Silica-supported Fe/Fe–O nanoparticles for the catalytic hydrogenation of nitriles to amines in the presence of aluminium additives

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The hydrogenation of nitriles to amines represents an important and frequently used industrial process due to the broad applicability of the resulting products in chemistry and life sciences. Despite the existing portfolio of catalysts reported for the hydrogenation of nitriles, the development of iron-based heterogeneous catalysts for this process is still a challenge. Here, we show that the impregnation and pyrolysis of iron(II) acetate on commercial silica produces a reusable Fe/Fe–O@SiO2 catalyst with a well-defined structure comprising the fayalite phase at the Si–Fe interface and α-Fe nanoparticles, covered by an ultrathin amorphous iron(III) oxide layer, growing from the silica matrix. These Fe/Fe–O core–shell nanoparticles, in the presence of catalytic amounts of aluminium additives, promote the hydrogenation of all kinds of nitriles, including structurally challenging and functionally diverse aromatic, heterocyclic, aliphatic and fatty nitriles, to produce primary amines under scalable and industrially viable conditions.

Catalysis plays a decisive role in many basic and applied chemical processes and is involved in the industrial production of more than 90% of fine and bulk chemicals as well as polymeric materials and many other everyday products23,24. In addition, the synthesis of bioactive compounds for life sciences and the success of sustainable energy technologies, including green fuels, depend on efficient catalytic processes1–5. Indeed, the success of organic synthesis in the last 100 years relied to a large extent on the discovery and application of suitable catalysts1–5. In this respect, specifically, the development of practical and cost-efficient hydrogenation strategies constitutes a key achievement of the last century4. Nowadays, a plethora of molecularly defined metal complexes as well as heterogeneous materials are frequently applied for the selective hydrogenation of alkynes25, olefins26,27,28, carbonyl compounds29–32, nitroarenes33,34, as well as (hetero)arenes35–37. Among these hydrogenation reactions, the transformation of nitriles to primary amines is particularly valuable because the latter products are privileged compounds in chemistry, medicine and biology38,39. In general, primary amines constitute important precursors and central intermediates in the chemical, pharmaceutical, agrochemical and materials industries40–42. After the original discovery of benzonitrile hydrogenation in the presence of nickel in 1905 (ref. 23), many catalysts were developed for this and related reactions (Fig. 1)24–42. These achievements were mainly possible due to the design of precious metal systems, which allow reactions to be performed at low temperature and pressure43,44,45. However, despite their tremendous success, their limited availability and higher price constitute major drawbacks. Thus, state-of-the-art catalysts for nitrile hydrogenation in industry continue to be Raney nickel26,44,45 and copper chromite27, which demand harsh conditions and suffer from toxicity issues. To solve these problems, alternative nickel- and cobalt-based heterogeneous catalysts have been reported in recent years46–48.

From a sustainability point of view, iron would be an ideal catalyst system for nitrile hydrogenation because of its abundance (at 4.7% it is the second-most abundant metal in the earth crust), low price and low toxicity49,50,51. Indeed, in the last decade, using sophisticated/synthetically demanding PNP pincer ligands, active iron complexes have been developed to hydrogenate nitriles49. In general, however, these metal complexes are less stable and difficult to use. In contrast, heterogeneous catalysts show improved stability and can be easily reused45,46,47,48,49,50. Unfortunately, to the best of our knowledge, analogous supported active iron centres for the hydrogenation of nitriles have not been created yet.

Here, we report a stable and convenient iron-based nanocatalyst obtained by the pyrolysis of iron acetate on commercial silica that shows excellent activity and selectivity for the hydrogenation of a large number of nitriles to produce primary amines in the presence of catalytic amounts of aluminium additives.

