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Ruthenium/magnesium–lanthanum mixed oxide: An efficient reusable catalyst for oxidation of alcohols by using molecular oxygen

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ABSTRACT

An efficient method for the oxidation of benzylic and secondary aromatic alcohols into their corresponding aldehydes or ketones has been achieved by using ruthenium supported magnesium–lanthanum mixed oxide as a heterogeneous catalyst in toluene, with molecular oxygen as the sole oxidant. This catalyst can also be operated in solvent free conditions at 393 K and reused for five cycles with consistent yield and selectivity.

1. Introduction

One of the most commonly practiced routes for the synthesis of carbonyl compounds is the oxidation of their corresponding alcohols [1,2]. Several transition metal-based oxidizing reagents have been developed, usually used in stoichiometric amounts, and lead to a large amount of waste. Molecular oxygen is an attractive and environmentally friendly oxidant. In this context, the oxidation of alcohols using molecular oxygen catalyzed by reusable heterogeneous catalysis is ideal from an environmental and atom economical point of view [3–5]. Solutions based on homogeneous catalysis are known [6–8], but heterogeneous processes are considered as more economical since they offer advantages such as ease of recovery and recycling. Most of the heterogeneous catalysts for oxidation reported so far are based on TEMPO supported by polymers or silicas [9–14], Ru [15–18] and Pd [19–25] employing molecular oxygen or air as a stoichiometric oxidant. Previously, we reported an effective method for the oxidation of alcohols using Ni–Al hydrotalcite catalyst with molecular oxygen [26]. Recently, Abad et al. reported an efficient method for the selective aerobic oxidation of alcohols by using Au/CeO_2 and Pd/CeO_2 [27,28]. Pioneering efforts from Baiker [17], Nishimura [19], Kaneda [20,21], Sheldon [22–24] and Uozumi [25] in aerobic oxidation of alcohols using reusable catalysts in the recent years resulted in great progress in this area. However, the development of a novel catalytic system that exhibits a wide range of substrate tolerance under mild conditions still remains a major challenge. Ruthenium is an attractive and efficient metal in catalyzing organic reactions. Ruthenium physico-chemically deposited on various supports such as hydroxyapatite (HAP) [29] showed a low activity but treatment with basic additives such as proline or prolinol significantly increased its catalytic activity. Recently we reported that ruthenium supported on nanocrystalline magnesium oxide modified by basic ionic liquids (Ru–CHNAP–MgO) was an active and recyclable catalyst whereas ruthenium supported onto pristine nanocrystalline magnesium oxide (Ru–NAP–MgO), though catalytically active was not recyclable as the metal leached into the solution [30]. It can be pointed out that ruthenium was stabilized by modifying the support with base [30]. Matsumoto et al. reported the oxidation of alcohols with polymer incarcerated ruthenium catalyst and TEMPO, in dichloroethane as solvent using oxygen [31]. However, leaching of ruthenium was observed and could be suppressed by treatment with a strong base (NaOH, 0.5 N) in the preparation step. Ru/Al_2O_3 has also been reported to give very good results [32]; however, the preparation of the catalyst included an additional step of hydrolysis of the adsorbed $RuCl_3$ precursor at pH = 13.2 by 1 M NaOH for 24 h, which is believed to increase the basicity of the support and stabilize Ru. It has been demonstrated that ruthenates are active species

