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Highly efficient and recyclable ruthenium-based supported catalysts

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Abstract

A highly efficient, recyclable layered double hydroxide (LDH)-supported ruthenium catalyst system (Ru-LDH) was developed for the facile transformation of 1,2-dihaloalkene moieties in tetrahalonorbornyl derivatives to the corresponding α-diketones. The efficiency of other supports such as LDH containing ruthenium(III) in a brucite layer (Ru–Mg–Al), commercial MgO (Ru–MgO), and montmorillonite K-10 (Ru-mont) was evaluated. Our results demonstrate that Ru-LDH and Ru–MgO are equally efficient, and the best turnover number (TON) reached was 5389. For $NaIO_4$ as the co-oxidant, MeCN-H_2O was the best solvent, whereas 1,2-dichloroethane/MeCN in a ratio of 5:1 gave superior results for NaOCl (household bleach).
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1. Introduction

Oxidative transformation of organic functional groups is an important tool for obtaining value-added products in both industry and academia. Among the transition metals, ruthenium complexes have emerged as highly efficient catalysts for a variety of transformations in the recent past [1]. We have recently reported a novel and efficient ruthenium-catalyzed conversion of dihaloalkene moiety in tetrahalonor-bornyl derivatives to the corresponding α-diketones [2]. We subsequently expanded the scope of this chemistry to a variety of interesting applications [3]. Initially we synthesized the norbornyl α-diketones, employing 7 to 11 mol% ruthenium catalyst and $NaIO_4$ as the stoichiometric cooxidant, corresponding to a turnover number (TON) of 12 to 14 [2]:

$$(1)$$
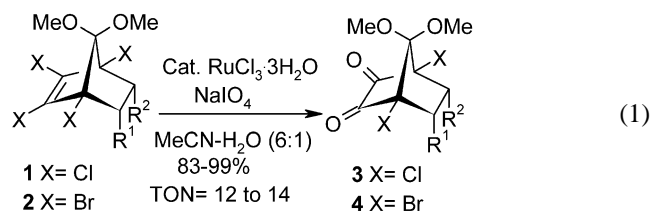
Because of growing environmental concerns and economical reasons, the current focus has been to develop catalytic processes involving recyclable catalysts, ideally with no by-products or at least with a minimum of nontoxic waste [4]. Extensive use of norbornyl α-diketones in several ongoing programs in our laboratory prompted us to develop an efficient, reusable, and cost-effective catalytic system. Layered double hydroxides (LDHs) or hydrotalcites (HT) have been used as heterogeneous basic catalyst systems in a variety of reactions [5]. LDHs have also been used as support for transition-metal-mediated reactions [6]. LDH-supported ruthenium catalysts have been reported in the recent past for the conversion of alcohols to carbonyl compounds [7,8], but

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to the best of our knowledge, there have been no reports of such systems for reactions mediated by RuO_4 as the active species. We report here a reusable Ru-LDH catalyst with a TON as high as 5389 and evaluate the efficiency of other supports, such as LDH containing ruthenium in a brucite layer, commercial MgO, and montmorillonite K-10.

2. Experimental

2.1. Materials

For the present study three types of supports were used: layered double hydroxide (LDH), MgO, and montmorillonite K-10. Layered double hydroxide (LDH) was prepared according to a procedure described in the literature [9], and commercially available MgO (from BDH) and montmorillonite K-10 (from Lancaster) were used as supports for ruthenium catalyst. Ruthenium(III) chloride was immobilized on these supports by treatment of the latter with aqueous solution of $RuCl_3 \cdot 3H_2O$ (from Arora-Mathey) followed by filtration. Catalyst Ru–Mg–Al was prepared by co-precipitation of chloride salts of ruthenium, magnesium, and aluminum according to a method described in the literature [7,8,10].

