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Introduction

Catalytic hydrogenation of olefins is one of the central synthetic methods in chemistry and intensively used in the petrochemical, pharmaceutical, agrochemical, fine chemical and food industries.^{1,2} Typically, these reductions are accomplished by using molecular hydrogen in the presence of sensitive RANEY® nickel or heterogeneous precious metal catalysts, predominantly based on palladium, rhodium, iridium, or ruthenium. Their limited availability, price, and sometimes toxicity created enormous interest in alternative technologies and catalysts.^{3,4} In this respect, design and development of Earth-abundant 3d-metal based hydrogenation catalysts are highly desirable. Among the different 3d metals, especially cobalt showed promising potential to be a good alternative to the noble metals regarding activity and generality. Therefore in the past decade, the development of efficient homogeneous^{5,6} and heterogeneous⁷ cobalt based catalysts⁸⁻¹⁰ has gained attention.¹¹ Exemplarily, efficient homogeneous complexes for directed or asymmetric olefin hydrogenation were synthesized by Chirik and co-workers.¹²⁻¹⁴ In addition, in recent years the groups of von Wangelin,¹⁵⁻¹⁸ Yang,^{9,10} and Lin¹⁹⁻²¹ reported notable advancements. Complementary to such molecularly

Biomolecule-derived supported cobalt nanoparticles for hydrogenation of industrial olefins, natural oils and more in water†

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Catalytic hydrogenation of olefins using noble metal catalysts or pyrophoric RANEY® nickel is of high importance in the chemical industry. From the point of view of green and sustainable chemistry, design and development of Earth-abundant, less toxic, and more environmentally friendly catalysts are highly desirable. Herein, we report the convenient preparation of active cobalt catalysts and their application in hydrogenations of a wide range of terminal and internal carbon–carbon double bonds in water under mild conditions. Catalysts are prepared on multi-gram scale by pyrolysis of cobalt acetate and uracil, guanine, adenine or L-tryptophan. The most active material Co-Ura/C-600 showed good productivity in industrially relevant hydrogenation of diisobutene to isooctane and in natural oil hardening.

defined systems, more stable and practical heterogeneous cobalt catalysts have attracted considerable attention. For example, the synthesis of olefin-stabilized Co nanoparticles¹⁸ and solid Zr-MTBC-CoH catalysts²⁰ has been reported for catalytic hydrogenations of alkenes, imines, carbonyls, nitroarenes, and heterocycles.^{9,16,22}

During the last decade, our group also developed novel cobalt-based homogeneous²³ and heterogeneous²⁴⁻³⁰ catalysts. In this regard, herein, we report the convenient preparation of novel heterogeneous catalysts *via* pyrolysis of cobalt acetate with biological N-containing ligands on different supports (carbon and aluminium oxides). N-Ligands were chosen from commercially available and relatively cheap amino acid tryptophan (Trp) and purine or pyrimidine nucleobases guanine (Gua), adenine (Ade) and uracil (Ura). To the best of our knowledge to date these nitrogen-rich ligands (Fig. 1) have not been used in the preparation of cobalt heterogeneous catalysts.³¹ Similarly, cobalt homogeneous complexes with nucleobases, *e.g.* uracil or modified uracil, have rarely been prepared before and have not been used in catalysis.³²⁻³⁴ For the first time, the



Fig. 1 N-Containing biological ligands used for catalyst preparation.

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catalytic activity of such materials is demonstrated in hydrogenations of a wide range of substrates. Advantageously, reactions can be performed in water without using any additives.^{35,36}

Results and discussion

We initiated our study on the development of new hydrogenation catalysts with the preparation of more than 20 potentially active cobalt catalysts.

All the materials were prepared in a straightforward manner on multi-gram scale starting from commercially available cobalt(II) acetate, the corresponding N-ligands (Fig. 1), and Vulcan XC72R or aluminium oxides as inorganic supports (see Experimental: catalyst preparation, ESI†). Then, the obtained cobalt pre-catalysts with a 3 wt% metal content were subjected to pyrolysis at 500, 600, 700, 800 or 1000 °C for 2 h under argon and are denoted as Co-ligand/support- $T_{pyrolysis}$ (additionally (a) or (b) was used, if the Al₂O₃ support was acidic or basic, respectively; dry – if non pyrolyzed; air – if pyrolyzed under static air, ESI†). The catalytic performance of all materials was evaluated in the industrially relevant diisobutene hydrogenation as a model reaction (Scheme 1).

