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Selective Transfer Hydrogenation of Carbonyl Compounds by Ruthenium Nanoclusters Supported on Alkali-Exchanged Zeolite Beta

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Abstract: Selective transfer hydrogenation of aromatic ketones and β-keto esters to the corresponding alcohols was achieved by using ruthenium nanoclusters supported on alkali-exchanged zeolite beta catalyst. The high activity and selectivity of the catalyst is due to the presence of highly dispersed ruthenium clusters in combination with the large number of Brønsted acidic sites of zeolite.

Keywords: chemoselectivity; nanoclusters; ruthenium; transfer hydrogenation; zeolite beta

Introduction

Selective hydrogenation of carbonyl compounds to alcohols is a synthetically important transformation both in the laboratory and in industry. Many homogeneous or heterogeneous catalysts have been studied for this transformation using molecular hydrogen as hydrogen source.[1] 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.[2] Both mono- and polynuclear Ru(II), Rh(I), and Ir(I) complexes have been successfully employed as catalysts for homogeneous asymmetric transfer hydrogenations.[3] Among these ruthenium complex-catalyzed transfer hydrogenations have proved to be particularly reliable.[3b–d] 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 mixtures and allows the efficient recovery and reuse of catalysts.[4] Examples of immobilized transfer hydrogenation catalysts are still rare. There are reports on transfer hydrogenations using catalysts non-covalently or covalently linked to the support.[5] In these systems, the catalysts are deactivated or the reactions are extremely slow. Later van Leeuwen and co-workers reported the solid-phase synthesis of asymmetric transfer hydrogenation catalysts as well as the use of these silica-supported systems in batch and flow reactors.[6] Ley and co-workers reported the heterogeneous transfer hydrogenation of aryl ketones using a recyclable [Pd(0)EnCat] catalyst.[7]

Zeolite-supported metal clusters are considered to be versatile heterogeneous catalysts because they offer conceptual links between molecular and surface catalysis[8] and provide the advantages of the two classes of catalysts. Zeolites and Al_2O_3-supported transition metal catalysts are excellent for selective hydrogenations[9] of various carbonyl compounds. Recently Ru-containing BEA zeolites were reported for the hydrogenation of a conjugated cyclic keto-enol[10] and it was shown that the acid properties of the zeolite and dispersion of the ruthenium particles were important for selective hydrogenation. It is also found that the presence of acidic conditions enhances the activity in the hydrogenation of β-keto esters.[11] In this paper, we report the selective transfer hydrogenation of aromatic ketones and β-keto esters by using ruthenium nanoclusters supported on alkali-exchanged zeolite beta.

Results and Discussion

Synthesis and Characterization of Ruthenium Nanoclusters Supported on Cesium Zeolite Beta Catalysts

The selection of zeolite beta (β) for the incorporation of ruthenium nanoclusters was based on the fact that this is a large-pore, tridimensional zeolite and upon exchange with cesium, the basicity of the zeolite increases to stabilize the supported metal species by generating stronger metal-support interactions, a consequence of which is a higher metal dispersion after reduction.[12] We have incorporated the ruthenium nanoclusters into cesium zeolite beta (Cs-β) by ion exchange (IE) and impregnation (IMP) methods using the precursors $RuCl_3$, $[Ru(NH_3)_6]Cl_3$ and $Ru_3(CO)_{12}$. The chemical composition and physical characteristics of these samples are given in Table 1. The surface area and pore volume values decrease slightly for Ru Cs-β(IMP-Cl) and Ru Cs-β(IMP-carbonyl) but largely for Ru Cs-β(IE-Cl). X-ray diffraction (XRD) patterns recorded for different types of ruthenium nanoclusters supported zeolite beta catalysts (Figure 1) show the typical zeolite beta structure even after incorporation of the ruthenium nanoclusters. Also, a new diffraction line at around 43°, was observed in the XRD patterns of Ru Cs-β(IE-Cl), Ru Cs-β(IE-amine) and Ru Cs-β(IMP-Cl), which is assigned to Ru crystallites.[13] However, the XRD pattern of Ru Cs-β(IMP-carbonyl) did not exhibit this diffraction line. The FT-IR spectra of Ru Cs-β(IMP-carbonyl) do not show any absorption bands in the carbonyl absorption region, which is similar to the earlier reported MCM-41 supported platinum carbonyl cluster.[14] These data reveal that free ruthenium clusters were dispersed in the Ru Cs-β(IMP-carbonyl) sample.

