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Chemoselective Hydrogenation of α,β-Unsaturated Carbonyls Catalyzed by Biomass-Derived Cobalt Nanoparticles in Water

Tao Song,[a] Zhiming Ma,[a,b] and Yong Yang[a]*

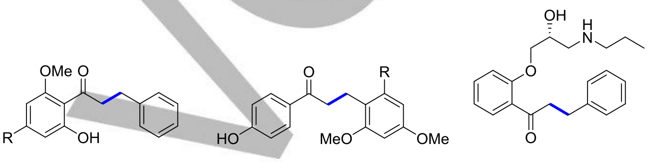
Dedication ((optional))

Abstract: Herein, we report highly chemoselective hydrogenation of α,β-unsaturated carbonyls to saturated carbonyls catalyzed by cobalt nanoparticles supported on the biomass-derived carbon from bamboo shoots with molecular hydrogen in water, which is the first prototype using a heterogeneous non-noble metal catalyst for such organic transformation as far as we know. The optimal cobalt nanocatalyst, CoO$_x$@NC-800, manifested remarkable activity and selectivity for hydrogenation of C=C in α,β-unsaturated carbonyls under mild conditions. A broad set of α,β-aromatic and aliphatic unsaturated carbonyls were selectively reduced to their corresponding saturated carbonyls in up to 99% yields with good tolerance of various functional groups. Meanwhile, a new straightforward one-pot cascade synthesis of saturated carbonyls was realized with high activity and selectivity via the cross-aldol condensation of ketones with aldehydes followed by selective hydrogenation. More importantly, this one-pot strategy is applicable for the expedient synthesis of Loureirin A, a versatile bioactive and medicinal molecule, from readily available starting materials, further highlighting the practical utility of the catalyst. In addition, the catalyst can be easily separated for successive reuses without significant loss in both activity and selectivity.

Introduction

The chemoselective hydrogenation of α,β-unsaturated carbonyls is a pivotal tactics both in the academic research and industry applications due to its extensive applications in the synthesis of fine chemicals, pharmaceuticals and functional materials.[1] In general, three types of product can be obtained from the hydrogenation of α,β-unsaturated carbonyls via either the selective reduction of the C=C or the C=O bond, or non-selective reduction of both bonds. The highly chemoselective reduction of one of the C=C and C=O bonds in the α,β-unsaturated carbonyls is still demanding yet can be challenging in some situations. Particularly, the selective hydrogenation of the C=C bond of α,β-unsaturated carbonyls with the C=O bond intact is one important synthetic transformation because the corresponding reduced products are valuable substructures for many pharmaceutically active molecules (Scheme 1)[2].

Over the past decades, great efforts have been made to contribute to the selective reduction of the C=C bond of α,β-unsaturated carbonyls to saturated carbonyls with various hydrogen donors, such as H_2, formic acid, alcohols, hydrosilanes, borohydrides, (para)formaldehyde, and other ones. However, in most cases, they generally employ noble metals, e.g., as Pt[3], Pd[4], Ru[5], Rh[6], Ir[7], with assistance of sophisticated and expensive organic ligands, such as N,N-bis(2,6-diisopropylphenyl)imidazol-2-ylidene,[4f] Pincer-ligands,[4j] dichlorotris(triphenylphosphine),[5e] N-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine,[6c] and so on, for the homogeneous catalysts, while with high expense of supports for the heterogeneous catalysts (Scheme 2a).



