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Transfer Hydrogenation of Carbonyl Compounds Catalyzed by Ruthenium Nanoparticles Stabilized on Nanocrystalline Magnesium Oxide by Ionic Liquids

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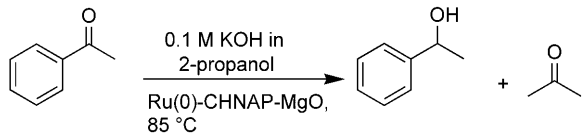
Abstract: Transfer hydrogenation of various carbonyl compounds was achieved in excellent yields by ruthenium nanoparticles stabilized on the nanocrystalline magnesium oxide by the incorporation of choline hydroxide, a basic ionic liquid. The procedure is simple, efficient and the catalyst can be recycled five times.

Keywords: choline hydroxide; nanocrystalline magnesium oxide; ruthenium nanoparticles; transfer hydrogenation

The selective hydrogenation of carbonyl compounds to alcohols is the foundation of many important current industrial and fine-chemical processes.[1] Many homogeneous or heterogeneous catalysts have been studied for this transformation using molecular hydrogen as the hydrogen source.[2] Recently most of the studies were concentrated on the transfer hydrogenation reaction because it is operationally simple and can avoid the use of molecular hydrogen.[3] The most efficient catalysts devised so far are centered on Ru,[4] Rh[5] and Ir[6] complexes. However, the application of such catalysts is limited, partly due to the problems of separation and recycling of the catalysts. To overcome such drawbacks, immobilization of homogeneous catalysts on insoluble supports has received considerable interest in recent years as it simplifies the separation of the catalysts from the reaction mixture and allows efficient recovery and reuse of catalysts.[7] There are only few reports on transfer hydrogenation using immobilized catalysts.[8–11]

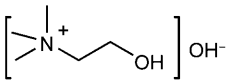
In recent years, room temperature ionic liquids (ILs) have attracted much attention for hydrogenation reactions.[12] ILs are also attractive media as they have been shown to stabilize nanoparticles.[13] Recently, we have reported aerobic alcohol oxidation by ruthenium species stabilized on nanocrystalline magnesium oxide by basic ionic liquids.[14] Herein we report the transfer hydrogenation of various carbonyl compounds (Scheme 1) using ruthenium nanoparticles stabilized on nanocrystalline magnesium oxide with ionic liquids.

Various magnesium oxide crystals[15] [commercial MgO, CM-MgO (specific surface area, SSA: $25\,m^2g^{-1}$), conventionally prepared MgO, CP-MgO (SSA: $252\,m^2g^{-1}$), and nanocrystalline aerogel-prepared MgO, NAP-MgO (SSA: $590\,m^2g^{-1}$)] were used as supports. The catalysts were prepared by treating magnesium oxide crystals with choline hydroxide (CH)[16] in dry THF. After filtration and washing several times with dry acetone, the CHNAP-MgO (1.0 g) was stirred with 75 mL of a 2.67×10^{-2} M aqueous $RuCl_3$ solution at 25 °C for 24 h. The solid was filtered, washed with deionized water, acetone and dried overnight at 110 °C to obtain Ru(III)-CHNAP-MgO. The final catalyst **1**, Ru(0)-CHNAP-MgO was obtained by reduction of the solid at 280 °C for 4 h in a flow of H_2 ($30\,mL\,min^{-1}$) and used for the selective



Scheme 1. Transfer hydrogenations of acetophenone with 2-propanol over Ru(0)-CHNAP-MgO catalyst.

Table 1. Transfer hydrogenation of acetophenone with different catalysts at 85 °C.[a]



Choline hydroxide (CH)

Entry	Catalyst	Time [h]	Yield [%][b]
1	Ru(0)-CHNAP-MgO	6	95
2	Ru(0)-CHCP-MgO	6	81
3	Ru(0)-CHCM-MgO	6	65
4	Ru(III)-CHNAP-MgO	6	30
5	$RuCl_3$	6	0
6	CHNAP-MgO	12	0
7	NAP-MgO	6	0
8	CH	12	0
9	Ru(0)-NAP-MgO	6	64

[a] *Reaction conditions:* substrate (1 mmol), 2-propanol (5 mL), KOH in 2-propanol (0.1 mol), catalyst (8.2 mol%), refluxed at 85 °C.
[b] Isolated yields.

transfer hydrogenation of the carbonyl compounds. A similar procedure was used to prepare different ruthenium catalysts and they were screened for transfer hydrogenation of acetophenone (Table 1).