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for this reaction [33]. In oxidizing atmosphere Ru is easily oxidized, probably to ruthenate species. These species being anionic are unstable on cation exchangers (solid acids) but are stabilized by solid bases. In such a case, the nature of the support should be important for determining its activity and recyclability. Indeed Ru/MCM-41 has been reported to be a selective catalyst for the oxidation of alcohols, but it has to be modified by anchored quaternary ammonium species to make it recyclable [34]. Mg–La mixed oxides have received much attention as basic catalysts and support materials. Recently, we efficiently carried out transesterification of diethyl carbonate by alcohols [35]. Michael addition reactions [36], aldol type reaction of aldehydes and imines with ethyl diazoacetate by using this highly basic Mg–La mixed oxide catalyst under recyclable conditions [37]. We have also used the Mg–La mixed oxide as a support for palladium catalyzed cross-coupling reactions [38,39]. This highly basic magnesium lanthanum mixed oxide was found to promote the activity of palladium. In this work, we report the oxidation of benzylic and secondary aromatic alcohols under heterogeneous conditions to aldehydes or ketones by O_2 or air in the liquid phase with a high efficiency using Ru/Mg–La mixed oxide catalyst at 353 K in toluene as solvent, or at 393 K without solvent. The catalyst was characterized by DSC, powder XRD, BET surface area, TEM, TPR, SEM-EDX, TPD of CO_2 and XPS analyses.

2. Experimental

2.1. Materials and methods

All solvents used in the catalytic test were of analytical grade and were used as received from Merck India Pvt. Ltd. High purity oxygen was used in the oxidation of alcohols. Purification of reaction products was carried out by flash chromatography using 100–200 mesh silica gel, and a mixture of ethyl acetate and petroleum ether as the eluting agent. All the products were characterized by ^{1}H-NMR spectroscopy. The ^{1}H spectra of samples were recorded on a Gemini 200 MHz, and/or a Bruker-Avance-300 MHz Spectrometer using TMS as an internal standard in $CDCl_3$. X-ray photoelectron spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. The pressure in the spectrometer was about 10^{-9} Torr. For energy calibration, we used the carbon 1*s* photoelectron line. The carbon 1*s* binding energy was taken to be 284.6 eV. Spectra were deconvoluted using the Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species were first determined using the spectrum of a pure sample. The location and FWHM of the products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible within ±0.1 eV. The TPR profile was recorded on Micromeritics (Auto Chem 2910) using 0.05 g of catalyst sample. In a typical method the catalyst was loaded in an isothermal zone of a quartz reactor (i.d = 6 mm, length = 300 mm) heated by an electric furnace at a rate of 10 °C/min to 300 °C/min in flowing helium gas at a rate of 30 cm^3/min, which facilitates desorption of the physically adsorbed water. After degassing, the sample was cooled to room temperature and the helium gas was switched to 36 cm^3/min reducing gas of 5% H_2 in argon and the temperature was increased to 725 °C at a ramping rate of 10 °C/min. Hydrogen consumption was measured by analyzing effluent gas by means of thermal conductivity detector. The consumption of hydrogen was calibrated measuring the TPR of Ag_2O (20 mg), with the same protocol. The XRD patterns of Mg–LaO and Ru/Mg–LaO samples were obtained on a Rigaku miniflex X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 0.15406 nm) from 2θ = 2–80°, at a scan rate of 2°/min, with the beam voltage and a beam current of 30 kV and 15 mA, respectively. The basicity of the support was investigated by calorimetry [40], using CO_2 adsorption at 303 K and samples activated in vacuum at 723 K. The instrument is a Tian–Calvet calorimeter. CO_2 is an acidic probe, which has been commonly used to measure basicity [41,42]. The heat of adsorption measures the strength of the interaction with basic sites and therefore the basic strength as a function of coverage. The TPD of CO_2 of Ru/Mg–LaO fresh and used samples are measured using an Auto Chem 2910 (Micromeritics, USA). In a typical method about 0.1 g of sample is reduced at 400 °C for 5 h in hydrogen at a flow rate of 30 mL min^{-1}. After reductive pre-treatment the sample is saturated with 9.9% CO_2 (balance helium) at 60 °C, at a flow rate of 50 mL min^{-1} and subsequently flushed with helium gas at 60 °C for 1 h. The TPD measurements are carried out from 60 °C to 700 °C at a ramping rate of 10 °C/min. The amount of desorbed CO_2 is calculated using GRAMS/32 software. GC analysis was done by GC-2010, gas chromatograph Shimadzu, with ZB5 capillary column, internal diameter 0.53 mm, film thickness 1.50 μm, length 30 m, initial temperature 70 °C (hold 2 min), ramp 7 °C/min → 279 °C (hold 7 min), injection temperature 250 °C, and detector temperature 280 °C (FID). For the transmission electron microscope (TEM) analysis, samples were dispersed in methanol solution and dropped on a 200-mesh Cu grid, and images were taken using JEOL JEM 2100F high-resolution transmission electron microscope at an acceleration voltage of 200 kV. For scanning electron microscopy (SEM) and the energy dispersive X-ray spectroscopy (EDX) analysis, samples were fixed on carbon tape and images were taken using JEOL JSM-6700FE.