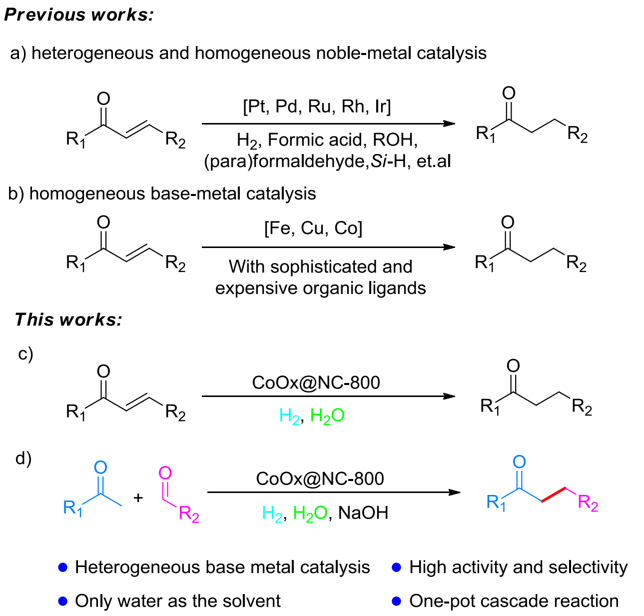
R = H Uvangoletin
R = Me Myriggalone H

R = H Loureirin A
R = OMe Loureirin B

***(R)*-Propafenone**

Scheme 1. Selected pharmaceutically active molecules contained the 1,4-diaryl ketone skeletons.

Under the increasing pressure of the energy crisis and economic constraints, the replacement of noble metals by inexpensive and earth-abundant non-noble metals would be preferable in sustainable catalysis and synthesis, especially for more widespread and industrial applications. Despite recent sporadic reports regarding ligand-enabled non-noble metal catalyzed selective hydrogenation of the C=C bond of α,β-unsaturated carbonyls,[8] a heterogeneous catalyst with high chemoselectivity remains elusive.[9] As a consequence, from both economic and environmental viewpoints, there is a strong incentive to develop a reusable heterogeneous non-noble-metal catalyst for highly efficient and selective hydrogenation of the C=C bond of α,β-unsaturated carbonyls.



Scheme 2. The strategies for chemoselective hydrogenation C=C bond of α,β-unsaturated carbonyls.

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Results and Discussion

In our continuation to develop green catalysis for sustainable organic synthesis, we very recently developed an efficient and recyclable inexpensive cobalt nanocomposites on N-doped hierarchical carbon derived from biomass for chemoselective hydrogenation of functionalized nitroarenes.[10] Inspired by the impressive results, we are eager to extend the application of this catalyst for the selective hydrogenation of α,β-unsaturated carbonyls. Herein, we report that this cobalt nanocomposites catalyst is capable of catalysing chemoselective hydrogenation of the C=C bond of α,β-unsaturated carbonyls in water (Scheme 2c). The present catalytic system shows outstanding catalytic activity with exclusive selectivity to C=C bond reduction and broad substrate scope for various α,β-unsaturated carbonyl compounds with good tolerance of functional groups. In addition, the cobalt nanocomposites catalyst also shows high activity for one-pot direct synthesis of saturated carbonyls from ketones and aldehydes as starting materials via a sequential cross-aldol condensation and selective hydrogenation (Scheme 2d). More importantly, this new straightforward one-pot cascade method is applicable for expedient synthesis of pharmaceutically active Loureirin A in a simple and green manner.

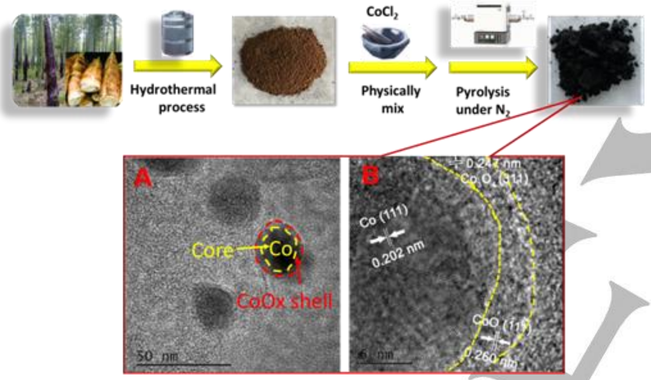
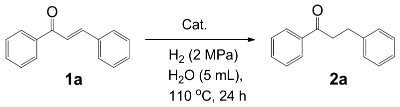


Figure 1. Schematic illustration of the preparation of CoO_x@NC.

