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Co_3O_4 Nanoparticles Supported on Mesoporous Carbon for Selective Transfer Hydrogenation of α,β-Unsaturated Aldehydes

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Dedicated to Professor Klaus K. Unger on the occasion of his 80th birthday

Abstract: *A simple and scalable method for synthesizing Co_3O_4 nanoparticles supported on the framework of mesoporous carbon (MC) was developed. Benefiting from an ion-exchange process during the preparation, the cobalt precursor is introduced into a mesostructured polymer framework that results in Co_3O_4 nanoparticles (ca. 3 nm) supported on MC (Co_3O_4/MC) with narrow particle size distribution and homogeneous dispersion after simple reduction/pyrolysis and mild oxidation steps. The as-obtained Co_3O_4/MC is a highly efficient catalyst for transfer hydrogenation of α,β-unsaturated aldehydes. Selectivities towards unsaturated alcohols are always higher than 95 % at full conversion. In addition, the Co_3O_4/MC shows high stability under the reaction conditions, it can be recycled at least six times without loss of activity.*

The production of high-value-added chemicals from biomass is of major interest since the dependence on petroleum-based chemicals can be reduced by replacing fossil feedstocks with renewable ones.[1] Furan derivatives of furfural (FAL) and 5-hydroxymethylfurfural (HMF), which can be produced from hemicellulose and cellulose, respectively, are considered as promising platform molecules to bridge the gap between biomass resources and bio-chemicals, since they can be converted into a variety of high-value-added chemicals and fuels.[2] Particularly, selective hydrogenation of FAL to furfuryl alcohol (FOL) and HMF to 2,5-bis-(hydroxymethyl)-furan (BHMF) has great potential for industrial applications. Because, FOL and BHMF can be used as precursors in the synthesis of polymers, resins and adhesives, and as intermediates for the generation of drugs and crown ethers.[1e,f] However, owing to the different functionalities of furan-based α,β-unsaturated aldehydes (e.g., furan ring, C=C and C=O bonds),[3] selective hydrogenation of only the C=O bond is very challenging. Many byproducts are often formed by hydrogenolysis of the -CH=O side chain to -CH_3, or hydrogenation of the furan ring and its opening,[4] leading to low yield of the desired unsaturated alcohols and increasing costs for product purification. Therefore, design of suitable catalysts and/or catalytic systems that facilitate selective hydrogenation of C=O bond in the presence of other functionalities is highly desirable.

In general, conventional hydrogenation catalysts based on transition metals (e.g., Pd, Pt, Ru, Rh, Cu, or Ni) show high activity but poor selectivity toward unsaturated alcohols.[4,5] To enhance the selectivity for unsaturated alcohols over such catalysts, additives,[6] stabilizers/ligands,[7] supplemental metal components,[8] and functional supports[9] were introduced into catalytic systems or catalysts. In some cases high selectivity toward unsaturated alcohols and high activity were indeed achieved using the above approaches. However, owing to the complexity of reaction mechanisms (e.g., competitive/non-competitive and dissociative/non-dissociative adsorption, side reactions), selectivities and activities in these cases can be affected by a series of factors, including the structure, texture and composition of the catalysts (e.g., particle size, shape, molar ratio of different components, crystal structure) and the reaction conditions (e.g., temperature, pressure and solvent).[10] In other words, dramatic decrease in selectivity and/or activity often occurs, because it is very difficult to predict and control the influence of these factors precisely, especially in large scale applications. Therefore, it is necessary to develop simple methods for scale-up of catalyst synthesis. Furthermore, the catalysts must be highly active and selective toward unsaturated alcohols in simple catalytic systems, which are also controllable and scalable.