As can be seen from Table 1, catalysts Ru(0)-CHCP-MgO, Ru(0)-CHCM-MgO and the ruthenium catalyst without choline hydroxide(CH), Ru(0)-NAP-MgO afforded 81%, 65% and 64% yields after 6 h (Table 1, entries 2, 3 and 9). The best result was obtained with the catalyst Ru(0)-CHNAP-MgO (95%). NAP-MgO is purely ionic and has a three-dimensional polyhedral structure which, having the presence of high surface concentrations of edge/corner and various exposed crystal planes (such as 002, 001, and 111), leads to inherently high surface reactivity per unit area.[17] The NAP-MgO has (i) Mg^{2+} sites of the Lewis acid type, (ii) O^{2-} sites of the Lewis base type, (iii) lattice bound hydroxy groups, (iv) isolated hydroxy groups and (v) anionic and cationic vacancies. The CM-MgO (SSA: 25 $m^2 g^{-1}$) samples are generally large cubic crystals, on the other hand CP-MgO (SSA: 252 $m^2 g^{-1}$) samples are thin hexagonal platelets about 150 nm long and 10 nm thick having large exposed areas of the (100) crystal face. Thus, NAP-MgO did indeed display the highest activity compared to CP-MgO and CM-MgO.

The Ru(0)-NAP-MgO catalyst without choline hydroxide showed rapid deactivation during recycling, which may be due to leaching of the active species during reaction. A strong synergistic effect between the ruthenium nanoparticles and CHNAP-MgO was observed. Ruthenium nanoparticles are distributed on the outer surface by a combination of strong electrostatic interaction and coordination between CH of surface functionalized CHNAP-MgO. Choline hydroxide not only acts as surface functionalizing agent but also stabilizes the metal nanoparticles.

The catalyst **1** is well characterized by FT-IR, SEM-EDX, XRD, TEM, XPS, and TPR (see the Supporting Information). During the preparation of these catalysts, the surface of NAP-MgO was hydroxylated, as indicated by non-H-bonded OH groups at 3698 cm^{-1} in the IR, this is consistent with the reactive profile of NAP-MgO (Figure S2b, Supporting Information).[18] The XRD of CHNAP-MgO and **1** samples also indicate the formation of $Mg(OH)_n$ during the preparative protocol (Figure S3, Supporting Information). The SEM-EDX (scanning electron microscopy-energy dispersive X-ray analysis) of catalyst **1** shows that Ru content in the catalyst was 1.64 mmol g^{-1} (Ru content: 16.6 wt%).

In order to know the influence of the reactants on the monodispersed Ru(0)-CHNAP-MgO catalyst, the fresh and used catalysts were analyzed by transmission electron microscopy (TEM). The TEM image of the fresh catalyst **1** (Figure 1a) shows Ru(0) nanoparticles (< 2 nm) uniformly dispersed and distributed on the CHNAP-MgO surfaces. The TEM image of the used catalyst (Figure 1b) also shows highly dispersed ruthenium particles (< 2 nm), which clearly indicates that the ruthenium nanoparticles retain their properties even after completion of the reaction and the catalyst shows consistent activity even after several cycles.

X-ray photoelectron spectroscopy (XPS) spectrum of catalyst Ru(III)-CHNAP-MgO for Ru 3*p* level shows a $3p_{3/2}$ line at 463.3 eV(Figure S4a, Supporting Information), which is attributed to Ru^{3+}.[12a] XPS high resolution narrow scan of the freshly prepared catalyst **1** shows broad and small valleys between the spin-orbit components, which clearly indicates that two different Ru species are present. As can be seen in Figure 2, on deconvolution the low (at 281.3, 286.0 eV) and high (at 282.2, 287.0 eV) binding energies of ruthenium with an intensity ratio of 3:2 clearly implies that Ru is coexistant both in Ru(0) and Ru(III) oxidation states, respectively in catalyst **1**. The binding energy peaks observed for Ru $3p_{3/2}$ at 461.3 and 466.7 eV (Figure S4b, Supporting Information) are also characteristic of Ru in the Ru(0) and Ru(III) forms, respectively, in the catalyst **1**.[12b,c] The binding energy components corresponding to the RuO_2 species, probably are due to oxidation of the surface of the free ruthenium nanoparticles upon exposure to air which is in consonance to the earlier report.[19] The temperature-programmed reduction (TPR) profile of the catalyst Ru(III)-CH-NAPMgO indicates the par-