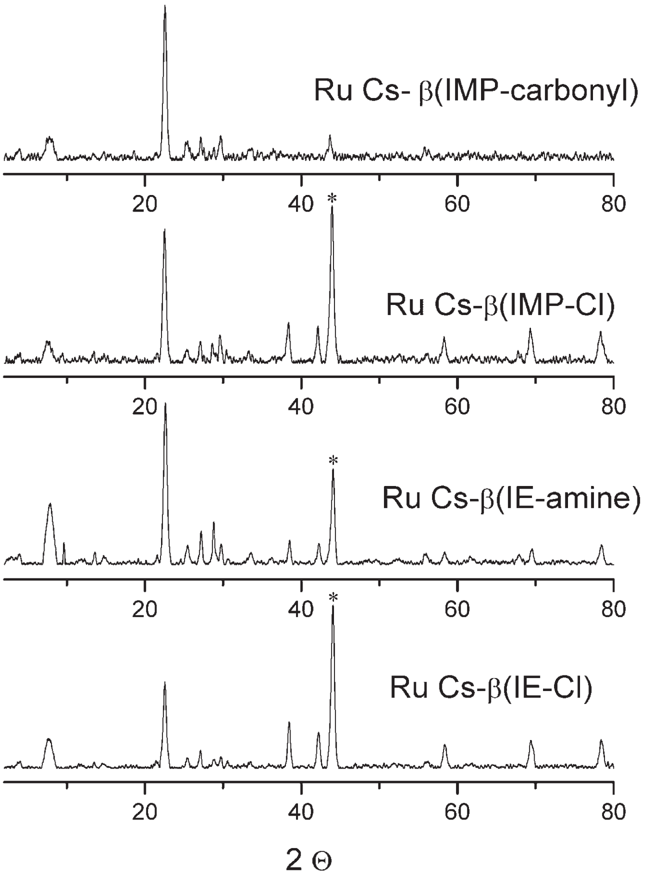


Figure 1. Powder XRD patterns of different zeolite beta catalysts (* indicates peaks due to Ru crystallites).

The binding energies (BE) of Ru ($3d_{5/2}$) in Ru Cs-β-(IE-Cl), Ru Cs-β(IE-amine) and Ru Cs-β(IMP-Cl) were close to 280.0 eV (Table 1), indicating the presence of metallic ruthenium. The BE of Ru Cs-β(IMP-carbonyl) shows broad and small valleys between the spin-orbit components, which clearly indicates that two different Ru species are present. Deconvolution shows the low (at 281.8, 285.8) and high (at 283.1, 287.8) eV binding energies of ruthenium with an intensity ratio of 3:2. These BE components correspond to the RuO_2 cluster species, probably formed by oxidation of the surface of the free ruthenium clusters upon exposure to air which is in agreement to the earlier report.[15] Transmission electron micrograph (TEM) images of Ru Cs-β(IE-Cl), Ru Cs-β(IE-amine) and Ru Cs-β(IMP-Cl) samples showed agglomerated ruthenium metal particles whereas highly

Table 1. Chemical composition, textural characteristics and binding energies of zeolite beta catalysts.

