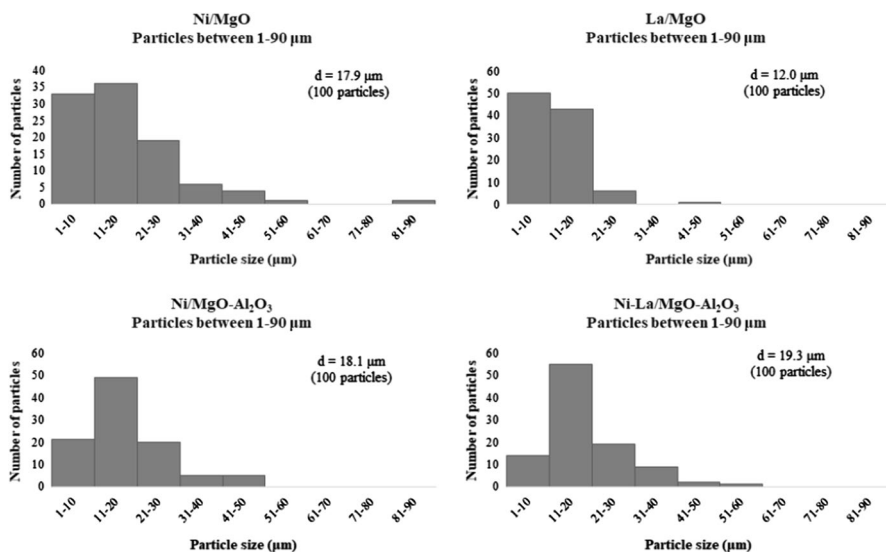
Fig. 3 shows the BET isotherms of the prepared catalysts. According to Brunauer, Emmett and Teller the S-shaped isotherms for Ni/MgO and La/MgO are Type II

**Table 1** Metal content and BET surface area of the catalysts

Entry	Catalysts	Theoretical values		Measured values (ICP)		Measured values (EDS)		BET surface area ( $\text{m}^2 \text{g}^{-1}$ )
		Ni (wt%)	La (wt%)	Ni (wt%)	La (wt%)	Ni (wt%)	La (wt%)	
1	Ni/MgO	5.53	–	5.3	–	7.37	–	51.8
2	La/MgO	–	12.19	–	12.2	–	14.43	33.7
3	Ni/MgO–Al <sub>2</sub> O <sub>3</sub>	5.53	–	4.9	–	6.56	–	196.7
4	Ni–La/MgO–Al <sub>2</sub> O <sub>3</sub>	5.53	12.19	5.0	10.9	8.22	12.70	160.9



**Fig. 1** SEM images of the catalysts: **a** Ni/MgO, **b** La/MgO, **c** Ni/MgO–Al<sub>2</sub>O<sub>3</sub>, **d** Ni–La/MgO–Al<sub>2</sub>O<sub>3</sub>