2.2. Preparation of catalyst

The magnesium-lanthanum mixed oxide was prepared by the co-precipitation method described earlier. It was calcined at 923 K in air [35,36]. The powder XRD pattern of the Ru/Mg–LaO calcined mixed oxide showed the diffraction lines of a lanthanum oxide carbonate and lanthanum hydroxides with parameters corresponding to those reported in the literature. This biphasic solid probably consists of a layer of lanthanum oxide deposited on magnesia. This mixed oxide has a surface area of 37.6 $m^2\,g^{-1}$. The calcined sample of Mg–LaO mixed oxide (1.78 g) was stirred with $RuCl_3$ (0.415 g, 2.67×10^{-2} M) in 75 mL of freshly prepared deionized water at 298 K for 24 h under nitrogen atmosphere. The catalyst was filtered, washed with deionized water, acetone and dried overnight at 383 K in an oven. The prepared Ru/Mg–LaO catalyst was grey in colour and from the elemental analysis the Ru content was found to be 1.0 mmol/g (Ru content: 10.10 wt%). The same procedure was used to prepare Ru supported on γ-alumina [Harshaw, 224 $m^2\,g^{-1}$], silica [Aldrich, 500 $m^2\,g^{-1}$], and titania [Aldrich P25 Anatase, 50 $m^2\,g^{-1}$] magnesia [NAP–MgO with a specific surface area (BET) ≥ 600 $m^2\,g^{-1}$ was purchased from "Nano Scale Corp., Manhattan, KS, USA." It was then calcined at 450 °C for four hours in air. The BET surface area obtained was 183 $m^2\,g^{-1}$ catalysts.

2.3. General procedure for the oxidation of alcohols

An oven dried 50 mL two-necked round bottomed flask equipped with a reflux condenser connected with a balloon filled with oxygen was charged with Ru/Mg–LaO catalyst (0.102 g), alcohol (1.0 mmol) and toluene (5.0 mL). The resulting mixture was stirred at 353 K. After completion of the reaction (as monitored by TLC and GC), the reaction mixture was centrifuged to separate the solid catalyst. The catalyst was washed with toluene (2 × 20 mL) for complete recovery of the organic materials. In case of recycling studies, the catalyst was washed with deionized water and dried prior to the reusability experiments. The combined filtrate was dried over anhydrous Na_2SO_4 and the solvent was removed

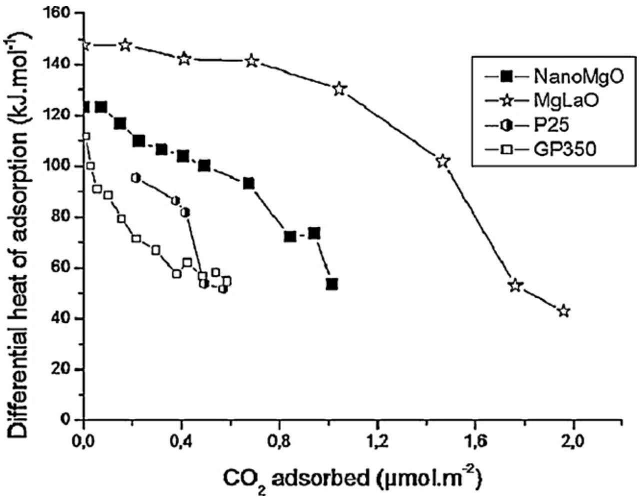


Fig. 1. The basicity of various support materials measured by CO_2 adsorption at 303 K.