Results

Synthesis and characterization of Fe-based nanocatalysts. In the last decade, the excellent catalytic performance of carbon-encapsulated core–shell 3d metal nanoparticles has been demonstrated in a variety of hydrogenation reactions52,53,54,55,56. These catalysts were prepared by the immobilization and pyrolysis of metal complexes or metal organic frameworks on inorganic supports (for example, carbon, SiO2 and Al2O3)52,53,54,55,56. In this context, we developed activated Fe2O3 nanoparticles, surrounded by...
nitrogen-doped graphene, as selective catalysts for the hydrogenation of nitroarenes to anilines. In addition, supported Fe-based nanoparticles have also been found active for the hydrogenation of quinolines. However, these and related Fe materials showed no activity for more challenging substrates, including nitriles (Supplementary Table 1, entries 1 and 2). To identify potential iron-based heterogeneous catalysts for nitrile hydrogenation, we prepared a series of iron nanoparticles supported on various supports. Specifically, commercially available neutral, acidic and basic inorganic supports, for example, Vulcan XC72R carbon powder, Aerosil silica (SiO$_2$), γ-Al$_2$O$_3$ and MgO, were impregnated with iron(II) acetate. Subsequently, these materials were pyrolysed at 800 °C under reductive (H$_2$) conditions. A schematic illustration of the synthetic procedure with the SiO$_2$ support is presented in Fig. 2. Hereafter, these materials are denoted as Fe(OAc)$_2$-support-$x$, where $x$ denotes the pyrolysis temperature.

As a benchmark reaction, the hydrogenation of 4-chlorobenzonitrile (1) to 4-chlorobenzylamine (2) was chosen (Fig. 3), not only to identify an active catalyst system, but also a selective one. Notably, 1 easily undergoes reductive dehalogenation in the presence of many known hydrogenation catalysts. To our surprise, during initial control experiments, we observed some activity (26% yield of 2) and high selectivity (>90%) for the primary amine in the presence of Fe(OAc)$_2$-SiO$_2$-800 (Fig. 3). To improve the conversion and yield, we varied the reaction conditions (temperature, solvent, catalyst loading) and investigated the influence of additives (Supplementary Tables 1–3). Applying higher catalyst loadings (up to 12.8 mol%), the product yield increased up to 50%, and the selectivity for the primary amine remained very good. Gratifyingly, in the presence of aluminium triisopropoxide, the yield of 4-chlorobenzylamine (2) dramatically increased to 96%.

Following this excellent result, several other metal alkoxides, aluminium compounds as well as Lewis acids and bases were tested as additives (Supplementary Table 2). Surprisingly, only a few additives, for example, $p$-toluenesulfonic acid, showed a positive effect on the reaction, while most, for example, bases, had a negative impact. Optimal results, with an almost quantitative yield of 2, were achieved in the presence of inexpensive aluminium foil (Fig. 3 and Supplementary Fig. 1). In this case, the aluminium foil completely dissolved in the solvent (isopropanol), which explains the similar positive effect of aluminium foil and aluminium triisopropoxide. Control experiments proved that this dissolution only takes place in the presence of ammonia (Supplementary Table 4). To elucidate the crucial role of aluminium additives, we performed kinetic investigations of the model reaction in the absence and presence of aluminium foil and aluminium triisopropoxide (Supplementary Figs. 2 and 3). Surprisingly, all the reactions needed a preactivation time (3–9 h) to start. Only in the presence of aluminium triisopropoxide was this preactivation drastically reduced. Based on these results and the testing of the different additives, we assume that both aluminium
trisopropoxide and aluminium foil are converted under the reaction conditions to an active Lewis acid co-catalyst that activates the nitrile group. These Lewis acidic centres can probably also be generated on the silica support close to the nanoparticles by reaction with Si–OH sites on the surface. Notably, catalytic (substoichiometric) amounts (20 mol%) of the aluminium additives were sufficient to achieve improved yields.