**Fig. 2** Particle size distribution of the catalysts

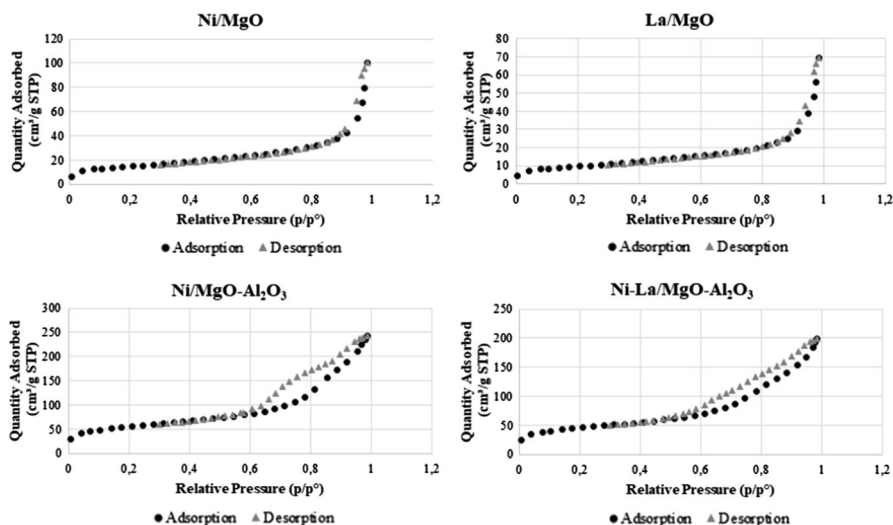


Fig. 3 BET isotherms of the catalysts

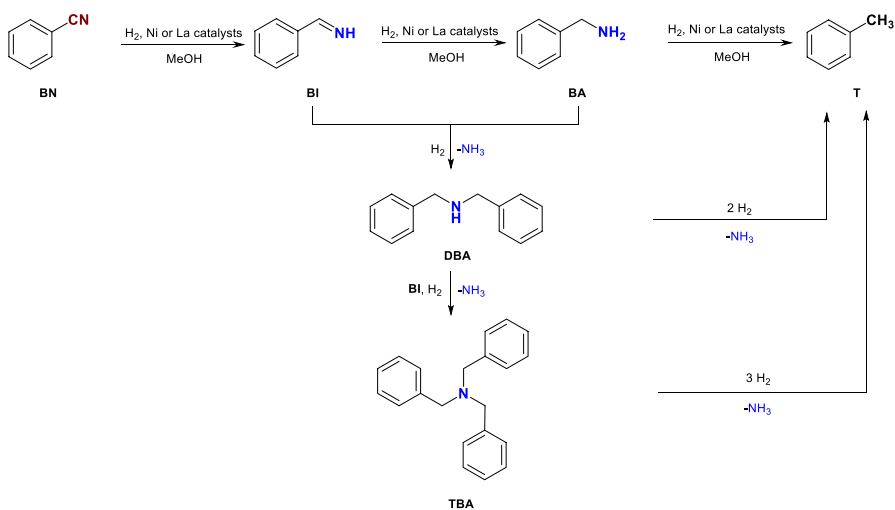


Fig. 4 Nickel–lanthanum-catalysed hydrogenation of benzonitrile (BN)—reaction pathway

BET isotherms, meaning that the low pressure portion of the isotherm is concave to the pressure axis, the higher pressure region convex and the intermediate region approximately linear [44, 45]. At the beginning by lower pressures the micropores are filled with nitrogen gas. At the knee of the isotherm the monolayer formation begins. After the complete monolayer coverage, a multilayer formation occurs. Lastly, at high pressures capillary condensation takes place. The other two isotherms



**Table 2** Hydrogenation of BN over magnesia(–alumina) supported Ni or La catalysts

Entry	Catalyst	Temperature (°C)	Reaction time (h)	Conversion (%)	Product		Selectivity to BA (%)
					Isolated yield (%)	BA-content <sup>a</sup> (%)	
1	Ni/MgO	30–130	8.0	100	73	68.1	50
2	Ni/MgO	100	5.0	100	96	44.8	43
3	La/MgO	100	5.0	98	96	47.9	47
4	Ni/MgO–Al <sub>2</sub> O <sub>3</sub>	100	5.0	100	96	53.5	52
5	Ni–La/MgO–Al <sub>2</sub> O <sub>3</sub>	100	5.0	100	95	52.6	50

Conditions: 2.0 g benzonitrile, 0.1 g·g<sup>-1</sup> catalyst/substrate ratio, 50 mL methanol, 10 bar

<sup>a</sup>The main by-product was dibenzylamine (DBA) and no formation of tribenzylamine (TBA) was observed

for Ni/MgO–Al<sub>2</sub>O<sub>3</sub> and Ni–La/MgO–Al<sub>2</sub>O<sub>3</sub> are Type IV BET isotherms with a hysteresis loop. In these cases capillary condensation occurs in the mesopores.