Diisobutene is formed by dimerization of isobutene and is generally available as an equilibrium mixture (~4:1) of its isomers, namely terminal olefin 1 (2,4,4-trimethylpent-1-ene) and its internal isomer 2 (2,4,4-trimethylpent-2-ene). In recent years, there has been increasing interest in the hydrogenation of diisobutene for the preparation of isooctane 3 (2,2,4-trimethylpentane) as an alternative anti-knock gasoline additive.³⁷ Due to environmental concerns of existing products, *e.g.* methyl *tert*-butyl ether (MTBE), the petrochemical industry is seeking more environmentally friendly octane booster compounds. In this respect, isooctane is one of the leading candidates because of its high octane number and economically attractive production using existing infrastructure. In fact, this process was successfully implemented in a world-scale plant (Fortum's NEXOCTANE technology).³⁸



Scheme 1 Dissobutene (mixture of isomers 1 + 2) hydrogenation to isooctane 3.

Diisobutene hydrogenation to isooctane **3** has been reported in the past mainly with noble-metal catalysts, such as Pd^{39,40} and Pt.⁴¹ Besides, studies on kinetics of diisobutene hydrogenation were performed by Lylykangas *et al.* using commercial nickel–alumina Ni/Al₂O₃⁴² and Co/SiO₂⁴³ catalysts. Other cobalt catalysts have scarcely been studied in this hydrogenation process, although there is an increasing interest in cobalt-catalysed hydrogenation.²³ As an example, in 2018, we reported the hydrogenation of different olefins including diisobutene in the presence of biowaste-derived cobalt chitosan catalysts. However, comparably harsh conditions (150 °C, 40 bar hydrogen) were necessary for the latter reaction.³⁰ To identify more active and improved cobalt catalysts, our newly prepared materials and commercial ones were screened in the model reaction (Scheme 1) under mild conditions in water as a green solvent (Table 1; ESI - Table S1[†]). More specifically, the experiments were performed in high pressure equipment in parallel vials, using 1.5 mmol diisobutene and 1 mol% of catalyst in 1.5 ml of water at 60 °C and under 30 bar of molecular hydrogen pressure for 18 h. As shown in Table 1, commercial catalysts (Table 1, entries 1 and 2), non-pyrolyzed materials (Table 1, entries 3 and 10) and cobalt samples prepared without biological ligands (Table 1, entries 4 and 11) were completely inactive, indicating the crucial role of ligands and importance of pyrolysis conditions in the formation of the catalytically active cobalt species. Among the pyrolyzed materials, adenine (Ade), guanine (Gua) and tryptophan (Trp) based cobalt catalysts demonstrated low or moderate catalytic activity (Table 1, entries 14–20). To our delight, uracil (Ura) based and Vulcan supported catalysts were more active. Furthermore, at 600 and 700 °C, pyrolyzed materials turned out to be excellent catalysts for diisobutene (1 + 2) hydrogenation ensuring quantitative conversions and excellent yields of isooctane 3 even with 0.5 mol% catalyst under very mild conditions (Table 1, entries 6 and 7).

 Table 1
 Hydrogenation
 of
 diisobutene
 (Scheme 1)
 in
 water
 with
 different supported and biomolecule ligated cobalt catalysts^a
 Image: Cobalt catalysts and biomolecule ligated cobalt catalysts and biomolecule ligated cobalt catalysts
 Image: Cobalt catalysts and biomolecule ligated cobalt catalysts
 Image: Cobalt catalysts and biomolecule ligated cobalt catalysts
 Image: Cobalt catalyst