Compared with hydrogenation reactions involving H_2, transfer hydrogenation is much safer and easier to handle because pressure is not an issue and the influence of H_2 pressure on selectivity is not relevant.[11] In transfer hydrogenation reactions, 2-propanol is often utilized as hydrogen donor, because it is cheap, environmentally friendly, and easy to remove.[11] Herein, we report on the transfer hydrogenation of furan-based α,β-unsaturated aldehydes over spinel-type cobalt oxide on mesoporous carbon (Co_3O_4/MC), where the selectivity toward unsaturated alcohol is always higher than 95 % at full conversion. The synthesis of Co_3O_4/MC involves a hydrothermal process, an ion-exchange, and a pyrolysis/reduction as well as a mild oxidation step (Figure 1 a). In the first step, a mesostructured polymer gel is synthesized using 2,4-dihydroxybenzoic acid and hexamethylenetetramine (HMT) as polymer precursors, and triblock copolymer (P123) as surfactant under hydrothermal conditions (130 °C for 4 h). Then, cobalt ammine complexes are introduced

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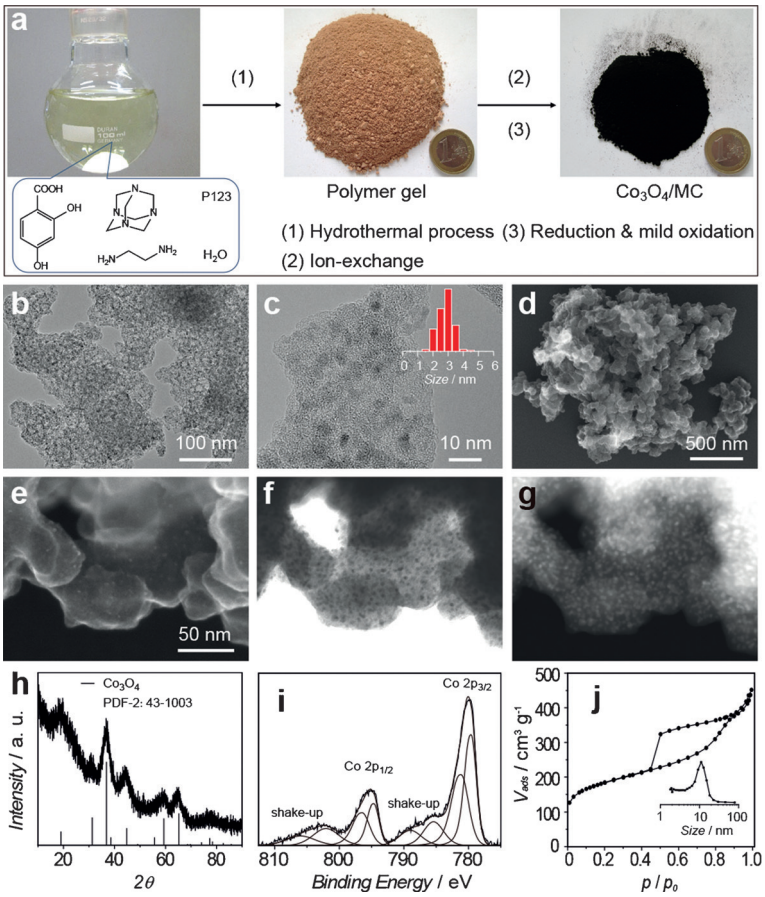

Figure 1. a) Synthesis of Co_3O_4/MC. b,c) TEM images, d) SEM image and e–g) STEM images of Co_3O_4/MC; inset in (c) shows the Co_3O_4 particle size distribution. h) XRD pattern, i) XPS spectrum, and j) N_2 sorption isotherm of Co_3O_4/MC; inset: the pore size distribution.

homogenously into the polymer framework via ion exchange. Next, the polymer containing the cobalt precursor is pyrolyzed at 500 °C (10 % H_2 in argon) to form the carbon, simultaneously the cobalt precursor is reduced to form metal nanoparticles supported on the mesopore framework of the carbon. Finally, Co_3O_4 nanoparticles are formed within the MC support after mild oxidation at room temperature (1 % O_2 in argon). These synthetic processes can be easily scaled up.