Catalyst	Precursor	% Ru[a] (w/w)	Pore volume [$cm^3 g^{-1}$]	Surface area [$m^2 g^{-1}$]	Binding energies Ru $3d_{5/2}$ [eV]
Hβ	-	-	0.962	463.1	-
Cs-β	-	-	1.000	436.4	-
Ru Cs-β(IE-Cl)	$RuCl_3$	1.80	0.462	267.1	280.8
Ru Cs-β(IE-amine)	$Ru[(NH3)_6]Cl_3$	0.62	0.899	486.7	280.5
Ru Cs-β(IMP-Cl)	$RuCl_3$	5.55	0.618	389.2	280.4
Ru Cs-β(IMP-carbonyl)	$Ru_3(CO)_{12}$	5.50	0.589	389.6	281.8, 283.1, 285.8, 287.8

[a] Analyzed by ICP-AES.

dispersed uniform ruthenium metal particles were observed in Ru Cs-β(IMP-carbonyl) (Figure 2 a).

Hydrogen chemisorption was employed to estimate the dispersion of ruthenium and the cluster size after reduction of the samples. The comparison of the results of hydrogen adsorption is presented in Table 2. The metal dispersion varies in the order, Ru Cs-β-(IMP-Cl) < Ru Cs-β(IE-Cl) < Ru Cs-β(IE-amine) < Ru Cs-β(IMP-carbonyl). The samples prepared by impregnation with $Ru_3(CO)_{12}$ adsorb large amounts of hydrogen and show high metal dispersion and the ruthenium cluster size is less than 5 nm. The samples prepared by ion exchange of ruthenium hexammine chloride also adsorb considerable amounts of hydrogen and the dispersion is also high compared to the samples prepared by ion exchange or impregnation with $RuCl_3$. This is in accord with the recent report that the hexammine chloride complex allows a better penetration into the mesopores of MCM-41 than $RuCl_3$ and ruthenium acetylacetonate.[16] The decrease in metal dispersion by using the $RuCl_3$ precursor might be a consequence of the agglomeration of undissolved $RuCl_3$ crystals on the surface of the Cs-β during the ion-exchange. The subsequent reduction results in the formation of larger ruthenium crystallites most likely located on the outer surface of Cs-β particles. The results of the hydrogen adsorption experiments were confirmed by powder XRD, N_2 adsorption and TEM measurements. The number of acidic sites was determined by means of NH_3-TPD method in the range of 150–650 °C and these results are condensed in Table 2. It is observed that the amount of NH_3 adsorbed on the Cs-β is decreased with a concomitant decrease in the maximum of the desorption temperature and therefore the acidic strength is also decreased.[17] The amounts of acidic sites in Ru Cs-β(IE-Cl), Ru Cs-β(IE-amine) are less than in Cs-β and this may be due to the partial shielding of acidic sites by ruthenium clusters present outside the pores. The numbers of acidic sites have increased slightly for Ru Cs-β(IMP-Cl) and largely for Ru Cs-β(IMP-carbonyl). The increase in the number of acidic sites in Ru Cs-β(IMP-carbonyl) may be due to the presence of electron-deficient sites which are formed by the interaction of small ruthenium clusters with electron acceptor sites of zeolite.[18]

Survey of the Reaction Parameters

Various ruthenium nanoclusters supported catalysts were prepared from different Ru precursors, *viz.* $RuCl_3$, $[Ru(NH_3)_6]Cl_3$ and $Ru_3(CO)_{12}$, and tested for the transfer hydrogenation of acetophenone (Table 3). The optimized reaction conditions are: 2-propanol as hydrogen donor, 10 mol % of KOH and catalyst con-

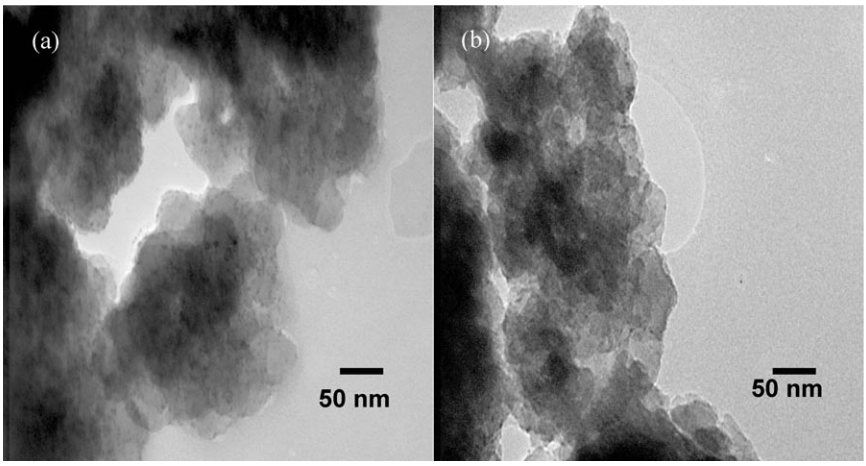
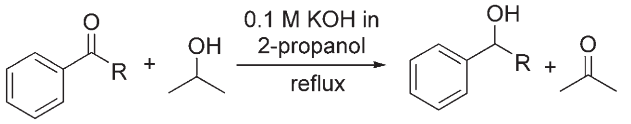


