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ORIGINAL PAPER

Synthesis and characterization of RuO_2@ZrO_2 core–shell nano particles as heterogeneous catalyst for oxidation of benzylic alcohols in different conditions

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Abstract In this study, new RuO_2@ZrO_2 core–shell nanoparticles have been produced using simple procedure and characterized by the spectroscopic methods (XRD and HR-TEM techniques). Catalytic activity of the synthesized nano powders has been investigated in the liquid-phase selective oxidation of benzyl alcohols. Also, the effect of some parameters such as optimum weight ratio for Ru doping, catalyst, oxidant type and various solvents was studied in room temperature, reflux, ultrasound, microwave conditions and UV–vis irradiation. The catalyst exhibits excellent activity and high conversion under mild conditions. Furthermore, this reagent was recycled and reused three times in the model reaction.

Keywords RuO_2@ZrO_2 · Heterogeneous catalysis · Selective oxidation · Benzyl alcohol

Introduction

Nowadays, the use of heterogeneous catalysts in the synthesis of chemical and pharmaceutical compounds has attracted much attention of chemists [1]. These catalysts are convenient to use on large scale and present high surface area of the catalytic active phase to the reactants. Also, they have many advantages such as easy separation and straight recycling process compared to homogeneous catalysts [2]. Many organic reactions are carried out using heterogeneous catalysis. Among them, the selective oxidation of benzyl alcohols to corresponding aldehydes is one of the most considerable transformations in organic synthesis and essentially useful in industry for preparing many drugs, vitamins, fragrances alcohols and esters [3, 4]. Carbonyl compounds such as acetophenone are useful and important intermediates in the food processing, cosmetics industry and in many complex syntheses [2].

However, catalytic oxidation of alcohols to carbonyl compounds on an industrial scale remains an important challenge because these processes need expensive metals, toxic organic solvents, long reaction times and in most cases, they require high temperature for effective catalytic activity.

On the other hand, modified transition metal oxides have gained much attention for their significant strength of acidity and excellent activity. The catalytic activity of heterogeneous catalysts such as magnesium oxides [5, 6], copper oxides [7], cerium oxides [8, 9] titanium oxides [10, 11], tungsten oxides [12], cobalt oxides [13], vanadium oxides [14], molybdenum oxides [15], niobium oxides [16, 17] and zinc oxides [18, 19] has been studied in the presence of different types of oxidants such as molecular oxygen and hydrogen peroxide as green oxidizing agent [20]. Among the inorganic oxides, zirconium oxide (zirconia), due to the characteristics of excellent chemical stability, biocompatibility, mechanical strength and low cost, has been considered as an important material [21–23]. However, pure zirconia could not be obtained at high temperature because of its low thermal stability and weak acid strength. In order to improve the catalytic properties of zirconia; we need modified zirconia by introducing different metals oxides such as Fe_3O_4, RuO_2, SiO_2, Al_2O_3, etc. which formed mixed oxides.

In our previous published research works [24–31], we synthesized some of nano catalysts and their activities were

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studied in different reactions. In this work, we investigated the synthesis of efficient RuO_2@ZrO_2 core–shell nanoparticles for the oxidation of benzylic alcohols to the corresponding aldehydes or ketones in room temperature, reflux, ultrasound, microwave and UV–vis irradiation. Therefore, we became interested in exploring the utility of RuO_2@ZrO_2 nanoparticles as a recyclable, economical, cheap and commercially available catalyst for this oxidation.

Experimental

Materials

All materials and solvents were purchased from Merck and Fluka and used without further purification.

Instrumentation

The particles sizes were obtained by high-resolution transmission electron microscope (HR-TEM) images on a JEM-2010F 200 kV (Cs = 0.5 mm). The crystal phase of the as-prepared products was identified by the powder X-ray diffraction method (XRD, Philips PW1840) using Cu Kα radiation (λ = 1.54060 Å) at a current of 200 mA and a voltage of 40 kV. The patterns were collected in the range of (2θ = 10–70), and continuous scan mode with a scanning rate of 8°/min. Yields of oxidation products were analyzed by gas chromatograph with a GC capillary column HP 6890 and FID detector.

Catalyst prepartion

For the preparation of Ru-doped ZrO_2, 1 g of Zirconium dioxide was dispersed in 30 ml deionized water with stirring for 30 min (solution A). Also, 20 mg of $RuCl_3.xH_2O$ was dissolved in 30 ml deionized water for preparation solution B. Then 100 µL of HCl 37 wt% was added with stirring for 30 min in solution B. In order to prepare RuO_2@ZrO_2 nanoparticles, solution A was added into solution B dropwise under constant stirring for 30 min. The obtained powder was filtered and washed with a large amount of deionized water. This grey powder was placed in a 100 mL beaker and 50 mL water was added. Under vigorous stirring, 1 M of NaOH was slowly added until the solution pH adjusted at 10. Then the solids were filtered and washed with deionized water. Finally, obtained precipitation was dried at 80 °C for 4 h.