Under the optimized conditions, other supported catalysts, such as Fe(OAc)2–C–800, Fe(OAc)2–Al2O3–800 and Fe(OAc)2–MgO–800 (Supplementary Figs. 4–6), did not show any activity (Fig. 3). In these samples we did not observe needle-like well-developed α-Fe nanoparticles growing from the matrix, as we did in the case of the optimal catalyst, Fe(OAc)2–SiO2–800. In contrast, the iron nanoparticles were highly aggregated and/or encapsulated within the matrix (Supplementary Figs. 4–6). Similarly, Fe(OAc)2 on SiO2 pyrolysed at 400 °C (Fe(OAc)2–SiO2–400) was completely inactive (Fig. 3). This is explained by a not fully developed active Fe nanostructure at low pyrolysis temperature, which is evident from the powder X-ray diffraction (PXRD) pattern (Supplementary Fig. 7) and transmission electron microscopy (TEM) image (Supplementary Fig. 8) of the Fe(OAc)2–SiO2–400 sample. By contrast, Fe(OAc)2–SiO2–600 and Fe(OAc)2–SiO2–1,000 exhibited comparable activities to that of Fe(OAc)2–SiO2–800, providing 93 and 94% yields of the desired product, respectively. This correlates well with the similar size and well-developed core–shell structure of the Fe(OAc)2–SiO2–600 and Fe(OAc)2–SiO2–1,000 samples (see the TEM images in Supplementary Figs. 9 and 10) compared with Fe(OAc)2–SiO2–800 (Fig. 4c). As expected, iron(II) acetate, unpyrolysed Fe(OAc)2–SiO2 and Al additives alone were completely inactive in the reaction (Fig. 3). Additionally, we prepared control samples, including pure amorphous Fe2O3 nanoparticles (NPs), fayalite (Fe5Si2O8) NPs and matrix-free Fe–Fe2O3 core–shell NPs with a very thin oxidic shell (Supplementary Figs. 11–13), and investigated their performance in the model reaction. Notably, the fayalite and Fe2O3 NPs were completely inactive, whereas the Fe–Fe2O3 core–shell NPs gave 30% yield (Supplementary Table 5, entries 1–3). This confirmed the crucial role of the Fe–Fe2O3 core–shell superstructure in triggering the catalytic process. We believe that the active material involves Fe centres and/or the Fe–O atomic interface48. The high activity of the catalyst incorporating the SiO2 matrix (Fe(OAc)2–SiO2–800) strongly indicates that the matrix regulates the size of the iron oxide crystallites49,50. Indeed, it has already been reported that the Cu–O–SiO2 interface in a silica-supported copper (Cu@SiO2) catalyst plays a key role in H2 dissociation to form Cu–H+ species51. Thus, we believe that the silica in Fe(OAc)2–SiO2–800 would contribute to the catalytic activity by forming such an active metal–support (Fe–O–SiO2) interface.

Next, we conducted a detailed characterization of the most active catalyst Fe(OAc)2–SiO2–800. TEM analysis revealed the formation of core–shell structures with globular and rod-shape morphologies, with the needle diameters ranging from 10 to 30 nm and lengths up to 100 nm (Fig. 4a–c). Energy-dispersive X-ray spectroscopy (EDS) of this material showed the presence of Si, O and Fe elements (Supplementary Fig. 14). The high-resolution TEM image (HRTEM; Fig. 4d) confirms that the metallic part of the catalyst is composed of an α-Fe core growing from the SiO2 matrix. Indeed, the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and elemental mapping images clearly verify that the Fe core nanoparticles are growing from the SiO2 matrix and are covered by a layer of ultrathin iron oxide with a thickness of a few nanometres (Fig. 4f–i). Based on this assignment, the most active Fe(OAc)2–SiO2–800 catalyst is abbreviated to Fe/Fe–O@SiO2 in the following text. A representative HAADF-STEM image of a globular particle and typical depth profile plot showing the intensity distribution of the Si, O and Fe elements at various distances from the surface are shown in Fig. 5a,b, respectively. The depth profiles confirm that the thickness of the oxidic Fe-O shell is less than 5 nm. Clearly, the catalyst surface is composed of iron nanoparticles, which grow from the SiO2 matrix, stabilized by an extremely thin iron oxide shell.

Furthermore, we performed very detailed chemical mapping with a focus on the iron-containing surface components that are responsible for the catalytic activity. All the identified Fe-bearing surface-active phase was composed of Fe nanoparticles covered with a very thin shell of iron oxide, irrespective of the size and morphology (globular, needle-like) of the Fe NPs (Supplementary Fig. 15).