Figure 2. TEM images of (**a**) fresh and (**b**) used catalyst.

Table 2. Metal dispersions, cluster sizes and acid properties of different ruthenium containing zeolite beta catalysts.

Catalyst	Hydrogen adsorbed [μmol g^{-1}]	Dispersion [%]	Cluster size [nm]	Acidity TPAD [mmol g^{-1}]
Hβ	-	-	-	0.859
Cs-β	-	-	-	0.508
Ru Cs-β(IE-Cl)	0.8	0.96	103.69	0.322
Ru Cs-β(IE-amine)	2.2	7.33	13.56	0.458
Ru Cs-β(IMP-Cl)	1.9	0.70	142.28	0.567
Ru Cs-β(IMP-carbonyl)	60.3	22.15	4.49	1.998

Table 3. Transfer hydrogenation of acetophenone with different ruthenium catalysts.[a]



Entry	Catalyst	Time [h]	Conversion[b] [%]
1	$Ru_3(CO)_{12}$	24	25
2	H β	24	0
3	Cs β	24	0
4	Ru Cs-β(IE-Cl)	24	0
5	Ru Cs-β(IE-amine)	24	0
6	Ru Cs-β(IMP-Cl)	24	14
5	Ru Cs-β(IMP-carbonyl)	20	100

[a] *Reaction conditions:* acetophenone (1 mmol), 2-propanol (5 mL), KOH in 2-propanol (0.1 mol), catalyst (2.5 mol% of Ru), refluxed at 82 °C.

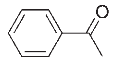
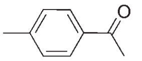
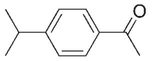
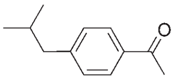
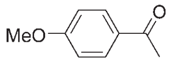
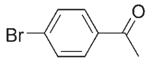
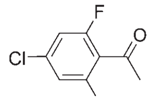
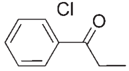
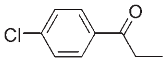
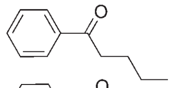
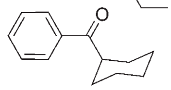
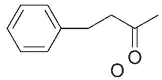
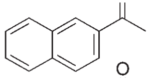
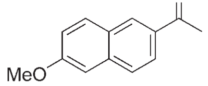
[b] GC yields.

taining 2.5 mol% of Ru at 82 °C. The Ru Cs-β(IE-Cl) and Ru Cs-β(IE-amine) catalysts do not give any product even after 24 h. The catalyst Ru Cs-β(IMP-Cl) has shown 14% conversion after 24 h while the catalyst Ru Cs-β(IMP-carbonyl) has shown complete conversion within 20 h. Even the homogeneous catalyst $Ru_3(CO)_{12}$ containing the same amount of Ru afforded 25% conversion after 24 h. Furthermore, there is no reaction by using Ru-free H-β or Cs-β catalysts. The reason for high catalytic activity of Ru Cs-β(IMP-carbonyl) catalyst is probably the high dispersion of ruthenium nanoclusters in combination with a large amount of acidic sites (Table 2).[10]