The cobalt nanoparticles (NPs) comprising of metallic cobalt as core covered with cobalt oxide as shell on N-doped hierarchical porous carbon derived from naturally renewable biomass, denoted as CoO_x@NC-T (where T represents pyrolysis temperature), were synthesized by a facile tandem hydrothermal-pyrolysis process as reported in our earlier work[10] (Figure 1, see details in the Supporting Information). Our previous work regarding the hydrogenation of nitro compounds catalyzed by the catalyst CoO_x@NC-T demonstrated that the synergistic effect between Co NPs and N,O atoms incorporated in the carbon framework dramatically improved the catalytic performance and the catalyst CoO_x@NC-800 gave the best outcome. We then decided to perform the hydrogeantion of 1,3-diphenylprop-2-en-1-one (chalcone, **1a**) as a model substrate to assess whether the catalyst CoO_x@NC-800 could enable selective hydrogenation of C=C or C=O bond with molecular hydrogen under similar conditions. To our delight, the reaction proceeded smoothly to convert **1a** to 1,3-diphenylpropan-1-one (**2a**) with 52% conversion and 100% selectivity using CH_3CN as solvent under 5 MPa of H_2 after 24 h (Table S5, entry 4). Rapid screening of the solvents showed that the reaction efficiency had a profound dependence on the polarity of the solvent (Table S5 in the Supporting Information) and increasing the polarity of the solvents was significantly beneficial to the improvement of conversion. Among all investigated solvents, H_2O, as a green and sustainable solvent, showed superior catalytic efficiency with complete conversion and exclusive selectivity to **2a**.

Interestingly, the pressure of H_2 can be reduced from 5 to 2 MPa with maintaining the equal activity and selectivity upon addition of an equivalent of tetrabutylammmonium iodide (TBAI) (with respect to **1a**) into the reaction mixture under otherwise identical conditions. This result indicates that TBAI might act as a surfactant to improve the solubility of organic substrate and dispersion of the catalyst in water, and the interfacial contact between the catalyst and substrate as well. To confirm this, the hydrogenation of **1a** in the absence of TBAI or the presence of 0.5 equivalent of TBAI was performed. A considerable lower conversion was observed in each case, especially for the reaction without TBAI (entries 1 and 3), demonstrating the importance of TBAI for the enhanced reaction efficiency. Other common surfactants, such as tetrabutylammonium bromide (TBAB), tetrabutylammonium fluoride (TBAF), sodium dodecyl sulfate (SDS), hexadecyl trimethyl ammonium bromide (CTAB), were also employed for the reaction (Table 1, entries 7-10). All showed a pronounced improvement in activity under identical conditions, while TBAI gave the maximum. Reducing the reaction temperature or the dosage of catalyst resulted in lower conversion under otherwise identical conditions (Table 1, entries 4-6). In line with our previous findings, the catalyst CoO_x@NC-800 also gave the best result compared with that pyrolyzed at 700 or 900ºC (Table 1, entries 11 and 12). In sharp contrast, the catalyst CoO_x@C-800, which was prepared form pyrolysis of the mixture of cobalt salt and the commercially available activated carbon without N-dopant, only achieved half of the reaction efficiency to that of CoO_x@NC-800 under identical conditions (Table 1, entry 13), indicating the critical role of N-dopant in the carbon framework for the reaction. Other control experiments showed that $CoCl_2$, pure Co_3O_4, pure nano Co_3O_4 (100 nm) as catalyst or in the absence of the catalyst led to considerably lower activity or even no reactivity (Table 1, entry 14-18), further reflecting the essential role of the catalyst CoO_x@NC-800 in catalysis. Therefore, upon rapid investigation of reaction factors, the optimal reaction conditions involve 10 mol% of CoO_x@NC-800 as the catalyst, an equivalent of TBAI as the surfactant, H_2O as solvent, at 110ºC reaction temperature, under 2 MPa of H_2 pressure (Table 1, entry 2).

Table 1. Optimization of reaction conditions.[a]