2.2. Preparation of supported ruthenium catalysts

We prepared ruthenium(III) supported on LDH by stirring a solution of 102 mg (0.43 mmol) of $RuCl_3 \cdot 3H_2O$ in 30 ml of distilled water and 900 mg of LDH in a 50-ml round-bottomed reaction flask at ambient temperature (34–37 °C). The heterogeneous mixture was stirred for 8 h under an argon atmosphere. The solid catalyst was filtered out, washed with distilled water, and dried at 80 °C for 10 h to obtain 950 mg of the immobilized ruthenium catalyst, Ru-LDH. Another sample was made with 10-fold reduced catalyst loading by a similar procedure with 10.2 mg and 900 mg of $RuCl_3 \cdot 3H_2O$ and LDH, respectively. Catalyst Ru–MgO was prepared by the addition of MgO (900 mg), after washing with distilled water and drying at 80 °C for 8 h, to a stirred solution of 102 mg of $RuCl_3 \cdot 3H_2O$ in 30 ml of distilled water at room temperature under argon. Stirring was continued for 10 h, after which it was filtered through a Buchner funnel, washed with 10 ml of distilled water, and dried at 80 °C for 6 h to get 945 mg of Ru–MgO. Another sample with 10-fold reduced catalyst loading was also prepared. We obtained ruthenium(III)-exchanged montmorillonite (Ru-mont) by stirring a solution of $RuCl_3 \cdot 3H_2O$ (50 mg) in 10 ml of acetonitrile with 950 mg of commercially available montmorillonite K-10 (from Lancaster, which is a mixture of montmorillonite, quartz, feldspars, and kaolinite) under an argon atmosphere at room temper-

ature. After 24 h of stirring, the solvent was removed and the residue was dried in vacuum to get 970 mg of Ru-mont.

2.3. General method for oxidation of 1,2-dihaloalkene moieties with $NaIO_4$ as co-oxidant

Ru-LDH (Ru 39 mg/g, 4 mg, 0.15 mol% Ru) was added to a vigorously stirred solution of substrate (1 mmol) in acetonitrile (12 ml). After 5 min, $NaIO_4$ (364 mg, 1.7 mmol) and distilled water (2 ml) were added, and the solution was allowed to stir at ambient temperature (34–37 °C) until the reaction was completed (monitored by thin-layer chromatography). The reaction mixture was filtered through a Buchner funnel, and the residue was washed with acetonitrile (5 ml). Filtrate (along with acetonitrile washing) was concentrated in a rotavapoure under reduced pressure, and the crude reaction mixture was dissolved in ethyl acetate and washed first with $Na_2S_2O_3$ solution and then with brine. The ethyl acetate layer was dried over anhydrous Na_2SO_4 and concentrated in vacuum to get a crude product, which after silica column chromatography (hexane and ethyl acetate as solvent) furnished pure product. The isolated products were characterized by a comparison of the IR and NMR (^1H NMR and ^{13}C NMR) spectra with those of authentic compounds [2].

2.4. Oxidation with NaOCl (5%) solution as co-oxidant (with 0.6 mol% catalyst)

To a magnetically stirred solution of starting material (1 mmol) in 5 ml of 1,2-dichloroethane and 1 ml of acetonitrile, 155 mg of Ru-LDH (0.6 mol% Ru, catalyst loading 0.39% Ru) followed by 2.2 ml of aqueous NaOCl solution (3 mmol, chlorine content 5% w/v) was added at ambient temperature. A further portion of NaOCl solution (3.6 ml, 5 mmol) was added batchwise at regular intervals of time with vigorous stirring until the completion of the reaction (tlc). After completion of the reaction, isopropanol (0.8 ml, 10.5 mmol) was added to the reaction mixture and was again stirred for 3 h. The reaction mixture was filtered through a sintered-glass crucible (G4), and residue was washed with dichloromethane (5 ml) followed by distilled water (5 ml). The organic layer was separated out, and the aqueous layer was extracted with dichloromethane (2×3 ml). The combined organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. The residue was purified by column chromatography (silica gel) with hexane–ethyl acetate as solvent to obtain the pure product in good yield. The residue in the crucible was washed further with distilled water (20 ml) and was dried in oven at 80 °C for 4 h to recover the active catalyst.