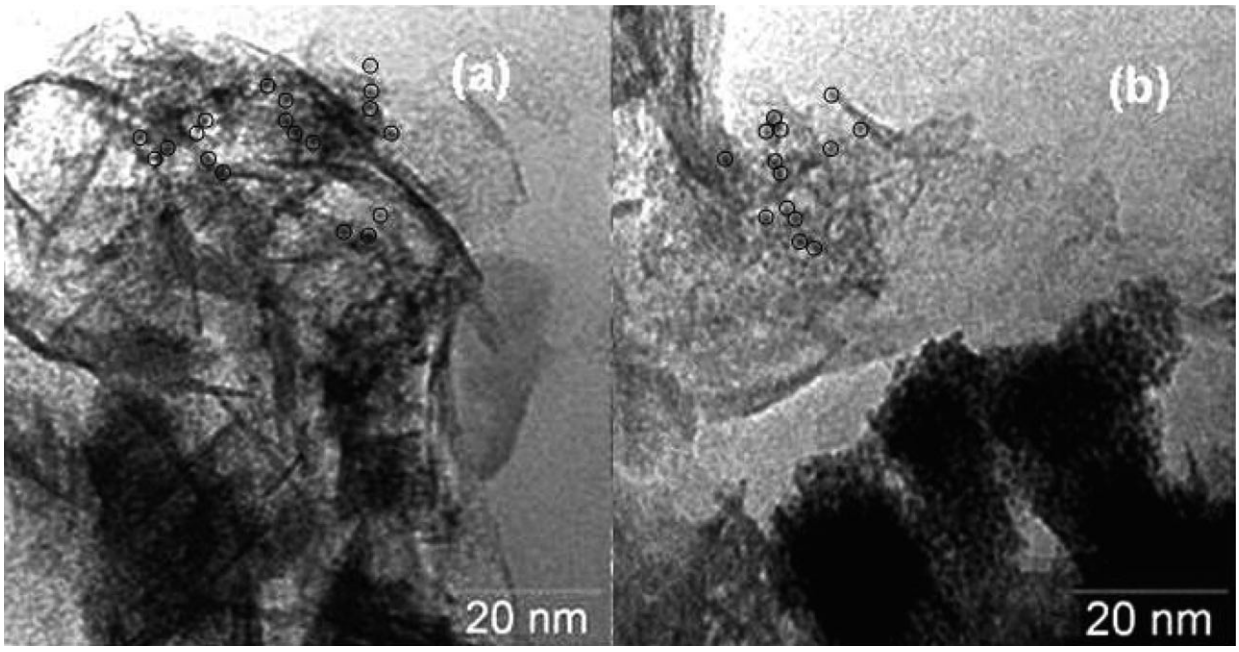


Figure 1. TEM images of (**a**) fresh and (**b**) used catalyst of Ru(0)-CHNAP-MgO.

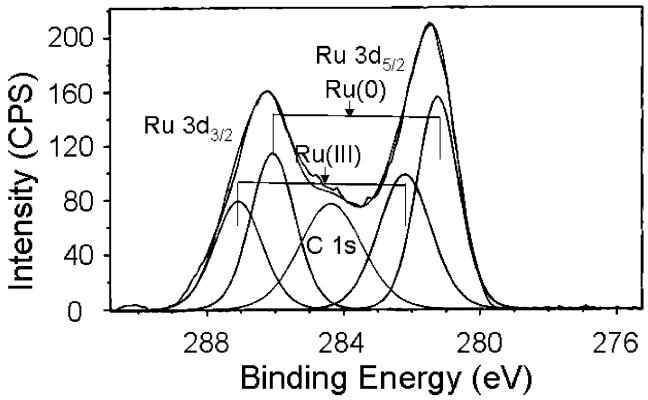


Figure 2. XPS high resolution narrow scan of Ru 3*d* of Ru(0)-CHNAP-MgO

tial reduction of Ru^{3+} at 280 °C (Figure S5, Supporting Information).