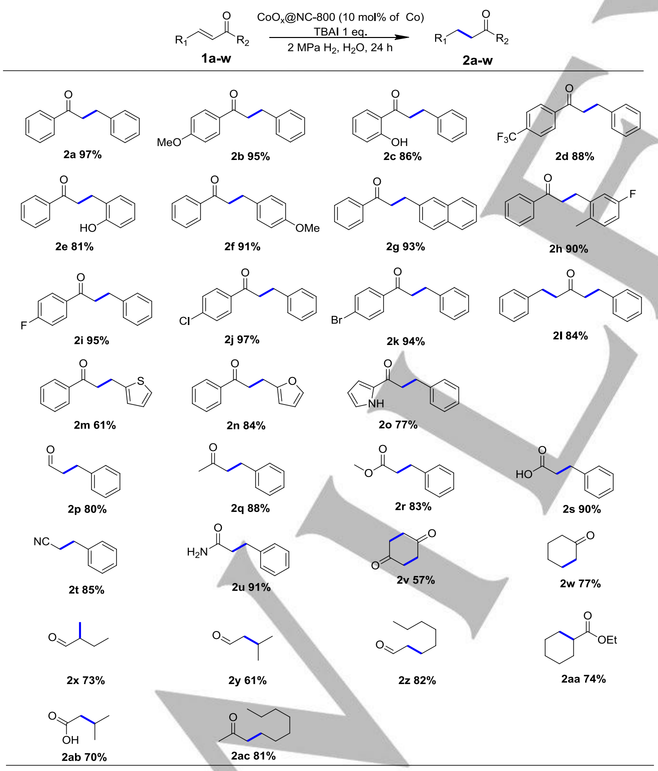
Entry	Cat.	Additive	Conv.(%)[b]	Selec.(%)[b]
1	CoO_x@NC-800	TBAI(0.5 eq.)	86	>99
2	**CoO_x@NC-800**	**TBAI(1 eq.)**	**100**	**>99**
3	CoO_x@NC-800	Blank	34	>99
4[c]	CoO_x@NC-800	TBAI(1 eq.)	88	>99
5[d]	CoO_x@NC-800	TBAI(1 eq.)	76	>99
6[e]	CoO_x@NC-800	TBAI(1 eq.)	62	>99
7	CoO_x@NC-800	TBAB(1 eq.)	95	>99

8	CoO_x@NC-800	TBAF (1 eq.)	69	>99
9	CoO_x@NC-800	SDS(1 eq.)	86	>99
10	CoO_x@NC-800	CTAB (1eq.)	82	>99
11	CoO_x@NC-700	TBAI(1 eq.)	76	>99
12	CoO_x@NC-900	TBAI(1 eq.)	83	>99
13	CoO_x@C-800	TBAI(1 eq.)	50	>99
14	$CoCl_2$	TBAI(1 eq.)	10	>99
15	Co_3O_4	TBAI(1 eq.)	13	>99
16	Nano Co_3O_4	TBAI(1 eq.)	11	>99
17	Blank	TBAI(1 eq.)	0	0
18	Blank	Blank	0	0

[a] Reaction conditions: chalcone **1a** (0.2 mmol), catalyst (20 mg, 10 mol% of Co), H_2O (5 mL), H_2 (2 MPa), 110ºC, 24 h. [b] Determined by GC and GC-MS using dodecane as an internal standard sample and confirmed with their corresponding authentic samples. [c] 100ºC. [d] 90ºC. [e] 10 mg of catalyst was used.

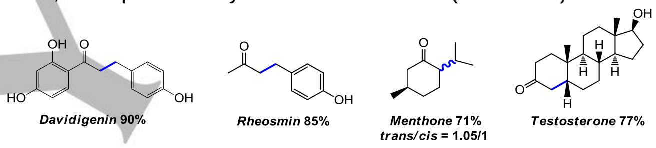
To explore the general applicability of this protocol, various α,β-unsaturated carbonyls were subjected to the optimized reaction conditions (Table 2). Both electron-donating and -withdrawing aromatic substituted α,β-enones (**1a-1h**) were reduced efficiently to provide the corresponding desired products in good to excellent yields. The steric effects have negligible effect on reactivity, especially for the ortho-substituted α,β-enones with either -OH or -Me group(**1c**, **1e,** and **1h**). Halogen-substituted chalcones (1h-1k) gave the corresponding saturated carbonyls in high isolated yields without detection of dehalogenated products. The two conjugated C=C bonds in diphenylpenta-1,4-dien-3-one (1l) were both selectively reduced. Heteroaromatic chacone-type derivatives (**1m**-**1o**) were also compatible with the present conditions and gave the corresponding saturated ketones in 61% to 84% yields, respectively. Moreover, a set of α,β-unsaturated aldehyde (**1p**), ketone (**1q**), ester (**1r**), acid (**1s**), nitrile (**1p**), and amide (**1u**) were also successful for the selective reduction of C=C bonds, giving the desired products in excellent yields under identical conditions. In addition, the aliphatic unsaturated aldehydes including terminal alkenyl (**1x**), disubstituted alkenyl (**1y**), and trisubstituted alkenyl (**1z**) were all exclusively reduced to the their respective saturated aldehydes in 61-82% yields. Other aliphatic unsaturated carbonyls, like ketones (**1v, 1w, 1ac**), ester (**1aa**), or carboxylic acid (**1ab**) were also smoothly converted to the saturated carbonyls.