In a second method, a mixture of ethyl acetate and acetonitrile (5 ml and 1 ml, respectively, for 1 mmol of substrate) was used as the reaction medium, and after completion of the reaction, the aqueous layer was extracted with

ethyl acetate (2×5 ml). The rest of the procedure was exactly like the one described above. In the third method, only acetonitrile was used as the solvent (12 ml/mmol). Here, after filtration, filtrate was diluted with 10 ml of distilled water and was extracted with ethyl acetate. The rest of the procedure was similar to that described above.

3. Result and discussion

3.1. Characterization of catalysts

Catalysts were characterized by various physical techniques like AAS, SEM, XRD, and BET surface area measurement. The amount of ruthenium adsorbed on LDH was determined to be 3.9 wt% by atomic absorption spectroscopy. The X-ray diffraction patterns of LDH and Ru-LDH were found to be similar ($2\theta = 10°$–$65°$), and the basal spacing was found to be ~ 7.8 Å. Scanning electron microscope images revealed the presence of catalyst clusters on the surface of agglomerated crystallites of LDH, but the clusters were not uniformly distributed. The BET surface area was found to be 60 m^2/g. The powder XRD study reveals magnesium oxide to be present in the brucite phase. There was no difference in the XRD pattern of MgO or Ru–MgO in the range of $2\theta = 10°$–$70°$. The basal spacing d_{101} for both compounds was found to be 2.4 Å. The BET surface area of catalyst Ru–MgO was determined to be 108.9 m^2/g. Catalyst loading in Ru-mont was calculated to be 2 wt%. Powder XRD for montmorillonite K-10 and Ru-mont was found to be the same.

3.2. Oxidation of norbornyl derivatives

The performance of the Ru-LDH was tested on a representative substrate, **1** [R^1, $R^2 = $–$(CH_2)_4$–], with the use of, initially, 5 mol% catalyst and 1.5 equiv. of NaIO$_4$ in acetonitrile–water (6:1). After completion of the reaction (tlc), the catalyst was filtered off and the filtrate was processed to obtain 95% of the analytically pure corresponding α-diketone **3**. When the catalyst (residue) was reused for the next runs after successive washing with acetonitrile and water, prolonged reaction times were required to achieve 100% conversion with a yield comparable to that of the first run, indicating leaching of the catalyst (Table 1, entries 1, 2, and 4).

To see the extent of leaching of the catalyst, a filtration experiment was carried out [11]. To a round-bottomed flask Ru-LDH (130 mg, 5 mol% ruthenium, catalyst loading Ru 3.9% w/w), NaIO$_4$ (428 mg, 2 mmol), acetonitrile (12 ml), and distilled water (2 ml) were added and stirred at room temperature. After 1 h the reaction mixture was filtered through a sintered-glass crucible (G4) and washed with 2 ml of water. To this filtrate substrate **1** (346 mg, 1 mmol) was added and stirred at room temperature. Reaction was found to be complete after 11 h (tlc monitoring), giving rise to the

Table 1
Ru-LDH catalyzed conversion of **1** [R^1, $R^2 = $–$(CH_2)_4$–] to **3**[a]

Entry	Run		Time (h)	Yield of **3** (%)
1	1st		3.5	95
2	2nd		13	94
3	2nd	Treated with ^{i}PrOH[b]	3.5	94
4	3rd		39	91
5	3rd	Treated with ^{i}PrOH[b]	4	95

[a] 5 mol% Ru-LDH, 1.5 equiv. of NaIO$_4$, MeCN–H$_2$O (6:1), ambient temperature (34–37 °C).

[b] Treated with 3 equiv. of ^{i}PrOH for 2 h prior to filtration.

corresponding diketone **3** (273 mg) in 89% yield, whereas a reaction carried out with the above solid residue as catalyst required 10 h for completion of the reaction. This decrease in activity of the recovered catalyst above and the occurrence of an oxidation reaction of substrate **1** with the filtrate (obtained from the blank reaction above) clearly indicated the leaching of the catalyst to the solution.