To identify the chemical and structural character of the catalyst, we analysed the Fe/Fe–O@SiO2 sample by PXRD, Mössbauer spectroscopy, X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) spectroscopy. The PXRD pattern of Fe/Fe–O@SiO2 (Supplementary Fig. 16) shows strong metallic α-Fe reflections at 2θ values of 52.33, 77.16 and 99.60°, corresponding to crystalline facets of the Fe (110), (200) and (211) planes, respectively (Joint Committee on Powder Diffraction Standards (JCPDS) card number 04-012-6482). Thus, α-Fe is the dominant crystalline phase involved in the catalyst superstructure. The low-crystalline SiO2 matrix is represented by a broad peak at 2θ ≈ 26°, indicating the presence of poorly crystalline crystallite (JCPDS card number 04-008-7643). The ultrathin iron oxide layer is, in accord with expectation, not identifiable in the PXRD pattern due to its mostly amorphous nature. However, detailed PXRD analysis clearly showed additional low-intensity diffraction peaks corresponding to fayalite (Fe5Si2O8) JCPDS card number 04-002-3681 and crystalline silicon (Si0), JCPDS card number 04-014-8844). In summary, PXRD provided a complex picture of the high-temperature chemistry of the Fe–Si–O system.

These observations are in line with the XPS analysis, which confirmed the presence of just Fe, Si and O elements in the survey spectrum (Supplementary Fig. 17a). The high-resolution O1s spectrum of Fe/Fe–O@SiO2 (Supplementary Fig. 17b) identifies peaks
at 530.72 and 533.14 eV, corresponding to Fe–O and Si–O bonds, respectively. Most importantly, the high-resolution Fe 2p spectrum (Supplementary Fig. 17d) reveals Fe 2p$_{3/2}$ peaks at 710.27 and 712.73 eV, and Fe 2p$_{1/2}$ peaks at 723.37 and 725.83 eV, which can be ascribed to Fe$^{3+}$ species$^{52}$, along with two satellite peaks at 717.41 and 730.51 eV. This is strong proof that the amorphous iron oxide phase covering the Fe(0) core corresponds to amorphous Fe$_2$O$_3$. The formation of iron(III) oxide was confirmed by the hyperfine parameters derived from room-temperature Mössbauer spectroscopy (Fig. 5c). The $^{57}$Fe Mössbauer spectrum of the sample shows a dominant sextet (68% of the relative spectrum area) and two doublet components. According to the Mössbauer hyperfine parameters, the sextet with zero isomer shift and a hyperfine field of 32.9 T can be unambiguously assigned to ferromagnetic $\alpha$-Fe. The doublet with high isomer shift (1.18 mm s$^{-1}$) and quadrupole splitting (2.64 mm s$^{-1}$) clearly belongs to Fe(II) ions in the fayalite structure formed at the Si–Fe interface$^{53}$, in perfect agreement with the results of the PXRD measurements. Finally, the doublet with an isomer shift of 0.35 mm s$^{-1}$ is typical of high-spin Fe(III) in amorphous iron(III) oxide with disordered symmetry of the iron environment, as proved by the high quadrupole splitting (1.31 mm s$^{-1}$)$^{54}$. It is worth mentioning that possible traces of Fe(III) ions usually involved in the fayalite structure would overlap the doublet of the iron(III) oxide phase. Finally, the EPR spectrum of Fe/Fe–O@SiO$_2$ shows broad anisotropic signals with g factor values of $g_c = 2.72$, $g_a = 2.04$ and $g_e = 1.8$ ($g_{\text{ms}} = 2.19$) at 77 K (Fig. 5d), which indicates the presence of ferromagnetic particles corresponding to Fe(0) with distinct size and morphology. In summary, HRTEM, HAADF-STEM, XPS, PXRD, EPR and Mössbauer spectroscopy allowed us to explore the chemical and structural character of the Fe/Fe–O@SiO$_2$ catalyst, being composed of a SiO$_2$ matrix, a fayalite interface (Fe$_2$SiO$_4$) and $\alpha$-Fe–amorphous Fe$_2$O$_3$ core–shell nanoparticles growing from the silica matrix and representing the surface-active phase participating in the catalytic process. The EPR and Mössbauer data confirm the ferromagnetic character of the sample, predetermining the catalyst for simple magnetic separation.