Entry	Catalyst	Conversion $1 + 2^{b} [\%]$	Yield 3 ^{<i>b</i>} [%]
1	Co_3O_4	0	0
2	CoO_4W	2	Traces
3	Co-Ura/C-dry	0	0
4	Co/C-600	5	0
5	Co-Ura/C-500	65	65
6	Co-Ura/C-600	$100(100^{\circ})$	>99 (>99 ^c)
7	Co-Ura/C-700	100	>99`
8	Co-Ura/C-800	96	94
9	Co-Ura/C-1000	37	35
10	Co-Ura/Al ₂ O ₃ (b)-dry	4	0
11	Co/Al ₂ O ₃ (b)-800	8	0
12	$Co-Ura/Al_2O_3(b)-700$	2	Traces
13	$Co-Ura/Al_2O_3(b)-800$	6	5
14	Co-Trp/C-700	3	2
15	$Co-Trp/Al_2O_3(a)-700$	33	31
16	$Co-Trp/Al_2O_3(b)-700$	40	38
17	$Co-Trp/Al_2O_3(b)-800$	64	62
18	Co-Ade/C-700	18	17
19	Co-Ade/Al ₂ O ₃ (a)-800	34	25
20	Co-Gua/C-700	10	0

^{*a*} Reaction conditions: 1.5 mmol substrate, 1.5 ml water, 1 mol% catalyst, 30 bar H₂, 60 °C, 18 h. ^{*b*} Yields were determined *via* GC, using hexadecane as the internal standard. ^{*c*} 0.5 mol% catalyst was used.

Having the first efficient catalysts in hand, we investigated the influence of critical reaction parameters for this transformation (Scheme 1; Table 2; ESI – Table S2†). Interestingly, testing various solvents showed that the active catalyst is effective in water even at 40 °C and 10 bars of molecular hydrogen (Table 2, entries 8 and 9). Other tested solvents gave

Table 2 Hydrogenation of diisobutene (1 + 2) in water with Co-Ura/C (Scheme 1), and reaction optimization^a

Entry	Catalyst	$p(H_2)[bar]$	Conversion $1 + 2^{b} [\%]$	Yield 3 ^b [%]
1	Co-Ura/C-600	50	100	>99
2	Co-Ura/C-700	50	100	>99
3	Co-Ura/C-800	50	83	82
4	Co-Ura/C-600	30	99 (90°)	99 (90°)
5	Co-Ura/C-700	30	98 (90 ^c)	98 (90 [°])
6	Co-Ura/C-600	20	98	97 ໌
7	Co-Ura/C-700	20	98	97
8	Co-Ura/C-600	10	64	63
9	Co-Ura/C-700	10	63	62

^{*a*} Reaction conditions: 1.5 mmol substrate, 1.5 ml water, 1 mol% catalyst, 10–50 bar H_2 , 40 °C, 18 h. ^{*b*} Yields were determined *via* GC, using hexadecane as the internal standard. ^{*c*} 0.5 mol% catalyst was used.

inferior results under identical conditions (ESI – Table S2†). Some of these solvents (propylene carbonate, acetonitrile or methanol) are even inactive at higher reaction temperature, which might be due to their adsorption/coordination behaviour on the catalyst surface (ESI – Table S2†). Consequently, all further experiments were performed in water. From the three most active catalysts (Table 1, entries 6–8) tested at 40 °C and 50 bar hydrogen, Co-Ura/C-800 still showed very good activity (Table 2, entry 3).

Furthermore, variations of hydrogen pressure and the catalyst amount (Table 2, entries 4 and 5) revealed Co-Ura/C-600 and Co-Ura/C-700 as the best catalytic systems with similar performances. As is evident from Table 2, both catalysts ensure excellent yields of the desired hydrogenation product 3 even at 40 °C/20 bar hydrogen pressure (Table 2, entries 6 and 7) and function equally throughout all experiments. Next, both Co-Ura/ C-600 and Co-Ura/C-700 were used in diisobutene hydrogenation under standard reaction conditions (1.5 mmol substrate, 1 mol% catalyst, 60 °C, 30 bar hydrogen, 1.5 mL water and 18 h) for four consecutive runs (Fig. 2, ESI –Table S5†).