### Catalytic test in the hydrogenation of benzonitrile

The four supported metal catalysts, Ni/MgO, La/MgO, Ni/MgO–Al<sub>2</sub>O<sub>3</sub> and Ni–La/MgO–Al<sub>2</sub>O<sub>3</sub> were tested in the hydrogenation of benzonitrile (BN) at different temperatures in methanol, without any additive (Fig. 4). First the activity and selectivity of the different catalysts were tested. The results are summarized in Table 2.

**Table 3** Hydrogenation of nitriles over La/MgO

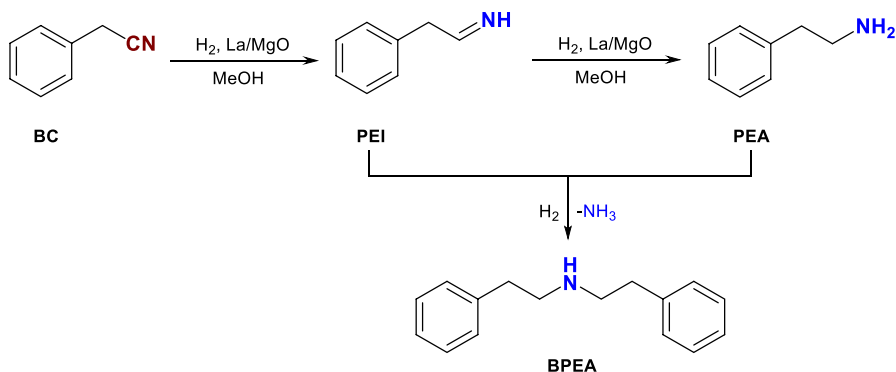
Entry	Substrate	Conversion (%)	Product		Selectivity to primary amine (%)
			Isolated yield (%)	Primary amine content (%)	
1	Benzyl cyanide	49	97	6.2 <sup>a</sup>	13
2	Cinnamionitrile	100 (C=C) 22 (CN)	97	10.6 <sup>b</sup>	46
3	Adiponitrile	12	99	0 <sup>c</sup>	0

Conditions: 2.0 g substrate, 0.1 g·g<sup>-1</sup> catalyst/substrate ratio, 50 mL methanol, 10 bar, 100 °C, reaction time: 5 h

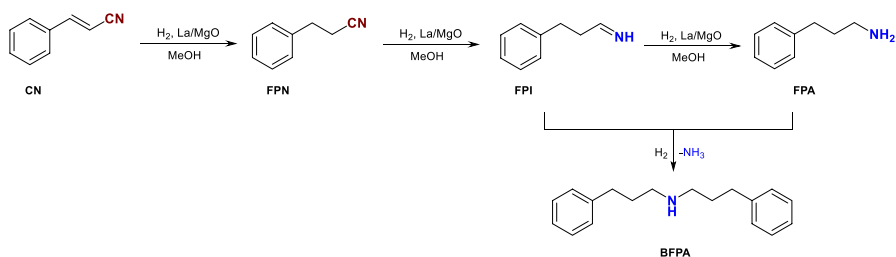
<sup>a</sup>The main by-product was bis(2-phenylethyl)amine (BFEA) and no formation of tris(2-phenylethyl)amine (TFEA) was observed

<sup>b</sup>The main by-product was bis(2-phenylpropyl)amine (BFPA) and no formation of tris(2-phenylpropyl)amine (TFPA) was observed

<sup>c</sup>The main product was 6-iminocapronitrile (ICN) and no formation of 6-aminocapronitrile (ACN) or 1,6-hexamethylenediamine (primary amines) was observed