Scope of the Reaction

The scope of the catalyst was established by using a wide range of aromatic ketones and in all cases the reaction was completed with in 20–48 h with exceedingly high yields (Table 4). As illustrated in Table 4, selective reduction of 4-methoxyacetophenone and 4-bromoacetophenone (entries 5 and 6) is possible to afford the corresponding alcohols in excellent yields albeit with longer reaction times. It is also important to note that the high yields were obtained in the reduction of 4-isobutylacetophenone, 6-methoxy-2-acetonapthone, 2,4-dichloro-5-fluoroacetophenone (entries 4, 7 and 14) and the corresponding alcohols are intermediates for ibuprofen, naproxen and ciprofloxacin, respectively. Moreover, the reduction of the compounds containing substitutents present either on the aromatic ring or in the α- position (entries 2–4 and 8–13) reveals that steric hindrance is less effective in the present reaction.

Table 4. Transfer hydrogenations of various aryl ketones with 2-propanol over Ru Cs-β(IMP-carbonyl) catalyst.[a]

Entry	Subsrate	Time [h]	Yield[b] [%]
1		20	99 (99, 97, 96)[c]
2		24	95
3		24	99
4		24	99 (93)[d]
5		36	92
6		48	95
7		48	85
8		24	99
9		36	92
10		30	98
11		24	95
12		20	99
13		30	96
14		48	65

[a] *Reaction conditions:* substrate (1 mmol), 2-propanol (5 mL), KOH in 2-propanol (0.1 mol), catalyst (50 mg, 2.5 mol% of Ru), refluxed at 82 °C.

[b] GC yields

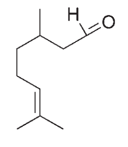
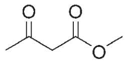
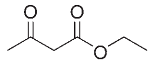
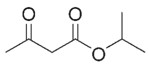
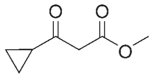
[c] Yields in parenthesis are for three successive cycles.

[d] Isolated yields.

Selective Transfer Hydrogenations

The active catalyst in the transfer hydrogenation of aromatic ketones was also tested for the chemoselective hydrogenation of various substrates with 10 mol% KOH in 2-propanol and the results are presented in Table 5. Citronellal, a non-conjugated unsaturated aldehyde, is selectively reduced to the corresponding unsaturated alcohol (citronellol). This is due to the high dispersion of ruthenium which selectively

Table 5. Selective transfer hydrogenations with 2-propanol over Ru Cs-β(IMP-carbonyl) catalyst.[a]

Entry	Substrate	Time [h]	Yield[b] [%]
1		30	95
2		17	99 (90)[c]
3		17	99
4		24	99
5		24	66

[a] *Reaction conditions:* substrate (1 mmol), 2-propanol (5 mL), KOH in 2-propanol (0.1 mol), catalyst (50 mg, 2.5 mol% of Ru), refluxed at 82 °C.

[b] GC yields.

[c] Isolated yields.

hydrogenates the carbonyl group.[19] Transfer hydrogenation of β-keto esters (entries 2–5) afforded complete conversion to β-hydroxy esters. The high activity can be attributed by the fact that the Brønsted acidic sites of zeolite protonate the carbonyl group to facilitate the hydride insertion.[11]

Reusability

The reusability is an important point concerning the use of the catalyst both for industrial and pharmaceutical applications. As the solid catalyst can be recovered easily from the reaction mixture, we examined the reusability of the catalyst in the transfer hydrogenation of acetophenone. After the first run, the catalyst was separated by filtration, washed with 2-propanol and dried in an oven. Table 6 presents the results of recycling of the catalytic system. Four cycles were performed without any significant loss of activity. ICP-AES analysis of the used Ru Cs-β(IMP-carbonyl) catalyst showed 1.1% of ruthenium leaching after the 4th cycle.

The ruthenium leaching was also studied as follows. The transfer hydrogenation of acetophenone using Ru Cs-β(IMP-carbonyl) catalyst was stopped after 8 h, and the conversion was 39%. At this juncture the catalyst was separated from the reaction mixture at the reaction temperature and the reaction was continued with the filtrate for additional 12 h. No further product formation was observed from GC analysis. Moreover, the absence of Ru in the filtrate was determined by ICP-AES.