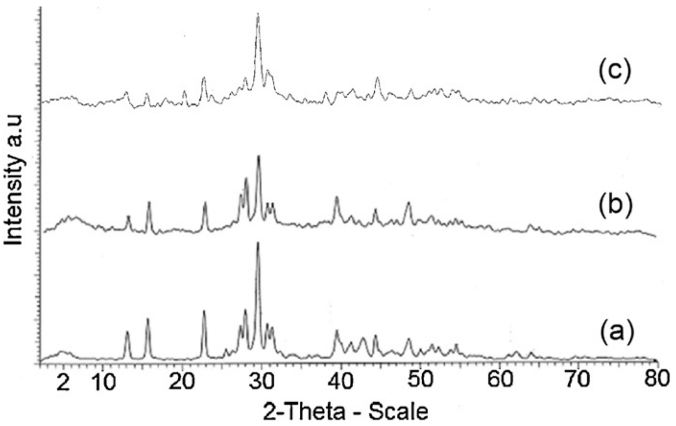


Fig. 2. XRD patterns of the (a) Ru/Mg–LaO fresh, (b) Mg–LaO and (c) Ru/Mg–LaO used samples.

under reduced pressure. The crude product was purified by column chromatography (silica gel: 100–200 mesh using ethyl acetate and petroleum ether) to give the corresponding aldehyde or ketone. For the solvent free oxidation of benzyl alcohol, a dry 100 mL three-neck round bottomed flask, equipped with a reflux condenser was charged with Ru/Mg–LaO catalyst (0.490 g) and freshly distilled benzyl alcohol (1.08 g, 10 mmol). The resulting mixture was stirred at 393 K under one atmosphere of oxygen. Conversion and selectivity were determined by GC using undecane as external standard. The combined organic layers were dried using anhydrous Na_2SO_4, filtered. The distillation of the residue gave pure benzaldehyde (75% yield).

3. Results and discussion

3.1. Catalyst characterization

The Ru/Mg–LaO catalyst was characterized by powder XRD, TPR, XPS and SEM–EDX in order to determine the nature of the ruthenium dispersed on the solid. The support was characterized by calorimetry in order to determine the basicity. The results are reported in Fig. 1, in which a nano MgO sample of high surface area ($183\,m^2\,g^{-1}$), TiO_2 ($50\,m^2\,g^{-1}$), SiO_2 ($500\,m^2\,g^{-1}$) and γ-alumina ($224\,m^2\,g^{-1}$) surface areas are added as reference. It appears clearly that the mixed oxide shows a higher basic strength than MgO.

The CO_2 uptakes of the fresh and used form of Ru/Mg–LaO are carried out by TPD of CO_2 in order to measure the basicity of the samples. The CO_2 uptakes of the fresh and used catalysts are found to be 240 and 214 µmol/g respectively.

The XRD diffractogram (Fig. 2a) of Ru/Mg–LaO fresh is similar to that of the support Mg–LaO (Fig. 2b) and used (Fig. 2c) samples, and it can then be concluded that the Ru oxide is dispersed as small particles.

This high dispersion of Ru is confirmed by the examination of scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDX) (Fig. 3). The ratio of Ru:Mg:La did not change dramatically before and after the reaction (before, 21.75:55.48:22.77, used, 21.49:60.33:18.18, respectively).

Fig. 4 shows the TEM micrographs of the fresh and used 10%Ru/Mg–LaO catalysts. It can be seen that the particles are almost spherical shape with a mean diameter of 15 and 30 nm for fresh and used catalysts respectively. Although some aggregation was observed in the used catalyst, it did not affect the product yield.

The oxidation state of Ru was investigated by two methods: TPR and XPS. The TPR profiles of the fresh and used Ru/Mg–LaO catalysts, reported in Fig. 5 shows one large peak at about 550 K, with a shoulder at 750 K. The high temperature peak at about 750 K, linked to a very stable Ru species, is assigned to the oxychloride, and the low temperature peak to Ru cations well dispersed at the surface [41,43].