The active catalyst **1** was tested for the selective transfer hydrogenation of various carbonyl compounds with 10 mol% KOH in 2-propanol and in all cases the reaction was completed within 6–10 h with high yields (Table 2). The efficiency and stability of the newly established catalytic system was examined in detail with acetophenone as the substrate. Reduction proceeds to completion giving excellent isolated yields through five successive cycles (Table 2, entry 1). The selective reduction of 4-methyl-cinnamaldehyde, 4-phenylbut-3-en-2-one and citronellal (Table 2, entries 8 to 10) afforded the corresponding alcohols in excellent yields albeit with longer reaction times. It is important to note that the high yields were obtained in the reduction of 4-isobutylacetophenone and 6-methoxy-2-acetophenone, (Table 2, entries 3 and 5) and the corresponding alcohols are intermediates for the synthesis of ibuprofen and naproxen, respectively.

Moreover, the reduction of the compounds containing substitutents present either on the aromatic ring or in the α-position (Table 2, entries 2–7) reveals that steric hindrance is less effective in the present reaction. Citronellal, a non-conjugated unsaturated aldehyde, is selectively reduced to the corresponding unsaturated citronellol (Table 2, entry 10). The average turnover number (TON) for our catalytic system is 11. Ru(0)-CHNAP-MgO catalyst was recovered and reused for four cycles under the same reaction conditions. Reusability studies are presented in Table S3 (Supporting Information).

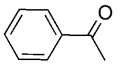
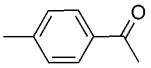
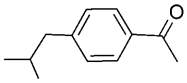
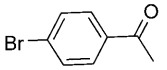
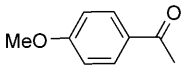
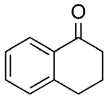
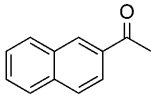
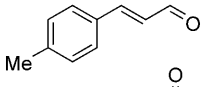
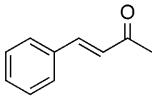
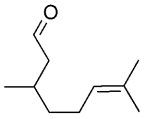
In summary, a highly efficient heterogeneous ruthenium catalyst, Ru(0)-CHNAP-MgO, was prepared and applied to transfer hydrogenation reactions. The catalyst has proven to be highly efficient and selective in the reduction of carbonyl groups.

Experimental Section

Preparation of the Catalyst

NAP-MgO (1.0 g) and choline hydroxide (0.5 mL) were taken in a 50-mL round-bottomed flask containing 25 mL of dry THF and stirred under a nitrogen atmosphere for 4 h. The CHNAP-MgO was then filtered and washed several times with acetone and dried under vacuum. CHNAP-MgO (1.0 g) was stirred with $RuCl_3$ (0.415 g) in 75 mL of freshly prepared deionized water at 25 °C for 24 h under a nitrogen

Table 2. Transfer hydrogenation of various carbonyl compounds with 2-propanol over Ru(0)-CHNAP-MgO catalyst.[a]

Entry	Substrate	Time [h]	Yield [%][b]
1		6	95, 91[c]
2		6	93
3		6	94
4		6	95
5		6	94
6		10	89
7		10	92
8		10	93
9		10	90
10		10	84

[a] *Reaction conditions:* substrate (1 mmol), 2-propanol (5 mL), KOH in 2-propanol (0.1 mol%) catalyst (0.05 g), refluxed at 85 °C.
[b] Isolated yields.
[c] Fifth cycle.

atmosphere. The solid was filtered, washed with deionized water, acetone and dried overnight at 110 °C to obtain Ru-(III)-CHNAP-MgO. The final Ru(0)-CHNAP-MgO catalyst was obtained after hydrogenation of the solid at 280 °C for 4 h. The prepared Ru(0)-CHNAP-MgO catalyst was gray in color and from the elemental analysis, the Ru content was determined to be 1.64 mmol g^{-1}(Ru content: 16.6 wt%).

General Procedure for the Transfer Hydrogenation of Carbonyl Compounds with Ru(0)-CHNAP-MgO Catalyst

A reaction mixture containing 1 mmol of the substrate, 5 mL of 2-propanol and KOH in 2-propanol (0.1 mol), was placed in a two-neck, round-bottomed flask equipped with a septum port, reflux condenser and a guard tube. To this mixture were added 50 mg of freshly vacuum-dried catalyst Ru(0)-CHNAP-MgO. The transfer hydrogenation reaction was carried under reflux at 85 °C. ^{1}H NMR, MS and IR analyses confirmed the identity of the products. The reusability of the catalyst was tested after washing the used catalyst with 2-propanol followed by drying at 100 °C.

Supporting Information

Characterization data of the catalysts are available in the Supporting Information

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