Transmission electron microscopy (TEM) images (Figure 1 b,c) show that the Co_3O_4/MC is highly mesoporous. The Co_3O_4 nanoparticles with a diameter of approximately 3 nm are finely dispersed on the framework of MC. Many macropores are also observed in the scanning electron microscopy (SEM) images (Figure 1 d and Figure S1a in the Supporting Information), which are caused by the gel structure of the polymer. Scanning transmission electron microscopy (STEM) images (Figure 1 e–g) further confirm that the Co_3O_4 nanoparticles are very homogeneously dispersed on the MC framework and that they have a narrow particle size distribution. Most importantly, no bigger Co_3O_4 particles are formed by the synthesis method (Figure 1 b,e–g and Figure S1 b). The X-ray diffraction (XRD) pattern (Figure 1 h) shows the typical reflections of the Co_3O_4 spinel (the lines under the diffraction pattern indicate reflections for the PDF-2 entry 43–1003). The very broad reflections prove the formation of small Co_3O_4 nanoparticles after the reduction and mild oxidation steps. The Co 2p X-ray photoelectron spectrum (XPS) shows peaks with binding energies at 779.6 eV and 794.6 eV corresponding to Co^{3+} $2p_{3/2}$ and $2p_{1/2}$, and peaks at 781.1 eV and 796.5 eV belonging to Co^{2+} $2p_{3/2}$ and $2p_{1/2}$ (Figure 1 i, Table S1), which further confirm the formation of Co_3O_4 nanoparticles. Nevertheless, the shake-up signal at 785.4 eV belonging to Co^{2+} is slightly higher than expected for an ideal Co_3O_4 surface, suggesting that Co^{2+} is enriched in the surface of the Co_3O_4 nanoparticles (Figure 1 i, Table S1). Based on AAS analysis (atomic absorption spectrometry, PerkinElmer AAnalyst 200), the Co fraction in Co_3O_4/MC is 15 wt %, corresponding to 20 wt % Co_3O_4. The N_2 sorption isotherm of Co_3O_4/MC (Figure 1 j) shows a type-IV curve, characteristic for mesoporous materials. The sorption isotherm does not level out in a plateau at relative pressures $p/p_0 > 0.9$, indicating the existence of macropores, fully consistent with the SEM observations. The surface area, pore volume and pore size of Co_3O_4/MC are 642 $m^2 g^{-1}$, 0.7 $cm^3 g^{-1}$ and 11 nm, respectively.

The synthesis methodology of Co_3O_4/MC can be extended to synthesize other metal catalysts supported on MC. Pd/MC (Figure S2) and Ru/MC (Figure S3) were prepared by this method as well, both of which have narrow particle size distribution (5 ± 0.8 nm for Pd; 1 ± 0.2 nm for Ru) and homogenous dispersion. Without introducing metals, MC with a surface area of 722 $m^2 g^{-1}$, a pore volume of 0.7 $cm^3 g^{-1}$ and a pore size of around 9.5 nm is generated directly after carbonization of the polymer gel at 800 °C in argon (Figure S4). Such carbon material has high potential for applications as catalyst support or adsorbent.

The catalytic performance of Co_3O_4/MC was evaluated for transfer hydrogenation of FAL to FOL and HMF to BHMF. First a blank reaction without catalyst was carried out; no reaction proceeded (Table S2, entry 1). In the presence of pure MC, the conversion of FAL was lower than 4 % after reaction for 8 h at 120 °C (Table S2, entry 2). However, when using Co_3O_4/MC as catalyst, full conversion of FAL into FOL (selectivity > 97 %) was achieved after reaction for 8 h at 120 °C (Figure 2 a). Also, a 97 % selectivity of BHMF at complete conversion of HMF was realized within 48 h at 120 °C (Figure 2 b). In both cases, only trace amounts of byproducts (< 3 %) generated from the aldol condensation of substrates and acetone were observed. Undesired saturated aldehydes and saturated alcohols were not observed by GC-MS (detection threshold 0.3 %), indicating that Co_3O_4/MC is a truly selective hydrogenation catalyst for the C=O bond. Extending the reaction time for FAL hydrogenation to 24 h, the selectivity towards FOL was unchanged (Figure 2 a), further confirming that the C=C bond is unaffected under the reaction conditions. It is unclear whether the surface under