The peak at about 550 K has been assigned due to the reduction of RuO_2. The integration of the area under the peaks in the interval 400–900 K, coupled with the calibration of the hydrogen consumption, permits to determine the number of H atoms required for the reduction of Ru. This determination gives a ratio H/Ru = 3.86, corresponding to the reduction of a mixture of 80% Ru^{4+} and 20%

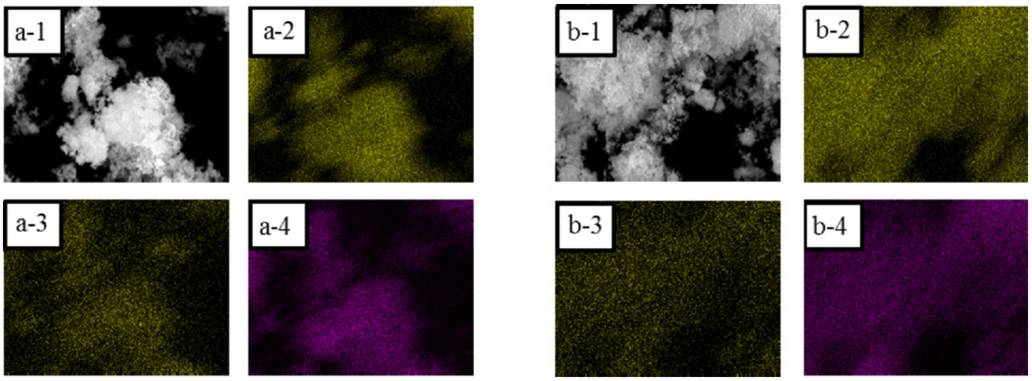


Fig. 3. Images of (a) fresh and (b) used Ru/Mg–LaO catalyst. SEM images of (a-1) fresh and (b-1) used catalyst. Element mapping of (a-2) and (b-2) Ru, (a-3) and (b-3) La, and (a-4) and (b-4) Mg.

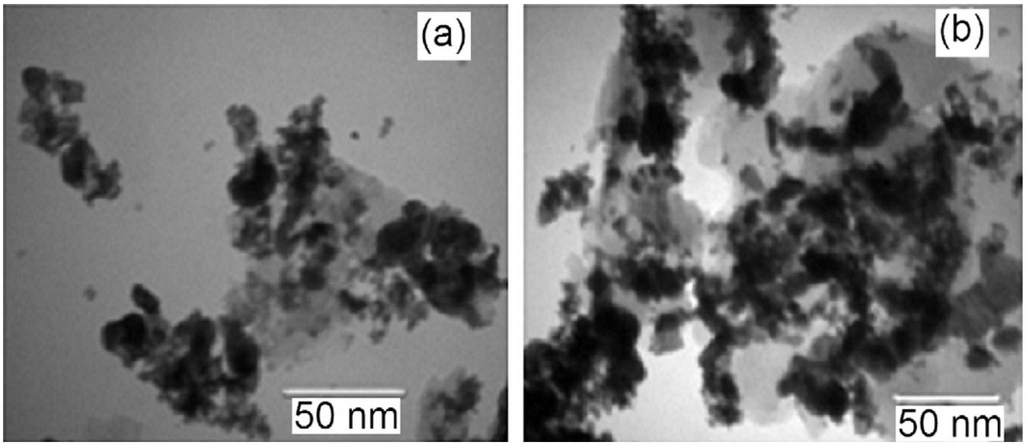


Fig. 4. TEM images of the (a) fresh Ru/Mg–LaO and (b) used Ru/Mg–LaO catalysts.