**Hydrogenation of benzonitriles and heterocyclic nitriles.** With an active Fe-based catalyst (Fe/Fe–O@SiO$_2$) in hand, we demonstrated its general applicability for the selective hydrogenation of all kinds of nitriles. Although in most of the reactions aluminium foil was used as an inexpensive additive, experiments performed for comparison in the presence of aluminium triisopropoxide gave similar product yields. First, we carried out the hydrogenation of a series of aromatic nitriles (Fig. 6). Simple benzonitriles as well as substituted ones bearing aromatic or alkyl groups gave the corresponding primary amines in yields of up to 96% (Fig. 6, products 3–7).

For the general applicability of any new catalyst, its chemoselectivity is an important aspect. Thus, from a synthetic point of view, it is important to note that this iron-based catalyst system is highly selective for the hydrogenation of the nitrile group in functionalized and multisubstituted substrates. As an example, amino-substituted and halogenated benzylic amines were prepared, which are versatile intermediates in organic synthesis as well as for pharmaceuticals and agrochemicals. Such products, including the more sensitive 4-iodobenzylamine, were easily produced from the corresponding...
benzonitriles in yields of up to 97% (Fig. 6, products 8–16). In addition, trifluoromethyl-substituted benzylamines were obtained in yields of 94 and 95% (Fig. 6, products 17 and 18, respectively). We were also pleased to find that the nitrile group was also selectively hydrogenated in the presence of the more challenging C≡C, ester, boronic ester, amide, ether, trifluoromethoxy and thioether groups (Fig. 6, products 19–30). Furthermore, when multisubstituted nitriles were subjected to hydrogenation, reduction of the CN group again took place highly selectively towards the corresponding benzylic amines in yields of up to 95% (Fig. 6, products 31–46).

Heterocyclic amines constitute versatile intermediates in the pharmaceutical and agrochemical industries. In this respect, the selective hydrogenation of cyano-substituted heterocycles, for example, quinolines, indoles, pyrroles, benzodioxoles, benzodioxanes, furans, morpholines and phthalanes, is of particular interest. The corresponding heterocyclic amines were obtained (except for 3-cyanofuran) in yields of 85–94% (Fig. 6).

Hydrogenation of aliphatic nitriles. Compared with aromatic nitriles, the hydrogenation of aliphatic nitriles is in general more challenging. Importantly, Fe/Fe–O@SiO$_2$ exhibited high activity and selectivity for these substrates, including dinitriles, under identical conditions (Fig. 7). Initially, several benzylic cyanides were hydrogenated to the corresponding primary amines in excellent yields (Fig. 7, products 57–72). Interestingly, the 2-arylethylamino motif is a common scaffold in many central nervous system-active compounds. Here, a variety of substituted derivatives were smoothly hydrogenated and furnished the corresponding primary amines in yields of up to 98% (Fig. 7, products 57–68). Phenylpropylamines are another important class of pharmaceutically relevant amines. For example, the parent compound (phenylpropylamine) is used in the synthesis of carboxypeptidase B-type enzyme inhibitors, muscarinic receptor antagonists and potential anticancer agents. Here, it was prepared in 94% yield from the corresponding nitrile (Fig. 7, product 69).

Although 3-(arylamino)propanenitriles are prepared in a straightforward manner from anilines and acrylonitrile, the hydrogenation of such substrates is difficult because retro-Michael additions can occur. However, this class of compounds was smoothly hydrogenated under our conditions to give the respective primary amines in good yields of up to 85% (Fig. 7, products 70–72). Finally, a selection of aliphatic nitriles was tested. Gratifyingly, Fe/Fe–O@SiO$_2$ also showed good-to-excellent activity and selectivity for these demanding substrates (Fig. 7, products 73–78). Particularly interesting is the selective reduction of 5-hexenitrile (Fig. 7, product 78). Notably, hexamethylenediamine (79), the key feedstock for the production of nylon 66, was prepared in 85% yield by direct hydrogenation of adiponitrile. Similarly, other diamines were obtained in 90–95% yield (Fig. 7, products 80 and 81).

Synthesis of fatty nitriles. With a worldwide production of fatty amines of >800,000 tons yr$^{-1}$, the hydrogenation of fatty nitriles constitutes an important industrial application$^{35}$. Fatty amines are valuable oleochemicals mainly used to produce fabric softeners, flotation agents, emulsifiers, corrosion inhibitors and lubricating additives$^{36}$.