After each run the catalyst was separated by filtration and thoroughly washed with acetone to remove traces of hexadecane (internal standard) and the product or substrate. The separated catalysts were dried at 60 °C under high vacuum for 4 h,



Fig. 2 Recycling tests of Co-Ura/C-600 and Co-Ura/C-700 catalysts by hydrogenation of diisobutene in water.

before being used in the next run. As shown in Fig. 2, in the second run Co-Ura/C-600 still showed >90% of the previous productivity, while that of Co-Ura/C-700 dropped down to 54%. However, during the third run a significant decrease of activity was observed for both materials, while in the fourth run the catalysts were almost inactive. To determine the reasons for this loss of activity, leaching tests were performed. Thus, the reaction mixtures were filtered, all volatile components were removed and the residues were dissolved in *aqua regia*.

The cobalt contents of the obtained aqueous solutions were determined *via* Atomic Absorption Spectroscopy (AAS), which confirmed that they were below the detection limit of 0.04 mg L^{-1} . Consequently, the observed productivity loss cannot be an effect of cobalt leaching.

Subsequently, for characterization of the active catalysts and their deactivation mechanism, detailed analyses of both fresh and recycled catalysts were performed by means of powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) (ESI – S10†).

The samples obtained after pyrolysis at different temperatures were investigated by powder X-ray diffraction in the first step. As seen from the diffraction pattern, Co_3O_4 is obtained as the main crystalline phase if a 500 °C temperature is applied in the synthesis procedure. If the pyrolysis temperature is further increased to 700 °C the Co-oxide is further reduced to metallic cobalt (cubic, ESI – Fig. S10B†). When the synthesis is performed at 1000 °C, the oxide seems to be fully reduced to cobalt. However, due to the low catalyst loading and broad overlapping diffraction peaks the presence of CoO or Co-carbide species cannot be ruled out from the diffraction data.

The XPS analysis of catalysts pyrolyzed at 500, 600, and 700 °C shows very similar results in their C 1s, N 1s and Co 2p spectra as well as in the quantitative analysis of the surface composition (ESI - S10C[†] for a quantification table). The C 1s spectra display strong peaks of carbon-carbon bonds (ESI -Fig. S10C-2[†]). In the N 1s region binding energies characteristic of pyridinic and pyrrolic nitrogen can be found in all spectra (ESI - Fig. S10C-4[†]). With increasing pyrolysis temperature an increasing oxygen concentration can be observed. When 1000 °C was used no cobalt and nitrogen could be detected at the surface of the catalyst while for carbon distinct C-O bonds could be found (ESI - Fig. S10C-2[†]). The Co 2p spectra for the fresh catalysts and pyrolysis temperatures up to 700 °C are quite similar and show two main features at 779.8 eV and 797 eV corresponding to Co $2p_{3/2}$ and Co $2p_{1/2}$, which are characteristic of Co₃O₄ (Fig. 4 for Co-Ura/C-600 and ESI - Fig. S10C-3[†]).⁴⁴

Analytical scanning transmission electron microscopy (STEM) was used to characterize the morphology of Co-Ura/C-600. The general overview confirms different types of structures, comprising Co oxide, Co metal and core-shell type particles with the Co metal at the core surrounded by a Co oxide shell (Fig. 3a, ESI – S10D-1†). Co metal surfaces not surrounded by its oxide are usually covered by several layers of carbon (Fig. 3b, ESI – S10D†).



Fig. 3 High angle annular dark field (HAADF) STEM image (a) showing the general morphology of fresh Co-Ura/C-600 and an annular bright field (ABF) STEM image (b) highlighting a Co metal core partially covered by carbon and Co oxide of the same sample. HAADF-STEM image of a one time used Co-Ura/C-600rec1 sample (c) shows formation of a Co oxide type structure growing around C-support particles. HAADF-STEM image of catalyst Co-Ura/C-600rec4 recovered four times (d) emphasizes further evolution of the new Co oxide phase.

To gain insights into the deactivation of the Co-Ura/C-600 catalyst the recycled material was studied by XRD, XPS and TEM after its fourth usage. X-ray diffraction reveals that no crystalline Co species can be found. This either indicates that the Co/Co-oxides are transformed into an amorphous state or their crystallite size drops significantly. After recycling of the catalyst Co-Ura/600 pronounced changes are observed in the XPS spectra of Co 2p indicating a change in the oxidation state of cobalt (see Fig. 4). The Co 2p signal is shifted to slightly higher binding energies and a new satellite feature around 803 eV becomes visible, indicating the formation of CoO or Co(OH)₂ phases⁴⁴ with each recycling step. Only minor changes can be observed in the C 1s (ESI – Fig. S10C-2†) and N 1s (ESI – Fig. S10C-4†) spectra after each cycle.