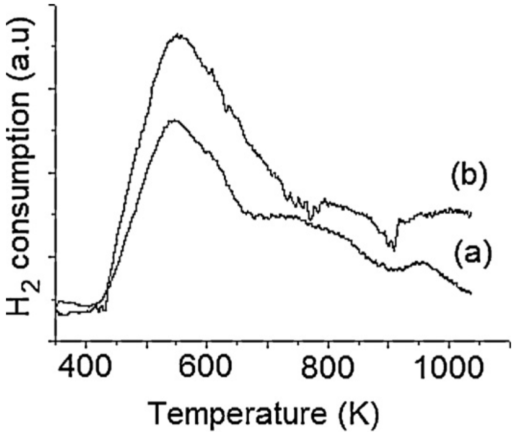


Fig. 5. TPR patterns of the (a) fresh and (b) used Ru/Mg–LaO catalyst.

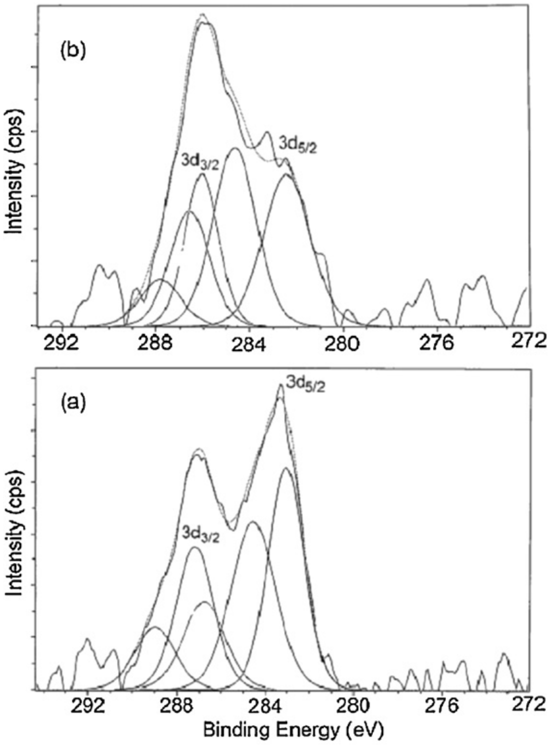
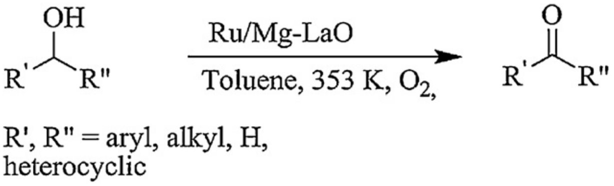


Fig. 6. X-ray photoelectron spectra of the (a) Ru $3d_{5/2}$ fresh and (b) Ru $3d_{5/2}$ used catalysts.



Scheme 1. Oxidation of alcohols over Ru/Mg–LaO catalyst.

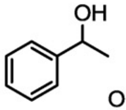
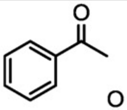
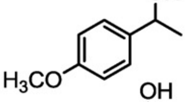
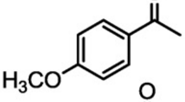
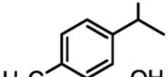
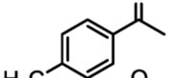
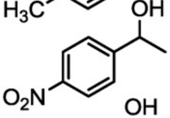
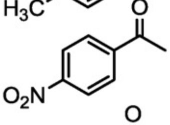
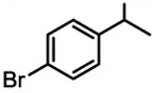
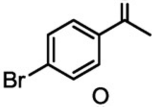
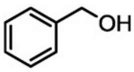
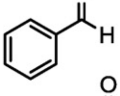
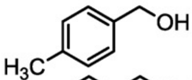
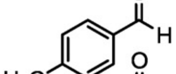
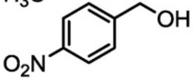
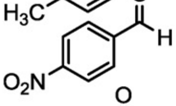
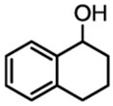
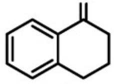
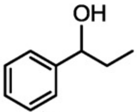
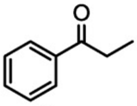
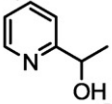
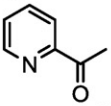
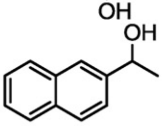
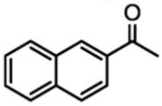
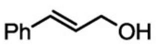
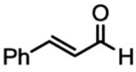
Ru^{3+}. In the XPS spectrum, the comparison of the surfaces of Ru *3d* peaks at 285 eV with that of the *2p* Cl peak at 199 eV gives a Ru/Cl atomic ratio of 61/38; using the Ru *3p* line at 466 eV, a similar result is obtained with Ru/Cl = 63/36. It can then be concluded that drying the solid at oven temperature induces hydrolysis of Ru—Cl bonds with formation of oxides. The strong basicity of the mixed oxides has induced the same effect as that of by NaOH treatment. It has been however known that chlorine is not completely eliminated from Ru supported on alumina [40] or silica [41,42] after calcination or even after calcination followed by reduction. The retention of Cl was attributed to the formation of an oxychloride, which should be present here in rather small amounts. This oxychloride can be responsible for the high temperature shoulder appeared in the TPR curve. The deconvolution of the XPS lines of Ru *3d* level (for fresh and used Ru/Mg-LaO mixed oxide catalysts) is reported in Fig. 6. It is observed that both fresh and used catalysts show common features, indicating that there is no change in the surface structure of the fresh catalyst after the reaction. These spectra contain three lines attributed to C; the one at 284.6 and 286.8 eV are due to pollution carbon, and a smaller peak at 289 eV