Until today, the industrial hydrogenation of fatty nitriles to amines has relied on well-established Raney Ni or Co catalysts as well as copper chromite$^{35}$. These materials have considerable toxicity issues for biological systems. Hence, alternative Ru-, Pd- and...
Hydrogenation of benzonitriles

- 3: 96% (93%)
- 4: 90%
- 5: 88% (89%)
- 6: 96%
- 7: 96% (95%)
- 8: 90%
- 9: 92%
- 10: 95% (95%)
- 11: 97% (96%)
- 12: 96%
- 13: 97%
- 14: 91%
- 15: 89% (90%)
- 16: 80%
- 17: 94%
- 18: 95%
- 19: 91%
- 20: 85%
- 21: 95%
- 22: 90%
- 23: 98%
- 24: 97%
- 25: 97%
- 26: 91%
- 27: 94%
- 28: 95%
- 29: 92%
- 30: 94% (92%)
- 31: 80%
- 32: 80%
- 33: 70%
- 34: 95% (93%)
- 35: 90%
- 36: 95%
- 37: 89%
- 38: 93%
- 39: 91%
- 40: 94%
- 41: 87% (84%)
- 42: 89%
- 43: 85%
- 44: 95%
- 45: 60%
- 46: 90%
- 47: 91%
- 48: 89% (91%)
- 49: 90%
- 50: 91% (93%)
- 51: 93%
- 52: 65%
- 53: 90%
- 54: 85%
- 55: 94%
- 56: 92%

Hydrogenation of heterocyclic nitriles

- 57: 91%
- 58: 89% (91%)
- 59: 90%
- 60: 91% (93%)
- 61: 93%
- 62: 65%
- 63: 90%
- 64: 85%
- 65: 94%
- 66: 92%

**Fig. 6 | Substrate scope.** Hydrogenation of (hetero)aromatic nitriles. Reaction conditions: 0.5 mmol nitrile, 40 mg Fe/Fe–O@SiO2 (8.5 mol% Fe), 3 mg Al foil (20 mol%), 5–7 bar NH3, 50 bar H2, 3 ml i-PrOH, 120 °C, 24 h. Isolated yields are given. *Yields were determined by GC using n-hexadecane as standard. †With 50 mg Fe/Fe–O@SiO2. ‡With 50 mg Fe/Fe–O@SiO2 and 5 mg Al foil. §At 135 °C. ¶With 60 mg Fe/Fe–O@SiO2 and 5 mg Al foil. ‡With 50 mg Fe/Fe–O@SiO2 at 135 °C. ‡Methyl 4-cyanobenzoate was used as substrate. Transesterification product with i-PrOH. Yields in parentheses refer to the reaction performed in the presence of 20 mol% Al(i-OPr)3. Products were isolated as free amines and converted to their hydrochloride salts for NMR and high-resolution mass spectrometry (HRMS) analysis.
Pt-based catalysts were developed. Unfortunately, none of these systems is commercially viable due to the high price of the precious metals. Gratifyingly, our catalyst is capable of hydrogenating fatty nitriles in a highly selective manner. As a result, seven different fatty amines were prepared in excellent yields of 95–97% (Fig. 8, products 82–88).

To further prove the synthetic utility and practicability of our Fe catalyst, we scaled up both the catalyst preparation (up to 12 g; Supplementary Table 6) and the nitrile hydrogenation protocol (up to 20 g). Regardless of the scale of preparation (1–12 g), all the Fe materials exhibited similar activity and selectivity (Supplementary Table 7). Next, the catalytic hydrogenation reactions of four selected aromatic and aliphatic nitriles were performed using quantities of up to 20 g nitrile. Again, similar conversions and yields were obtained to those achieved with small-scale reactions using up to 100 mg nitrile (Supplementary Fig. 18).

Finally, catalyst recycling was investigated at full and half conversions, which is an important aspect for any heterogeneous catalyst. Indeed, the Fe/Fe–O@SiO2 catalyst could be reused up to the fourth run. After that, a decrease in the product yield was observed. Recycling tests performed at half conversion for 14 h showed a drop in activity from the third run onward (Supplementary Fig. 18).