Table 2. Substrate scope [a].



[a] Reaction conditions: substrates (0.2 mmol), CoO_x@NC-800 (20 mg, 10mol% of Co), TBAI (73.8 mg, 0.2 mmol), H_2O (5 mL), H_2 (2 MPa), 110ºC, 24 h. Yields of isolated products are given.

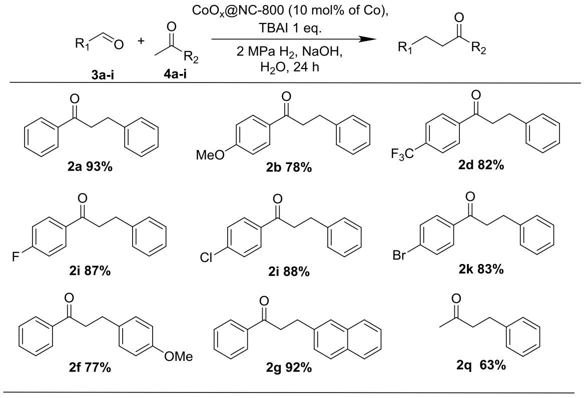
Meanwhile, natural and/or biologically active compounds, such as *Davidigenin, Rheosmin, Menthone,* and *Testosterone*, could also be efficiently and chemoselectively synthesized from their respective α,β-unsaturated carbonyls in good to high yields under the standard reaction conditions. Remarkably, Testosterone was synthesized with exclusive diastereoselectivity, affording *cis*-isomer as the sole product in the present catalysis system. Note that the trisubstituted unsaturated ketone was hydrogenated as effectively and efficiently as the disubstituted ones, exemplified as synthesis of *Menthone* (Scheme 3).



Scheme 3. Synthesis of natural and/or bioactive compounds under the standard conditions.

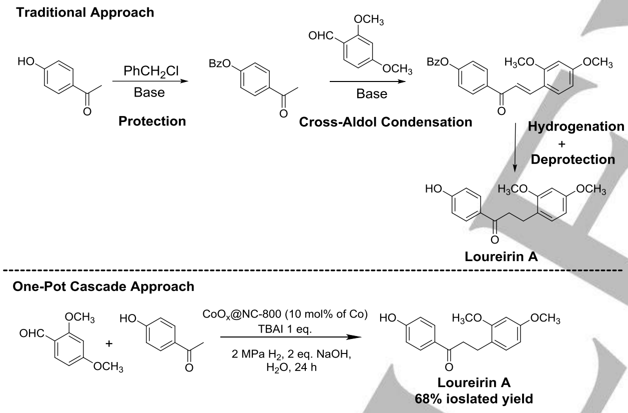
The impressive results for the direct hydrogenation of α,β-unsaturated carbonyls as demonstrated above clearly suggest that the catalyst CoO_x@NC is inactive for reduction of the C=O bond. It is well-known that the α,β-unsaturated carbonyls are usually synthesized via the cross-aldol (or Claisen-Schmidt) condensation between ketones and aldehydes in the presence of base or acid[11]. The unique selectivity of this catalyst inspired us to develop one-pot cascade synthesis of saturated carbonyls by the cross-aldol condensation of ketones with aldehydes and sequential selective hydrogenation. We then chose benzaldehyde and acetonphenone as the model substrates to perform the one-pot cascade reaction for the synthesis of saturated carbonyls. To our delight, the 1,3-diphenylpropan-1-one (**2a**) could be obtained with nearly quantitative yield under slightly modified optimal conditions catalysed by the catalyst CoO_x@NC-800 upon addition of NaOH as a base (Table S6). Subsequently, various typical aldehydes and ketones were employed as the substrates to proceed the reaction. We found that this protocol is suitable for both electron-donating and -withdrawing aromatic substituted benzaldehydes and acetonphenones to deliver the desired saturated ketones in good to excellent yields. Furthermore, the aliphatic acetone was also applicable for the synthesis of 4-phenylbutan-2-one (**2q**) with 63% isolated yield (Table 3).