**Fig. 5** Hydrogenation of benzyl cyanide (BC) over La/MgO



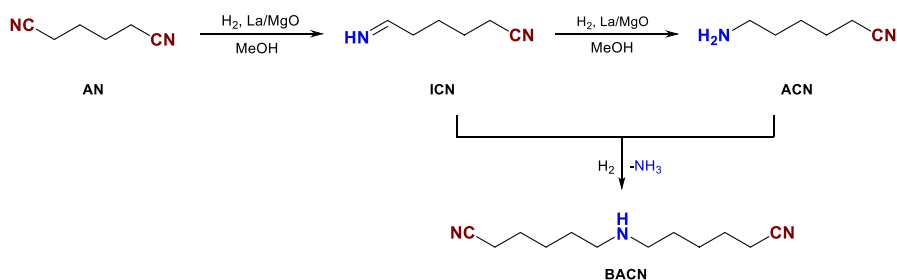
**Fig. 6** Hydrogenation of cinnamionitrile (CN) over La/MgO

As seen, all catalysts were active in the hydrogenation of benzonitrile. It was found that it is expedient to perform the Ni/MgO-catalysed reduction at 100 °C and 10 bar pressure, because at higher temperature (130 °C) the isolated yield was only 73%, due to a hydrogenolytic side reaction resulting in the formation of toluene (T). In the latter case, the BA-content was the highest (68.1%) and the selectivity to BA was 50%. Whereas, complete conversions, excellent yields (95–96%), as well as very similar primary amine selectivity (43–52%) were achieved with all catalysts at lower temperature (100 °C).

Among these results the most interesting was the remarkable hydrogenation activity of lanthanum (entry 3). Thus, the scope of the reaction in the presence of the La/MgO catalyst was extended to the hydrogenation of other nitriles, such as benzyl cyanide, cinnamionitrile (the homologues of BN) and adiponitrile (dinitrile). The reaction was carried out under the same conditions as described above. The results are summarized in Table 3.

As seen, much lower conversion of the nitrile group was obtained as the aliphatic properties of the starting materials increased.

When benzyl cyanide (BC) was hydrogenated (Fig. 5) over La/MgO, the conversion was 49% and only 13% selectivity to 2-phenylethylamine (PEA) was achieved and mainly the secondary amine, bis(2-phenylethyl)amine (BFEA) was formed with 87% selectivity.



**Fig. 7** Hydrogenation of adiponitrile (AN) over La/MgO

During the La-catalysed hydrogenation of cinnamionitrile (CN) (Fig. 6), the saturation of the C=C double bond took place completely resulting in 3-phenylpropionitrile (FPN), but the conversion of the nitrile group was low (22%). Whereas, the selectivity to 3-phenylpropylamine (FPA) was 46%, and the by-product was the secondary amine [bis(3-phenylpropyl)amine (BFPA)] only with 54% selectivity.

In the hydrogenation of adiponitrile (AN) over La/MgO (Fig. 7), very low conversion was obtained (12%), and only one nitrile group was reduced to 6-imino-capronitrile (ICN) with 75% selectivity. In addition, a secondary amine [bis(6-aminocapronitrile) (BACN)] was detected as a by-product, but no formation of 6-aminocapronitrile (ACN) or 1,6-hexamethylenediamine (primary amines) was observed.

## Conclusions

Ni or La on MgO and MgO–Al<sub>2</sub>O<sub>3</sub> and Ni–La on MgO–Al<sub>2</sub>O<sub>3</sub> catalysts have been prepared and characterized. The EDS measurements showed that the metal is located mostly on the surface of the supports. The activity of the catalysts was tested in the heterogeneous catalytic hydrogenation of benzonitrile in methanol without any additives. The La/MgO catalyst was found to be very effective in the reaction, which is unprecedented in the literature. The reaction scope was broadened the hydrogenation of benzyl cyanide, cinnamionitrile and adiponitrile was studied over this La/MgO catalyst. However, in these cases only a low amount of the desired primary amine could be identified in the reaction mixture. During the hydrogenation of cinnamionitrile the main product was 3-phenylpropionitrile instead of the 3-phenylpropylamine. In conclusion, the prepared supported base metal catalysts, especially the La/MgO, can be used in the hydrogenation of benzonitrile with 43–52% primary amine selectivity.

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**Declarations**

**Conflict of interest** The authors declare that they have no conflict of interest.

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