Table 1
Effect of the support on the catalytic properties of ruthenium for the selective oxidation of 1-phenylethanol to acetophenone.[a]

Entry[a]	Catalyst	Solvent	Yield (%)[b]
1	MgLaO	Toluene	n.r.[c]
2	$RuCl_3$	Toluene	n.r.[c]
3	Ru/MgLaO	Toluene	96, 95[d]
4	Ru/MgLaO	Trifluorotoluene	95
5	Ru/MgLaO	DMF	80
6	Ru/SiO_2	Toluene	45
7	Ru/Al_2O_3	Toluene	40
8	Ru/MgO	Toluene	36
9	Ru/TiO_2	Toluene	22

[a] Reaction conditions: alcohol (1.0 mmol), catalyst (0.1 g), toluene (5.0 mL), 353 K, O_2 balloon.
[b] Isolated yield after column chromatography.
[c] Determined by NMR spectroscopic integration.
[d] Yield in fifth cycle.

Table 2
Oxidation of various alcohols using molecular oxygen using Ru/Mg–LaO mixed oxide catalyst.[a]

Entry	Alcohol	Carbony compound	Yield (%)[b]
1			96
2			99
3			96
4			80
5			84
6			92
7			82
8			90
9			94
10			92
11			86
12			90
13			82

[a] Reaction: alcohol (1.0 mmol), catalyst (0.1 g), toluene (5.0 mL), 353 K, O_2 atmosphere, reaction time 4 h.
[b] Isolated yield.

can be attributed to carbonates adsorbed at the basic sites of the support. Due to spin–orbit interactions, the transition corresponding to Ru is composed of two doublets [44], the relative weight of which are 60% for Ru $3d_{5/2}$ at 283.06 eV attributed to Ru^{3+} and 40% for Ru $3d_{3/2}$ at 284.2 eV ascribed to Ru^{4+} [45–48] (Fig. 6). This XPS analysis therefore confirms that Ru could exist as RuO_2 at the surface.

3.2. Catalytic activity of Ru/Mg–LaO for oxidation of alcohols

The oxidation of various alcohols in oxygen atmosphere on different supported Ru catalysts has been performed with the non-reduced catalyst at 353 K (Scheme 1) and the results are reported in Table 1.