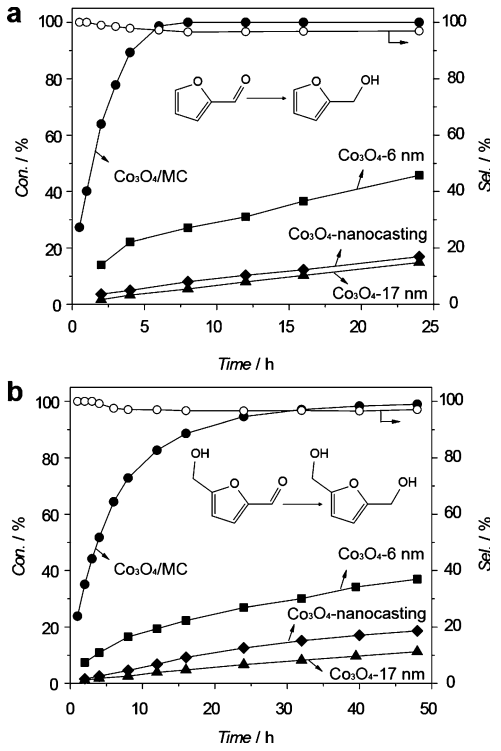

Figure 2. Catalytic performance in transfer hydrogenation reactions at 120 °C: a) FAL to FOL and b) HMF to BHMF over Co_3O_4/MC, Co_3O_4-nanocasting, Co_3O_4-6 nm, and Co_3O_4-17 nm. Reaction conditions: 1 mmol substrate, 10 mL 2-propanol, 50 mg Co_3O_4/MC, 25 mg for Co_3O_4-nanocasting, Co_3O_4-6 nm, and Co_3O_4-17 nm, respectively.

reaction conditions consists of Co_3O_4 or somewhat reduced species. The presence of metallic cobalt, however, is highly improbable, since comparison experiments using the materials prior to the final oxidation step resulted in a much inferior activity (Figure S6).

For comparison, mesoporous Co_3O_4 synthesized by nanocasting (Co_3O_4-nanocasting, Figure S5a,b)[12] was used as catalyst in the same system. The activity of Co_3O_4-nanocasting was much lower than that of Co_3O_4/MC. Conversions of FAL and HMF were only 17% and 19% after reaction for 24 h and 48 h, respectively (Figure 2a,b). From the XRD pattern of Co_3O_4-nanocasting one can infer, that its crystalline domain sizes are bigger than those of Co_3O_4/MC (Figure S5b). Furthermore, Co_3O_4 nanoparticles with different sizes (6 nm and 17 nm) synthesized by a reported preparation method without any surfactants (Figure S5c–f)[13] were also tested. The conversions of FAL over Co_3O_4-6 nm and Co_3O_4-17 nm were 46% and 15% within 24 h, indicating that smaller Co_3O_4 nanoparticles show higher activity (Figure 2a). Similar results were found for the transfer hydrogenation of HMF, the Co_3O_4-6 nm shows higher activity (Figure 2b). In all cases, the selectivities for FOL and BHMF were always higher than 97% (Table S2, entries 6–8, 12–14), indicating that the selectivity over Co_3O_4 is structure insensitive.