Table 3. One-pot synthesis of saturated ketones from various aldehydes and ketones [a].



[a] Reaction conditions: aldehyde (0.2 mmol), ketone (0.4 mmol), CoO$_x$@NC-800 (20 mg, 10 mol% of Co), NaOH (0.2 mmol), H_2O (5 mL), H_2 (2 MPa), 110°C, 24 h. Yields of isolated products are given.

To demonstrate the practical applicability of the one-pot cascade protocol, we extended it for the direct synthesis of Loureirin A, an important bioactive and medicinal molecule, from readily available starting materials (Scheme 4).[12] Under the slightly modified conditions, 68% of isolated yield of Loureirin A was achieved. Compared with the traditional synthetic method,[13] (de)protection of free hydroxyl group, separation and purification of the intermediate are no need, making this protocol more time-saving and cost-effective. Therefore, it provides an alternative and attractive synthetic method for preparation of Loureirin A and other important bioactive saturated carbonyls, further highlighting its practical importance and utility.



Scheme 4. Synthesis of Loureirin A by one-pot cascade strategy.

Durability and recyclability of a catalyst is critical for practical applications. The catalyst CoO$_x$@NC-800 was recollected by centrifugation, washed, and dried after completion of a selective hydrogenation experiment for subsequent cycles. As shown in Figure 2, the selectivity remained with negligible changes after five recycling experiments, demonstrating the high durability of the catalyst because of that the N atoms in carbon structure can act as basic coordination sites for stabilizing highly dispersed Co NPs.[8,14-16]A slight decrease in reaction efficiency is most likely due to the loss of catalyst during the recycle process.

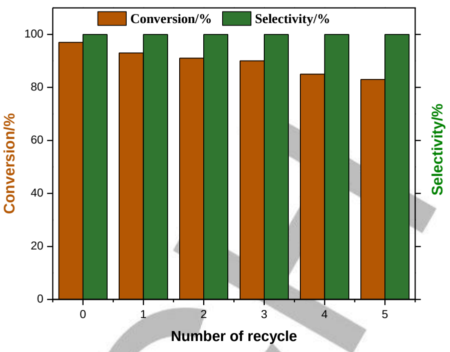
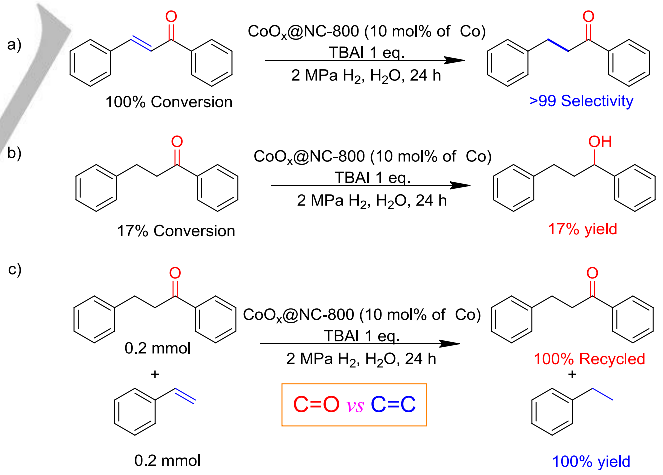


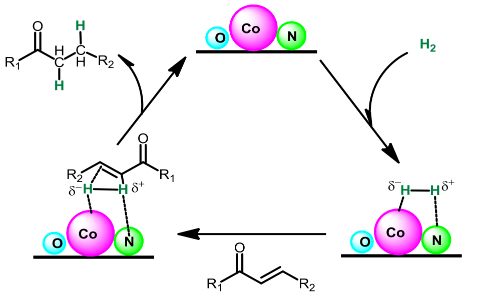
Figure 2. Recyclability of the catalyst CoO$_x$@NC-800 for the selective hydrogenation of α,β-unsaturated carbonyls under the standard conditions.