Table 6. Analysis of Ru in Ru Cs β(IMP-carbonyl) catalyst in transfer hydrogenation of acetophenone.[a]

Reusability	Ru[b] $[\mathrm{mmol\,g}]^{-1}$	Yield[c] [%]
Fresh reaction	0.544	99
1st recycle	0.543	99
2nd recycle	0.542	97
3rd recycle	0.538	96
Hot filtered catalyst	0.544	39[d]
Filtrate	-	39[e]

[a] *Reaction conditions:* acetophenone (1 mmol), 2-propanol (5 mL), KOH in 2-propanol (0.1 mol), catalyst, refluxed at 82 °CC.

[b] Analyzed by ICP-AES.

[c] GC yields.

[d] After 8 h.

[e] Reaction conducted with the filtrate.

XPS analysis of the used Ru Cs-β(IMP-carbonyl) catalyst shows low (at 282.0, 285.8 eV) and high (at 283.2, 288.0 eV) binding energy values of ruthenium similar to the binding energies observed for the fresh catalyst, which corresponds to the RuO_2 cluster species. No metallic ruthenium (~280.0) was observed. The TEM image of the used catalyst (Figure 2 b) also shows highly dispersed ruthenium particles (<2 nm). These results demonstrate that the used catalyst is the same as the fresh catalyst and highly dispersed ruthenium nanoclusters retain their properties even after completion of the reaction and the catalyst is active for several cycles.

Conclusions

Ruthenium nanoclusters supported on alkali zeolite beta catalysts were prepared by using ion exchange and impregnation methods with various precursors. Highly dispersed ruthenium nanoclusters were obtained using the $Ru_3(CO)_{12}$ precursor and the number of acidic sites increased four-fold with respect to the parent support (Cs-β). Ru Cs-β(IMP-carbonyl) showed high activity in the transfer hydrogenation of aromatic ketones and chemoselective hydrogenation of citronellal and β-keto esters.

Experimental Section

Preparation of Supports

The parent zeolite beta (β) having an SiO_2/Al_2O_3 ratio of 25 (Zeolyst International) was exchanged twice with a 0.5M

$NaNO_3$ solution (70 mL/g, 80 °C, 2 h, under stirring). After washing with water, the solid (Na-β) was recovered by centrifugation and dried overnight. Cesium zeolite beta (Cs-β) was obtained by exchanging Na-β with a 0.5 M solution of cesium acetate (Aldrich 99.9 %). The exchange procedure was the same as that mentioned above. The Cs-β was then calcined in a flow of air at 450 °C for 2 h.

Ruthenium was introduced in the so-obtained Cs-β zeolite by ion exchange and impregnation methods. The ion exchanged samples were obtained by stirring Cs-β in an aqueous solutions of $RuCl_3$ or $[Ru(NH_3)_6]Cl_3$ at 70 °C for 24 h. The solids were recovered by filtration and washed thoroughly with distilled water, dried and calcined in a flow of air at 450 °C for 2 h. These samples were then reduced at 450 °C for 6 h in a flow of H_2 (30 mL min^{-1}). The impregnated samples were also prepared by the same procedure and water was evaporated in a rotary vapor. The sample was calcined at 450 °C for 2 h and then reduced at 450 °C for 6 h in a flow of H_2 (30 mL min^{-1}). The impregnated samples were also prepared by stirring Cs-β in an solution of *n*-pentane containing $Ru_3(CO)_{12}$ at 30 °C for 24 h and then dried in a rotary vapor.

Reaction Conditions

A reaction mixture containing 1 mmol of the substrate and 5 mL of 2-propanol 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. The transfer hydrogenation reaction was carried under reflux at 82 °C. Aliquots were removed at different reaction times and products were analyzed by gas chromatography (Shimadzu 2010) fitted with an OV-17 column. The identity of the products was confirmed by NMR and MS analyses. The reusability of the catalyst was tested after washing the used catalyst with 2-propanol followed by drying at 100 °C.

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