The surface area of Co_3O_4 nanoparticles, assumed to be spherical, is used to normalize the reaction rate for FAL conversion. Basing the normalization on surface areas determined by nitrogen sorption for both pure samples gives essentially identical results. The rates (calculated based on the conversion reached over a certain period of time selected so that conversion over different catalysts were approximately identical) over Co_3O_4-6 nm and Co_3O_4-17 nm are 14.0×10^{-3} (22% conversion in 4 h) and 4.5×10^{-3} mmol m_{Co3O4}^{-2} h^{-1} (15% conversion in 24 h; Table S2, entries 7,8), respectively. For HMF conversion, the reaction rates over Co_3O_4-6 nm and Co_3O_4-17 nm are 4.0×10^{-3} (19% conversion in 12 h) and 1.7×10^{-3} mmol m_{Co3O4}^{-2} h^{-1} (11% conversion in 48 h; Table S2, entries 13, 14), respectively. Thus, intrinsic activities of the smaller particles seem to be by about a factor of three higher. Surprisingly, the reaction rates for FAL and HMF conversions over Co_3O_4/MC are 114.5×10^{-3} (64% conversion in 2 h) and 33.9×10^{-3} mmol m_{Co3O4}^{-2} h^{-1} (64% conversion in 6 h; Table S2, entries 3,9), respectively, which are much higher than those over unsupported Co_3O_4 nanoparticles. This suggests a synergistic effect between Co_3O_4 and MC, where the porous structure and surface functional groups (Figure S7) of MC may favor the accumulation of reactants through spatial confinement,[14] and even favor the formation of intermediates because of the interaction between support and reactants,[15] leading to the enhancement of transfer hydrogenation activity over Co_3O_4 supported on MC. The synergistic effect is studied in detail in ongoing work. Notably, compared with conventional impregnation methods, where the Co_3O_4 particle size distributions are generally very broad, the present synthesis method is simple and generates Co_3O_4 nanoparticles with narrow size distribution (ca. 3 nm) and homogeneous dispersion, which allows a highly efficient utilization of Co species on the Co_3O_4/MC.

The effect of temperature on the transfer hydrogenation reactions was also examined. By increasing the temperature to 140 °C and 160 °C, the conversions of FAL reached 100% within 3 h and 1 h, respectively (Figure S8a). For HMF to BHMF, the conversions were 100% after reaction for 12 h and 6 h when increasing the temperature to 140 °C and 160 °C, respectively (Figure S8b). Most importantly, the selectivities towards FOL and BHMF were still higher than 97% in all cases. These results indicate that increasing temperature to 160 °C only enhances the reaction rate without affecting the selectivity. For FAL conversion, the reaction rates over Co_3O_4/MC were calculated. They increase strongly from 37.5 (64% conversion in 2 h), to 148.2 (63% conversion in 0.5 h) and 401.4 mmol g_{Co3O4}^{-1} h^{-1} (57% conversion in 0.167 h) by increasing the temperature from 120 °C to 140 °C, and to 160 °C (Table S2, entries 3–5). Also the reaction rates for HMF conversion over Co_3O_4/MC increase from 11.1 (64% conversion in 6 h), to 57.5 (63% conversion in 1 h) and to 133.3 mmol g_{Co3O4}^{-1} h^{-1} (73% conversion in 0.5 h), respectively (Table S2, entries 9–11). These values are one or two orders of magnitude higher than those of Co_3O_4-nanocasting, Co_3O_4-6 nm, and Co_3O_4-17 nm (Table S2, entries 6–8, 12–14). Notably, the activity of Co_3O_4/MC is comparable to the activities of catalysts for hydrogenation systems involving H_2, and higher than activities of other transfer hydrogenation catalysts (Table S3). Moreover, the transfer hydrogenation system using Co_3O_4/MC as catalyst is much more stable and insensitive to factors (e.g., structure/component of catalysts

and reaction conditions) than the hydrogenation system involving H_2 (Table S3, entries 5–9).