To gain insight into the exclusive selectivity to C=C bond in the hydrogenation of unsaturated carbonyls, control experiments were performed (Scheme 5). When 1,3-diphenylpropan-1-one (**2a**) was subjected to the optimized conditions, only 17% conversion of **2a** was reduced to its respective alcohol after 24 h, clearly indicating the significantly preferable selectivity to C=C bond (Scheme 5b). In contrast, full conversion of styrene to ethylbenzene with completely recovery of **2a** was observed, when the reaction of the mixture of **2a** and styrene (1:1 molar ratio) was conducted under the optimized conditions, further confirming the outstanding selectivity to C=C bond of the catalyst (Scheme 5c). Based on our previous works and other reported results, N,O-doped hierarchically structured porous materials could modify the selective adsorption properties of catalyst for the C=C bond and C=O bond,[17] and also provide large surface areas for reaction, interfacial transport, or dispersion of active sites at different length scales of pores[2b]. The comprehensive effects might be decisive for the outstanding selectivity and activity.



Scheme 5. Control experiments under the standard conditions

A plausible reaction pathway is proposed as shown in Scheme 6. Initially, the H_2 is dissociated on the surface of CoO$_x$@NC-800, further generates the activated hydrogen species, such as cobalt hydride species [Co-H_2]. Meanwhile, the substrate interacts with the heterogeneous catalyst preferentially via the selective adsorption of the C=C bond other than C=O bond of α,β-unsaturated carbonyls by the catalyst surface. Subsequently, the C=C bond is chemoselectively hydrogenated by the activated hydrogen atoms. The formed saturated ketone desorbs from the surface of catalyst, thereby completing the entire catalytic cycle.



Scheme 6. Proposed reaction pathway of selective hydrogenation of α,β-unsaturated carbonyls.

Conclusions

In conclusion, we have developed highly chemoselective hydrogenation of α,β-unsaturated carbonyls to saturated carbonyls catalyzed by an inexpensive, active, and heterogeneous cobalt nanostructured catalyst. A broad set of α,β-aromatic and aliphatic unsaturated carbonyl compounds was selectively reduced to their corresponding saturated carbonyls in high yields with good functional groups tolerance. Meanwhile, the optimal catalyst CoO_x@NC-800 is also applicable for one-pot direct synthesis of saturated ketones starting from readily available aldehydes and ketones, including an important bioactive and medicinal Loureirin A, in a cost-effective and green manner. To the best of our knowledge, this is the first example using a heterogeneous non-noble metal catalyst for the chemoselcetive hydrogenation of C=C bond of α,β-unsaturated carbonyls.

Acknowledgements

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Keywords: nanostructured cobalt catalyst • selective hydrogenation • unsaturated ketones • ketones• one-pot method

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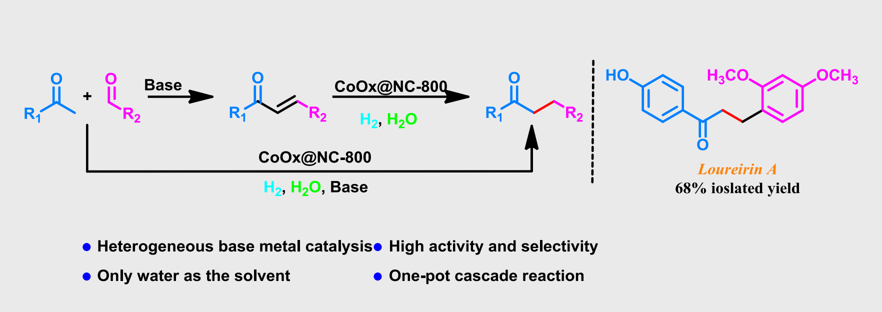

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Chemoselective Hydrogenation of α,β-Unsaturated Carbonyls Catalyzed by Biomass-Derived Cobalt Nanoparticles in Water

A heterogeneous and reusable biomass-derived non-noble cobalt nanoparticles has been firstly developed for efficient and selective hydrogenation of α,β-unsaturated carbonyls to saturated carbonyls, and the direct one-pot synthesis of saturated ketones including important bioactive and medical *Loureirin A* starting from aldehydes and ketones have also been realized in a sequential, cost-effective, and green manner.