STEM measurements of recovered catalysts Co-Ura/ C-600rec1 and rec 4 further support the XRD and XPS results as the morphology of Co phases changes during the reaction. After recovering once used Co-Ura/C-600rec1 a veil like structure attached to the surface of Vulcan support particles could be identified (Fig. 3c). Electron energy loss spectroscopy of these structures indicates a Co–oxygen bond (ESI – D-2†) although a content of hydrogen is also possible. However, it is not possible to verify the hydrogen content by this method. The four times recovered catalyst Co-Ura/C-600rec4 shows further evolution of the veil type structure at the cost of other Co metal or Co oxide particles (Fig. 3d; ESI – S10D-3†).

Next, kinetic investigations on diisobutene hydrogenation were performed under our standard conditions. The hydrogenation of diisobutene (1 + 2) to isooctane 3 was stopped after 1 h, 2 h, 4 h, 7 h and 18 h reaction times and the reaction mixture was analysed by GC (Fig. 5). As expected, terminal olefin 1 is more reactive than the internal one 2 and after 4 h



Fig. 4 Co 2p XPS spectra of fresh Co-Ura/C-600, and recycled Co-Ura/C-600rec1 and Co-Ura/C-600rec4 from top to bottom, respectively. The dashed lines at 779.8 eV and 803 eV mark pronounced changes in the spectra from predominantly Co_3O_4 in the fresh catalyst to CoO or Co(OH)₂ in the catalyst recycled four times.



Time (h)

Fig. 5 Reaction profile for the hydrogenation of diisobutene over Co-Ura/C-600 at 30 bar $\rm H_2,\,60~^{\circ}C,\,1-18~h.$

both substrates reached 96% and 42% conversion, respectively. After 7 h, the reaction mixture consisted of 96% of desired product isooctane 3 along with 4% of remaining internal olefin 2.

To explore the scope and limitations of our catalyst Co-Ura/ C-600, it was applied in the hydrogenation of 15 diverse olefins including various functional groups. The results shown in Table 3 demonstrate excellent catalytic activity of this material often leading to full conversion and quantitative yield under mild conditions in water (Table 3, entries 1–4, 6, and 11). A number of functional groups such as alcohol, amine, nitrile, ether, ester, aldehyde, and sulfonamide groups are well tolerated.

 Table 3
 Co-Ura/C-600
 catalyzed
 hydrogenations
 in
 water: substrate

 scope^a

Entry	Products	$T(^{\circ}C)$	Conversion ^{b} (%)	$\operatorname{Yield}^{b}(\%)$
1	Me 4	60	100	>99
2	Me 5	60	100	>99
3	MeO 6	60	100	>99
4	O OMe 7	60	99	99
5	Me 8	60	96	86
6	Me EtO O O O O EtO O O Et O O Et	60	100	98
7	O N O 10	60 100	16 100	10 56
8	Ph Ph 11	60 120	0 21	0 21
9	Me Me 12	60 140	0 99	0 81
10	H ₂ C Me 13	60 80 100	52 52 80	43 36 8
11	Me 14	60	100	>99
12	Me Me 15	60	100	92
13	Me Me	60	83	72

Entry	Products	$T(^{\circ}C)$	Conversion ^{b} (%)	$\operatorname{Yield}^{b}(\%)$
14	CN CN	60	50	48
15	16 MeNH ₂ 17	60	98	98

^{*a*} Reaction conditions: 1.5 mmol substrate, 1 mol% catalyst, 30 bar H_2 , 1.5 ml water, 18 h. ^{*b*} Yields were determined *via* GC or NMR, using hexadecane or mesitylene, respectively, as the internal standard. Bonds in blue indicate sites of double bond hydrogenation.