Co_3O_4/MC is also broadly applicable for hydrogenation of other α,β-unsaturated aldehydes. As examples, the conversions of cinnamaldehyde and citral were 99% with selectivities to the corresponding unsaturated alcohols of more than 95% (Figure 3a; Table S2, entries 15 and 16). These unsaturated alcohols are industrially important chemical intermediates for production of pharmaceuticals, flavors and cosmetics.[10b,c] In addition, never were traces of saturated aldehydes and/or saturated alcohols observed by GC-MS (detection threshold 0.3%). Therefore, the present catalytic system is highly promising for use in industrial production of α,β-unsaturated alcohols.

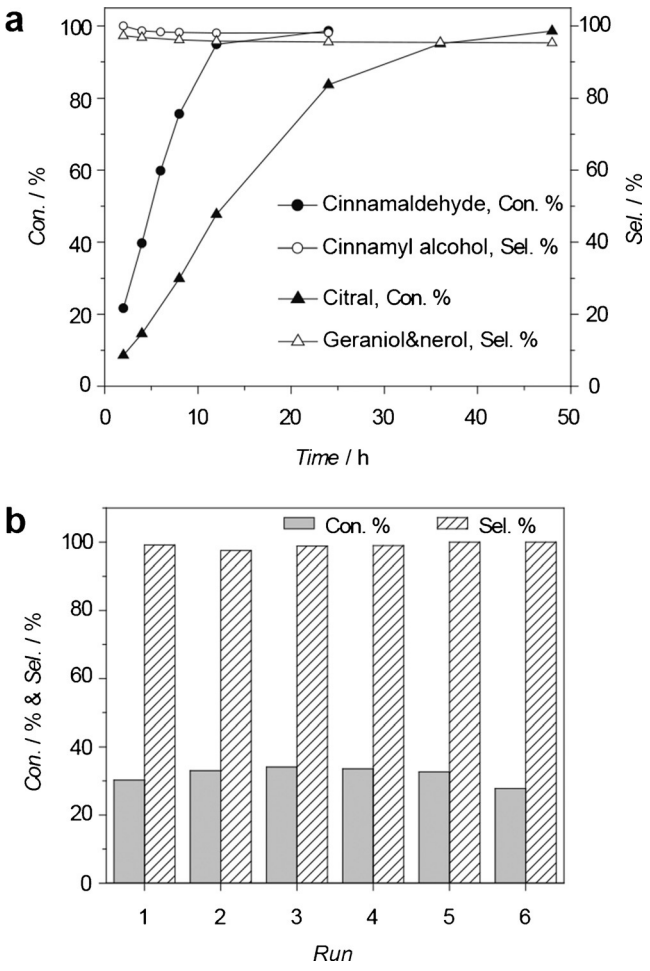

Figure 3. a) Catalytic performance in the transfer hydrogenation of cinnamaldehyde and citral over Co_3O_4/MC. Reaction conditions: 1 mmol substrate, 10 mL 2-propanol, 50 mg Co_3O_4/MC, 120°C. b) Recycling results for transfer hydrogenation of FAL over Co_3O_4/MC. Reaction conditions: 1 mmol FAL, 10 mL of 2-propanol, 50 mg Co_3O_4/MC, 120°C for 1 h.

The reusability of the Co_3O_4/MC catalyst was investigated using FAL as substrate. For each run, the reaction was carried out at 120°C for only 1 h. The catalyst after reaction was filtrated and washed with 2-propanol, followed by drying and treatment under H_2/Ar at 300°C for 2 h to remove residues from the surface of the used Co_3O_4/MC. In this way, the Co_3O_4/MC catalyst was recycled at least six times without considerable change in conversion of FAL (the conversions were ranging from 28% to 34% after 1 h), and the selectivity toward FOL was always above 97% (Figure 3b). The TEM images, XRD patterns and N_2 isotherm of Co_3O_4/MC after six runs (Figure S9) indicate that the mesoporous structure and the particle size of Co_3O_4 were unchanged, confirming the high stability of Co_3O_4/MC under reaction conditions. In addition, a hot-filtration test was carried out to verify the heterogeneous nature of the reaction. After removal of the solid catalyst, no reaction proceeded in the filtrate (Figure S10). Moreover, no Co species was present in the filtrate (< 0.2 ppm by AAS analysis). These results indicate that the catalytic effect in this system results from the Co_3O_4 nanoparticles and not from leached metal species.