To our gratification, we effectively overcame this problem by re-immobilizing the leached catalyst back on the solid support by treating the reaction mixture with 3 equiv. of isopropanol before filtration. In this case, the catalyst activity remained unaltered for the subsequent runs (Table 1, entries 3 and 5).

The following experiment further demonstrates the efficiency of isopropanol in re-immobilizing the leached catalyst back on the support. Ru-LDH (130 mg, 5 mol% ruthenium, catalyst loading Ru 3.9% w/w), NaIO$_4$ (428 mg, 2 mmol), acetonitrile (12 ml), and distilled water (2 ml) were placed in a reaction flask and stirred at room temperature for 1 h. Then isopropanol (240 mg, 4 mmol) was added to the reaction mixture and stirred for 1 h at room temperature, after which it was filtered through a sintered-glass crucible (G4) and was washed with 1 ml of distilled water. This filtrate (along with the washings) was treated with substrate **1** [R^1, $R^2 = $–$(CH_2)_4$–] (346 mg, 1 mmol) and an excess of NaIO$_4$ (856 mg, 4 mmol) and stirred at room temperature for 16 h. No reaction took place, and the unreacted substrate **1** was recovered, indicating the absence of the catalyst in the filtrate.

To study the ruthenium species present in the supported catalyst, X-ray photo-electronic spectroscopy (XPS) measurement was performed on the fresh Ru-LDH and on the Ru-LDH recovered from the isopropanol-treated reaction. XPS of fresh Ru-LDH shows lines at 280.7 and 282.1 eV, indicating ruthenium to be present in +3 and +4 oxidation states. The presence of later species is due to the aerial oxidation of RuCl$_3$ [12]. On the other hand, XPS of recovered catalyst shows Ru ($3d_{5/2}$) signals at 280.5 eV and 281.9 eV, along with a line at 283.3 eV, suggesting the presence of ruthenium in +3 and +4 states along with the higher oxidation state [13]. The presence of ruthenium in +3 and +4 states in the recovered catalyst is due to the reduction of ruthenium tetroxide to Ru^{+3} in the presence of isopropanol followed by aerial oxidation to the +4 state [12,14].

Table 2

Catalyst screening for the conversion of monosubstituted derivative **1** [$R^1 = -CH_2Cl$; $R^2 = H$] to **3**[a]

Entry	Catalyst	Mol%	Run	Time (h)	Yield of **3**[b] (%)	TON
1	Ru-LDH	0.15	1st	1.5	95	633
2			2nd	2	93	620
3			3rd	2	95	633
4	Ru-LDH	0.018		3.5	95	5278
5	Ru–MgO	0.15		1.5	95	633
6	Ru–MgO	0.018	1st	3.5	97	5389
7			2nd	4	94	5222
8			3rd	4	89	4944
9	Ru–Mg–Al	0.15		3	91	607
10	Ru-mont	0.15		8	85	567

[a] Catalyst, 1.5 equiv. of $NaIO_4$, MeCN–H_2O (6:1), ambient temperature (34–37 °C).

[b] Isolated yield of analytically pure **3**.

Table 3

Ru-LDH catalyzed oxidation with aq. NaOCl (household bleach) as co-oxidant[a]

Entry	Substrate **1** or **2** (R^1, R^2)	X	Solvent	Time (h)	Yield[b] (%)
1	–$(CH_2)_4$–	Cl	MeCN	7	40, 20[c]
2		Cl	EtOAc:MeCN (5:1)	8	79
3		Cl	1,2-dichloroethane:MeCN (5:1)	8	91
4		Br		28	84
5	–CH_2–O–CH_2–	Cl		5	88
6		Br		12	73
7	Ph, H	Cl		4.5	83
8		Br		31	85
9	CH_2Cl, H	Cl		2	77
10	CO_2Me, H	Br		4.5	72

[a] 0.6 mol% Ru-LDH, 6-8 equiv. of 5% aq. NaOCl, ambient temperature.

[b] Isolated yield of analytically pure **3** or **4**.