In the case of vinylphthalimide (2-vinylisoindoline-1,3dione), hydrogenation led to low conversion under standard conditions (Table 3, entry 7). However, increasing the temperature to 100 °C ensured 56% yield of product **10** due to partial polymerization of the substrate. Even the highly hindered double bond in triphenylethylene could be hydrogenated to give product **11**, albeit elevated temperature was required for this hydrogenation (Table 3, entry 8).

The hydrogenation of substrates with multiple double bonds is a demanding task, which is of interest in the valorisation of natural terpenes. Thus, we were pleased to find that our best catalyst was able to ensure high regio- and chemoselectivity in the hydrogenation of monocyclic terpene *R*-(+)-limonene ((*R*)-1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene) (Table 3, entry 9), which is the main component of essential oils from the rinds of citrus fruits. Both limonene and its mono-hydrogenation product p-menthene 12 ((R)-4-isopropyl-1-methylcyclohex-1-ene) are valuable products and widely used in cosmetics and in the fragrance industry⁴⁵ as well as in the synthesis of fine and bulk chemicals, *e.g.* aviation biofuel.⁴⁶ Notably, selective hydrogenation of R-(+)-limonene to (+)-p-1menthene has recently been reported by Leitner⁴⁷ using commercially available noble metal catalysts Pt/C and Pt/Al₂O₃, as well as by Feldmann, von Wangelin¹⁸ and Wolf¹⁶ using unsupported cobalt nanoparticles.

The Co-Ura/C-600 catalyst performed preferred reduction of the external double bond against the internal one to yield partially hydrogenated versatile product (+)-*p*-1-menthene **12** in 81% yield (Table 3, entry 9). In addition, a tiny amount (\sim 6%) of fully hydrogenated product *p*-menthane (mixture of isomers) was also formed. Similarly, selective hydrogenation of allyl methacrylate was achieved, which occurred preferably at the allylic double bond to form product **13** as a single product. At higher temperature mainly polymerization of the substrate/ product was observed, which demonstrates the importance of running such hydrogenations at lower temperature (Table 3, entry 10).

An example of another relevant hydrogenation is the selective reduction of myrcene (7-methyl-3-methyleneocta-1,6diene) (Table 4). Myrcene is an important natural monoterpene and represents a substantial component of the essential

Table 4 Co-Ura/C-600 catalyzed hydrogenations in water: substrate scope - natural monoterpenes^a

	Substrate CH ₂ CH ₂ Me Me	Product C Me	ets H ₂ Me (Me Me ² a 1	Me Me Me M Me M	Me Me Me Me 18c	Me Me Me 18d
Entry	T (°C)	Yields of 18a–d and total ^{b} (%)				
1	40	20	18	49	3	90
2	60	0	10	61	17	88
3	120	0	0	0	98	98

^a Reaction conditions: 1.5 mmol substrate, 1 mol% catalyst, 1.5 ml water, 30 bar H₂, 18 h. ^b Yields were determined via NMR, using mesitylene as the internal standard. Bonds in blue indicate sites of double bond hydrogenation.

oils of several plants including wild thyme, lemon grass, mango, cannabis, parsley, cardamom, hops and more.48 Structurally, this triene consists of two isoprene units like other monoterpenes. Myrcene and its hydrogenation products are highly valued as raw materials for the preparation of pharmaceuticals, and flavour and fragrance chemicals such as menthol, citronellal and nerol.⁴⁹⁻⁵¹ In this respect, selective hydrogenation of myrcene is of commercial importance, since the obtained products are potential precursors for further functionalized oxygenated derivatives. However, since myrcene contains three different carbon-carbon double bonds, the selective hydrogenation is highly challenging. Previous studies on myrcene hydrogenation made use of precious metal catalysts,⁵² such as Pd/SiO₂,⁵³ palladium nanoparticles,⁵⁴ or chiral phosphine complexes of rhodium and ruthenium.⁵⁵ Furthermore, also unsupported cobalt(0) nanoparticles were applied for the non-selective, complete hydrogenation.16



Scheme 2 Co-Ura/C-600 catalyzed hydrogenations in water: substrate scope - natural oils and fatty acid derivatives.^{a,b} ^a Reaction conditions: a) 1.5 mmol substrate, 1 mol% catalyst, 1.5 ml water, 30 bar H₂, 100 °C, 18 h; b) 300 mg substrate, 30 mg catalyst, 1.5 ml water, 30 bar H₂, 100 °C, 18 h; c) similar to b) at 120 °C; d) similar to b) at 140 °C; and e) similar to b) at 150 °C, 50 bar H₂. ^b Conversions and yields were determined via NMR, using mesitylene as the internal standard.