Conclusions

We have presented here the development of a heterogeneous iron-based catalyst for the hydrogenation of nitriles. Key to success was the use of silica-supported Fe nanoparticles covered with an ultrathin shell of amorphous iron(III) oxide (Fe/Fe–O@SiO2). These core–shell nanoparticles were prepared by simple impregnation of iron(II) acetate on commercial silica and subsequent pyrolysis under reductive conditions. The low cost and environmentally friendly character of the catalyst, easy recycling as well as upscaling of the synthetic process represent key advantages and make the material attractive for many applications. Importantly, the developed silica-supported Fe–O core–shell material exhibited high chemoselectivity for the reduction of functionalized and structurally diverse aromatic, heterocyclic and aliphatic nitriles, including industrially relevant fatty nitriles, to produce the corresponding primary amines in good-to-excellent yields. Aluminium alkoxide species generated in situ from aluminium foil or aluminium triisopropoxide proved to be important for the co-catalytic activation of the nitrile substrate.

Methods

General considerations. All nitriles were obtained commercially from various chemical companies. Before using, the purity of all the nitriles was checked. Iron(II) acetate (99.99%, cat no. 517933-25G) was obtained from Sigma Aldrich. Silica (Aerosil OX-50) was obtained from Evonik. Carbon powder (VULCAN XC72R, with code XVC72R) was obtained from Cabot Corporation. y-Al2O3 and MgO were obtained from Sigma-Aldrich. Al foil was obtained from Sigma-Aldrich (Mini Bin, HS23534A). For comparison purposes, Al foil used for food covering was also purchased from a local store (Kaufland, ALUFOLIE; ICP). The percentage of aluminium in Al-foil was determined by inductively coupled plasma (ICP) and it was found to be 99.97%. DMF was obtained from Acros Chemicals. Pyrolysis experiments were carried out in a Lenton tube furnace.

PXRD patterns were measured at room temperature with an Aeris diffractometer (PANalytical) in Bragg–Brentano geometry equipped with...
an iron-filtered Co Kα radiation source (40 kV, 15 mA, \( \lambda = 0.1789 \) nm) and PIXCell detector. Some samples were measured employing an X’PertPRO MPD diffractometer (PANalytical) in Bragg–Brentano geometry equipped with a Co Kα radiation source (40 kV, 30 mA, \( \lambda = 0.1789 \) nm), programmable divergence, diffracted beam anti-scatter slits and X’Celerator detector. The angular range of measurement was 5–105° 2\( \theta \), measured with a pass energy of 187.850 eV and an electronvolt step of 0.8 eV, for all measurements. All spectra were recorded in a vacuum of 1.3 \( \times \) 10\(^{-6}\) bar.

The same procedure was employed for the preparation of Fe(OAc)\(_2\)-Al\(_2\)O\(_3\)-800, Fe(OAc)\(_2\)-MgO-800.

**Preparation of Fe(Fe–O@SiO\(_2\)) on the 1.5 g scale.** A magnetic stirring bar and 280.33 mg Fe(OAc)\(_2\), were transferred to a 50 ml round-bottomed flask and 30 ml DMF was added. The reaction mixture was stirred at 50 °C to dissolve the iron acetate. To this solution, 1.2 g SiO\(_2\) (Aerosil OX 50) was added, followed by 10 ml DMF. Next, a reflux condenser was fitted to the round-bottomed flask containing the reaction mixture, which was then placed in an aluminium block preheated at 150 °C and stirred for 4 h. Next, the reflux condenser was removed and the round-bottomed flask containing the reaction products was allowed to stand without stirring or closing for 20 h at 150 °C for the slow evaporation of DMF. After evaporation of the solvent and ensuring complete drying, the solid material was cooled to room temperature and ground to a fine powder. This powder was pyrolysed at a defined temperature (400, 600, 800 or 1,000 °C) for 4 h in a tubular furnace under the flow of 20% H\(_2\)/N\(_2\) (ramp: 5 °C min\(^{-1}\), total flow: 3 l h\(^{-1}\)) and then cooled to room temperature.

Elemental analysis of Fe(Fe–O@SiO\(_2\)) by ICP and CHN analysis revealed the following (wt%) distribution: Fe = 6.09%; Si = 37.73%; C = 0.11%; H = 0.41%. The Brunauer–Emmett–Teller surface area was measured to be 46.04 m\(^2\) g\(^{-1}\).