[c] Product arising from dione cleavage followed by bridged lactone formation was obtained.

All of these experiments reveal that during reaction, the ruthenium species present on the supported catalyst Ru-LDH undergoes oxidation to ruthenium tetroxide, which, because of its solubility in the reaction medium [15], partly leaches out into the solution, causing a decrease in the catalytic activity of the recovered catalyst (Table 1). The leached catalyst was re-immobilized back on the support after treatment with isopropanol.

For comparison, the ruthenium-supported LDH catalyst was also prepared by a co-precipitation technique (abbreviated as Ru–Mg–Al) similar to the reported one [7,10], in which ruthenium is present inside the inert matrix (brucite layer). We also prepared the supported catalysts by immobilizing ruthenium salt on commercial MgO (Ru–MgO) and montmorillonite K-10 (Ru-mont) and evaluated their efficiency (Table 2). The results summarized in Table 2 reveal that Ru-LDH and Ru–MgO are equally effective (entries 1–8). These catalysts were successfully recycled three times with no noticeable decrease in activity or yield (entries 1–3 and 6–8). A very high substrate/catalyst ratio (5555) with TON 5389 could be achieved (Table 2, entry 6). When the ruthenium loading was reduced by 10-fold (0.39 wt%) to facilitate easy handling (weighing and recycling) of 0.018 mol% quantity, the time required to accomplish 100% conversion increased from 1.5 to 3.5 h (entries 4 and 6), but without diminishing yield or TON. The Ru–Mg–Al catalyst (0.15 mol%) required a longer reaction time when compared with Ru-LDH (Table 2, entries 1 and 9), perhaps because of the presence of ruthenium inside the brucite layer in the former, and a change in oxidation state would destroy the LDH structure. This view was supported by completely different XRD patterns of initial and recovered Ru–Mg–Al catalyst. On the other hand, montmorillonite K-10-supported catalyst did not prove fruitful, exhibiting the lowest TON among the catalysts screened (entry 10).

A variety of derivatives of **1** and **2** were transformed into the corresponding diones **3** and **4** with the use of Ru-LDH and Ru–MgO. It is interesting to note that several derivatives with ether functionality [R^1, R^2 = –CH_2–O–CH_2–; –CH_2–O–CH_2–O–CH_2–; –CH_2–CH_2–CH_2–O–] could be selectively converted to α-diketones **3** or **4** in high yield without affecting the α-position of the ether moiety.

3.3. Use of NaOCl as a co-oxidant

Although O_2 and H_2O_2 are the ideal co-oxidants from an environmental viewpoint, they are not useful in the present system, where Ru(VIII) is needed for the desired transformation. We therefore opted for NaOCl (household bleach), which is an inexpensive co-oxidant used for in situ generation of Ru(VIII) from its low-valent precursors and produces innocuous waste (NaCl). The results with 0.6 mol% Ru-LDH and 6–8 equiv. of aq. NaOCl are summarized in Table 3. The choice of the solvent was crucial for the success of the reaction; MeCN–H_2O, which is the solvent of choice for $NaIO_4$ (Table 1 and 2), gave a mixture of products in unsatisfactory yield (Table 3, entry 1). When EtOAc/MeCN (5:1) was probed, the yield improved to 79% (entry 2). The best solvent system that furnished an excellent yield of the α-diketone was found to be 1,2-dichloroethane/MeCN in a ratio of 5:1 (entries 3–10). In general, tetrabromo derivatives **2** required a relatively longer reaction time compared with tetrachloro derivatives **1** (entries 4 and 8).

In summary, recyclable ruthenium-supported catalyst systems were developed through the use of LDH and commercial MgO for the facile transformation of 1,2-dihaloalkene moieties in tetrahalonorbornyl derivatives into the corresponding α-diketones with high turnover numbers. For $NaIO_4$ as the co-oxidant, MeCN–H_2O is the best solvent, and 1,2-dichloroethane/MeCN in a ratio of 5:1 gave superior results for NaOCl (household bleach).

Acknowledgments

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