In contrast, the Co-Ura/C-600 catalyst showed excellent activity and good selectivity towards mono-, di- or full hydrogenation of myrcene leading to isolated dienes, internal alkenes or branched alkanes depending on the reaction temperature (Table 4). Thus, at 40 °C high regioselectivity toward mono- and dihydrogenated products 18a-c was observed with a very good combined selectivity of 90%. Product distribution showed that the selectivity to 18c was 49% which is the highest value and dienes 18a and 18b were formed roughly in the same proportion (18-20% each). The alkyl-substituted double bond remained almost intact. Then, at 60 °C predominantly the dihydrogenated product 18c was formed in 61% yield along with diene 18b (10%) and internal alkane 18d (17%). Increasing the reaction temperature to 120 °C led exclusively to the complete hydrogenation product 18d in an excellent 98% yield. This full hydrogenation of myrcene to 2,6-dimethyloctane 18d can be considered as a renewable route to synthesize fuel additives.56

Finally, we were attracted by the highly important hydrogenation of vegetable oils, fatty acid esters and their triglycerides under our mild conditions. Oils still constitute one of the most important renewable raw materials of the chemical industry. Their hardening over catalytic hydrogenation is a fundamental industrial bulk scale process for the production of important chemicals, such as stabilizers and surfactants, environmentally friendly industrial fluids and lubricants or eatable fats, such as margarine.⁵⁷⁻⁵⁹ Since biodiesel (commonly fatty acid methyl esters) and oil based bio-paraffins are nontoxic, biodegradable renewable alternatives to fossil based fuel, their feedstock diversification has become an important topic for scientists in industry and academia.⁶⁰ In this context, also the potential of apricot kernel,61 linseed or castor62 oils was explored, besides their use as important components in cosmetic preparations or pharmaceutical formulations.

The following industrially relevant substrates were explored: fatty acid methyl esters (Scheme 2A); triglyceride glycerine trioleate and trilinoleate (Scheme 2C) as well as natural apricot kernel, linseed and castor oils (Scheme 2B and C; ESI - Fig. S4, Table S6[†]). As is evident from Scheme 2, Co-Ura/C-600 turned out to be a very good catalyst for hydrogenation of fatty acid derivatives applied in our study. Hence, methyl oleate and its isomer methyl elaidate were hydrogenated at 100 °C to the corresponding methyl stearate 19 and methyl ricinoleate to produce 20 quantitatively (Scheme 2A). Moreover, methyl oleate and methyl ricinoleate were hydrogenated already at 60 °C with almost 90% yield, whereas methyl elaidate conversion was 55% (Scheme 2A; ESI - Table S6†). Additionally, hydrogenation of glycerine trioleate led to glycerine tristearate 22 in 88% yield at 60 °C (ESI - Table S6[†]) and to excellent quantitative yield at 100 °C. In the case of multiply unsaturated glycerine trilinoleate, the hydrogenation degree increased with temperature and conversion (Scheme 2C).

To our delight, natural vegetable oils also were hydrogenated smoothly. Their main component triglycerides are shown in Scheme 2 and their detailed composition and NMR spectra are available in the ESI in the S9 section.[†] Hence, refined castor oil was easily hydrogenated and converted to the white solid product **21** almost quantitatively (Scheme 2B). Finally, hydrogenation of apricot kernel oil was performed both at 120 °C and 150 °C with 77% and 87% conversion, respectively, as determined by ¹H NMR (ESI – S9†). Here, the main product glycerine tristearate **22** was obtained as a waxy, white solid. Moreover, the hydrogenation degree of linseed oil was very high at 150 °C and the conversion to product **22** was almost complete.