As can be seen from Table 1, Ru supported on acidic silica or on weak solid bases such as Al_2O_3, MgO and TiO_2 afforded low yields reaching 45%, 40%, 36% and 22% yields after 4 h (Table 1, entries 6–9). It can be pointed out that $RuCl_3$ has not suffered here any treatment with NaOH, so that the low basicity of alumina is retained, and this puts in evidence the strong effect of this treatment. The best result was obtained with the catalyst Ru/Mg–LaO (96%, Table 1, entry 3). The efficiency and stability of this newly established catalytic system was examined in detail with 1-phenylethanol as substrate. Oxidation proceeds to

Table 3
Reusability of the Ru/Mg–LaO catalyst.[a]

Trial	Time (h)	Yield (%)[b]
1	4	96
2	4	96
	4	95
4	4	95
5	4	95

[a] Reaction conditions: 1-phenyl ethanol (1 mmol), catalyst (0.1 g), toluene (5 mL), 353 K, O_2 atmosphere

[b] Isolated yields.

completion giving excellent isolated yields through five successive cycles (Table 1, entry 3).

The particularity of Mg–LaO is tentatively attributed to its strong basicity which would stabilize Ru as ruthenates at the surface of the solid. The activity pattern of Ru/Mg–LaO was investigated on a series of alcohols (Table 2). All aromatic secondary alcohols were converted to their corresponding ketones in short reaction times, with nearly quantitative yields (Table 2, entries 1–5 and 9–12). It is worth mentioning here that benzyl alcohol was cleanly converted to benzaldehyde and was obtained in 92% isolated yield (Table 2, entry 6), which is a significant improvement compared to our previous protocol which involved the use Ni–Al hydrotalcite wherein only 36% yield was obtained [26]. Substituted benzyl alcohols also afforded the corresponding aldehyde product in good yields (Table 2, entries 7 and 8). We were also pleased to find that nitrogen containing heterocyclic alcohol, i.e. 1-(pyridin-2-yl) ethanol could be selectively oxidized to its corresponding ketone in good yields (Table 2, entry 11). These results encouraged us to evaluate the oxidation of long chain aliphatic alcohols such as1-hexanol, 1-heptanol, 1-octanol and 1-nonanol under similar reaction conditions and also at high temperatures but unfortunately no catalytic activity was observed in these cases. The oxidation reaction was also conducted under solvent free conditions taking benzyl alcohol as the substrate. The results show only 75% of conversion with 69% yield of benzaldehyde at 393 K, analyzed by GC using undecane as an external standard. This lower conversion, compared to the diluted system, was attributed to the production of water by the reaction, leading to an inhibition of the reaction rate. The solvent free reaction was then performed at 393 K, giving a high conversion (>99), attributed to desorption of the water at this temperature. The best catalyst reported so far for this type of reaction is Au/CeO_2 [27,28], which consists small particles of metallic gold of about 4–5 nm in size, deposited on ceria of high surface area. The active sites, identified to Au^{3+} cations, are supposed to be localized at the interface of ceria and gold. In solvent free conditions Corma and coworkers observed esters during the oxidation of 1-phenylethanol over Au/CeO_2. On Ru/Mg–La mixed oxide this substrate produced selectively ketone (Table 2, entry 1).

The described methodology illustrates a very simple oxidation procedure, using a simple catalyst preparation. This solid consisting of Ru exchanged on to the Mg–LaO support is believed to sustain at high temperatures if required. The effect of the organic solvents on the oxidation was examined, where toluene and trifluorotoluene gave high yields. For safety and environmental reasons, we routinely made the reactions with toluene, but as demonstrated the solvent can be omitted. We have conducted the hot filtration experiment for leaching studies. After 1 h, the catalyst was filtered out of the reaction mixture; the filtrate was stirred under the same reaction conditions for 3 h. No propagation of the reaction was observed by GC analysis. The catalyst Ru/Mg–LaO was reused four times with consistent activity under the same reaction conditions without any detectable metal leaching (Table 3). There is no reaction with the filtrate, when a fresh amount of the reactant was added.

4. Conclusions

In conclusion, mild and efficient green oxidation of various benzylic and secondary aromatic alcohols to aldehydes or ketones can be obtained by using Ru supported on a strong basic Mg–La mixed oxide and molecular oxygen as an oxidant. The catalyst can be used for five cycles with consistent activity and selectivity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2012.03.013.

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