The same procedure was employed for the preparation of Fe(OAc)\(_2\)-C-800, Fe(OAc)\(_2\)-γ-Al\(_2\)O\(_3\)-800 and Fe(OAc)\(_2\)-MgO-800.

**Preparation of Fe(Fatty amines) on 6 and 12 g batches.** The same procedure was used for the preparation of Fe(Fatty amines) (Fe(OAc)\(_2\)-SiO\(_2\)) on the 6 and 12 g scale with a slight modification of the pyrolysis procedure, as described in Supplementary Table 6.

**General procedure for the hydrogenation of nitriles.** A magnetic stirring bar and 0.5 mmol of the corresponding nitrile were transferred to a 7 ml glass vial and then 3 ml i-PrOH was added. Next, 40 mg Fe(Fe–O@SiO\(_2\)) (8.5 mol% Fe) and 3 mg Al foil (the Al foil was cut into small pieces and used in the reactions) or 20.42 mg Al(i-OPr)(20 mol%) were added and the vial was fitted with a septum, cap and needle. Then, the reaction vials were placed in a 300 ml autoclave (eight vials containing different substrates at a time). The autoclave was closed, flushed twice with 20 bar hydrogen and then pressurized with 5–7 bar ammonia gas and 50 bar hydrogen. The autoclave was placed in an aluminium block preheated at 133 °C and the reactions were allowed to proceed for the required time under stirring.
During the reactions, the inside temperature of the autoclave was measured to be 120°C, and this temperature was considered to be the reaction temperature. After completion of the hydrogenation reactions, the autoclave was cooled to room temperature. The remaining ammonia and hydrogen were discharged, and the reaction products were removed from the autoclave. The substance was filtered and washed thoroughly with methanol and ethyl acetate. The reaction products were purified by column chromatography (silica, dichloromethane–methanol) and characterized by GC–MS and NMR analysis. To convert the amines to the hydrochloride salts, 1–2 mL methanolic HCl (0.5 M HCl in methanol) was added to the ethyl acetate solution of the respective amine and the mixture stirred at room temperature for 4–5 h. Then, the solvent was removed and the resulting hydrochloride salt was dried under high vacuum. For selected amines, the yields were determined by GC using the same protocol. After completing the reaction, n-hexadecane was added as standard to the reaction vials and the reaction products purified by column chromatography (silica, dichloromethane–methanol) and characterized by NMR and GC–MS analysis.

**Catalyst recycling.** A magnetic stirring bar and 10 mmol benzonitrile were transferred to a glass-fitted 300-ml Parr autoclave and 15–50 ml i-PrOH was added. Next, the required amount of catalyst (Fe/Fe–O@SiO2, 8.5–10 mol%) and Al foil (20 mol%); the Al foil was cut into small pieces and used in the reactions) were added. Then, the autoclave was closed, flushed twice with 20 bar hydrogen and then pressurized with 7–bar NH3, followed by 50 bar hydrogen. The autoclave was placed in an aluminium block preheated at 133–147°C (placed 30 min before counting the reaction time to achieve the reaction temperature) and the reactions were stirred for 24 h. During the reactions, the inside temperature of the autoclave was measured to be 120–135°C. After completion of the reactions, the autoclave was cooled to room temperature. The remaining ammonia and hydrogen were discharged, and the reaction products were removed from the autoclave. The solid catalyst was filtered and washed thoroughly with methanol and ethyl acetate. The reaction products were purified by column chromatography (silica, dichloromethane–methanol) and characterized by NMR and GC–MS analysis.

**Data availability**

All data are available from the authors upon reasonable request.

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**Author contributions**

R.V.J. and M.B. supervised the project. V.G.C., R.V.J. and M.B. planned and developed the project. V.G.C. developed and prepared the catalytic materials and performed the catalytic experiments. T.S. assisted in the catalyst preparation and catalytic experiments and also reproduced the results. R.G.K., J.K., O.M., M.B.G. and R.Z. characterized the catalysts. R.V.J., V.G.C. and M.B. wrote the paper with contributions from M.B.G., R.G.K. and R.Z.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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