In addition, the transfer hydrogenation process can be easily scaled up since no high pressure (as in hydrogenation with H_2) is required. A gram-scale experiment was carried out using 1 mL of FAL (ca. 1.16 g) as substrate at 160°C for 4 h. The conversion of FAL and selectivity for FOL were 100% and > 97%, respectively (Table S2, entry 17). After isolation by rotary evaporation at 80°C under reduced pressure (50 mbar), 1.02 g of FOL (Figure 4a) with purity of approximately 95% was obtained (calculation based on NMR data,

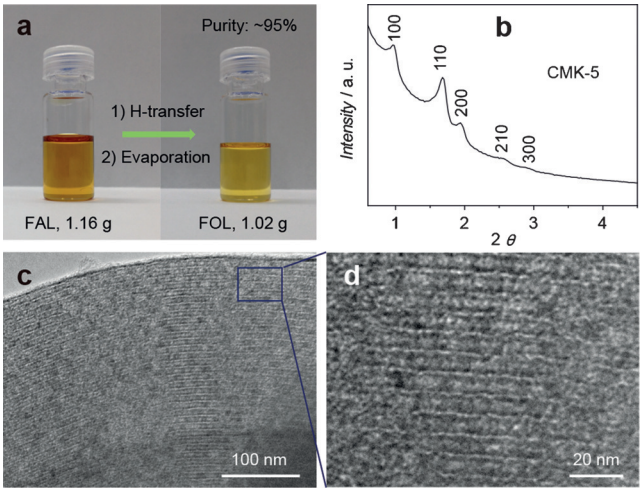

Figure 4. a) Photographs of FAL and the product FOL after transfer hydrogenation and evaporation. Reaction conditions: 1.16 g FAL, 100 mL 2-propanol, 500 mg Co_3O_4/MC, 160°C for 4 h. After isolation by rotary evaporation at 80°C under reduced pressure (50 mbar), 1.02 g of FOL with purity of around 95% was obtained. b–d) XRD pattern and TEM images of CMK-5 using the as-obtained FOL as precursor.

Figure S11). The as-obtained FOL was used as polymer precursor directly without further purification to synthesize ordered mesoporous carbon (CMK-5) via a previously reported method.[16] The obtained carbon material possesses the typical highly ordered mesoporous structure (Figure 4b–d).

In conclusion, we have developed a simple and scalable method to synthesize Co_3O_4 nanoparticles supported on the

mesopore framework of the MC. Benefiting from the ion-exchange process, by which cobalt precursor is introduced homogeneously into the polymer framework, Co_3O_4 nanoparticles with diameters of around 3 nm are generated which are finely dispersed on the MC framework. The as-obtained Co_3O_4/MC is an efficient catalyst for transfer hydrogenation of furan-based α,β-unsaturated aldehydes. Selectivities towards unsaturated alcohols are always higher than 95% at full conversion. Furthermore, Co_3O_4/MC is highly stable under the reaction conditions and can be recycled several times without loss of activity. The gram-scale preparation of FOL over Co_3O_4/MC indicates that the transfer hydrogenation system is scalable. The as-obtained FOL can be used as polymer precursor directly without further purification to synthesize CMK-5. Thus, the transfer hydrogenation system over Co_3O_4/MC appears to have potential for applications in industry. In addition, the synthesis route for Co_3O_4/MC, which is also scalable, can be extended to synthesize other metals or metal oxide catalysts supported on MC.

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