Conclusions

Novel heterogeneous cobalt catalysts were prepared by impregnation of inorganic supports with cobalt salts in the presence of 4 different bioorganic ligands (tryptophan (Trp), guanine (Gua), adenine (Ade), and uracil (Ura)) and subsequent pyrolysis. Among the resulting materials, specifically Co-Ura/C-600 showed excellent catalytic activity for hydrogenation of diverse substrates, such as industrially relevant olefins (diisobutene), natural oils, fatty acid derivatives and monoterpenes in water, without any additives. Broad functional group tolerance and often high selectivity towards hydrogenation of terminal olefins have been shown. The easy preparation of the Co-Ura/ C-600 catalyst in multi-gram scale, no need for special handling, long shelf life, and high air- and water-stability, makes it an attractive alternative to presently used homogeneous and noble metal based catalysts.

Experimental

General preparation of Co-Ura\C catalysts (3 wt% cobalt-based, uracil ligated and Vulcan supported)

In a 500 mL two-neck round bottomed flask, equipped with a reflux condenser and a magnetic stir bar, Co(OAc)₂·4H₂O (762.2 mg, 3.06 mmol, 1.0 equiv.) and ligand uracil (692.9 mg, 6.12 mmol, 2.0 equiv.) were dissolved in ethanol (360 mL). The flask was immersed in an oil bath and heated at 70 °C. After 30 min, 4.77 g of Vulcan powder was added to the reaction mixture and the resulting heterogeneous mixture was heated for 4 h at 80 °C. The solvent was removed using a rotary evaporator and the residue was dried overnight at 65 °C under high-vacuum. The dried sample was ground in an agate mortar to a fine powder (5.9 g), from which a 0.5 g portion was transferred to a ceramic crucible and pyrolyzed at temperatures between 500 and 1000 °C (the oven was evacuated to ca. 5 mbar and then flushed with argon three times, and the heating rate was 25 °C per minute and held at pyrolysis temperature for 2 h under an argon atmosphere). The pyrolyzed catalysts were ground again in an agate mortar, and stored in glass vials in air, without special protection. The catalysts were labelled as Co-ligand\support-temperature (e.g. Co-Ura\C-600).

General procedures for hydrogenation reactions

A 4 mL screw-cap vial was charged with a catalyst (30 mg, \sim 1 mol%), a substrate (1.5 mmol), 1.5 mL of deionized water

(or screened solvent) and a Teflon-coated stirring bar. The vial was closed with a phenolic cap with a PTFE/white rubber septum (Wheaton 13 mm septa) and for the connection to the atmosphere the septum was punctured with a syringe needle. The vial was fixed in an alloy plate and then transferred into a Parr 4560 series autoclave (300 mL). At room temperature, the autoclave was flushed with hydrogen three times before it was pressurized at the required hydrogen pressure. The autoclave was placed into an aluminum block on a heating plate and heated up to required temperature. The heating was continued for 18 h under intensive stirring (1000 rpm). Afterwards, the autoclave was cooled in an ice bath to room temperature, the hydrogen was discharged and the vials containing reaction products were removed. In the case of GC analysis, to the crude reaction mixture an internal standard *n*-hexadecane (100 µL) was added, the mixture was diluted with ethyl acetate and a GC sample was analyzed. For ¹H and ¹³C NMR analyses, mesitylene (20 μ L) was taken as the internal standard. To the reaction mixture 2 mL CDCl₃ was added and the organic phase was subjected to NMR and GC analyses, after filtration through a 0.2 µm PTFE syringe filter. The obtained chromatograms and NMR spectra were compared with the reported ones.

Catalyst recycling procedure

The reaction was performed according to the general procedure using the Co-Ura/C-600 or Co-Ura/C-700 catalyst (30 mg, ~1 mol%) and diisobutene (169 mg, 1.5 mmol) in 1.5 mL of deionized water. After 18 h, to the crude reaction mixture the internal standard *n*-hexadecane (100 μ L) was added, the reaction mixture was diluted with ethyl acetate and a sample was analyzed by gas chromatography. Reported GC yields are the average of at least three runs. Afterwards, the reaction mixture was filtered off and the obtained catalyst was washed with 10–15 ml acetone. The recycled catalyst was then dried at 60 °C under high vacuum for 4 h before using for the next run.

Conflicts of interest

There are no conflicts to declare.

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