General procedure for the oxidation reaction

A mixture of benzyl alcohol (1 mmol), t-BHP 70 % (0.3 ml) and RuO_2@ZrO_2 4 wt% (20 mg) in acetonitrile (5 ml) was stirred magnetically into the reactor through a septum. The progress of the reaction was followed using thin layer chromatography and after completion of the reaction, the products were filtered out from the catalyst. Then, the obtained oxidation products were analyzed using a gas chromatograph with a GC capillary column HP 6890 and FID detector.

Results and discussion

Catalyst characterization

X-Ray diffraction studies

Figure 1 shows the XRD patterns of the pure ZrO_2 and the supported Ru catalysts. All the XRD patterns consist of the diffraction peaks implies the monoclinic and tetragonal phase of the pure ZrO_2 nano particles (Fig. 1a, b) [32]. The weak diffraction peaks of Ru^{4+} species at 2θ = 28° was observed in Fig. 1b and it is indicated that Ru^{4+} particles are probably well dispersed on the zirconia supports [33]. No diffraction peaks corresponding to impurities are present. The average crystalline sizes of RuO_2@ZrO_2 were obtained from XRD data with the Scherrer equation and found to be 31 nm as confirmed by HR-TEM.

HR-TEM analysis

In order to obtain detailed information about the exact size and morphology of the as-synthesized catalyst, HR-TEM images are presented. Figure 2 depicts transmission electron micrographs of Ru-doped ZrO_2 (4 wt%). In this figure the morphology of RuO_2@ZrO_2 showed the core–shell structure and demonstrated that the ZrO_2 is covered by a dense layer of Ru. The average particles size derived

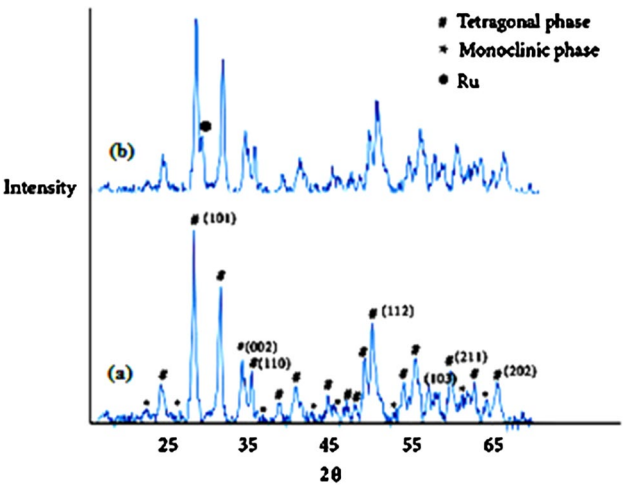

Fig. 1 XRD patterns of ZrO_2 (*a*) and RuO_2@ZrO_2 (*b*)

from HR-TEM analysis were about 35 nm, which is comparable with the crystallite size calculated from X-ray spectrum.

Oxidation of alcohols

Our paper survey revealed that there are no reports on the application of this efficient and effective catalyst in the oxidation of alcohols. To explore our studies towards the development of useful nano catalysts for oxidation, benzhydrol (diphenylmethanol) was selected as a model alcohol to optimize the reaction conditions in ethanol and the results are listed in Table 1. First investigations clarified that the catalytic activity is proportional to the amount of the catalysts. Because a negligible conversion of benzhydrol (only 5 %) was obtained in the absence of the catalysts, it indicated that the presence of catalyst is necessary for the benzhydrol oxidation (Table 1, entry1).

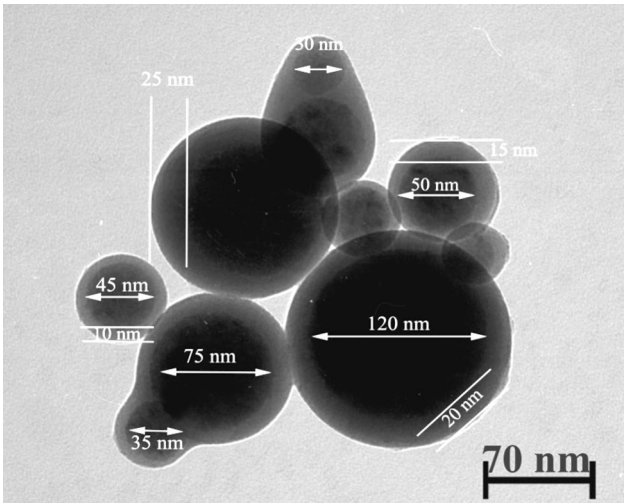

Fig. 2 HR-TEM images of RuO_2@ZrO_2

To evaluate the catalytic activity of the Ru-doped ZrO_2, the optimum amount of Ru doping is studied from 1 to 10 wt% in the model reaction. Ru loading amount had a remarkable effect on benzhydrol conversion and the oxidation reaction did not occur with pure ZrO_2, but the increase of Ru content in synthesized catalysts enhanced the conversion of alcohol significantly. In fact, the catalyst properties are closely associated with the amount of metal active sites and the size of Ru. Higher Ru loading obviously ensures sufficient active Ru sites [34]. As shown in Table 1, the 4 wt% of Ru-doped ZrO_2 sample had suitable catalytic efficiency and the optimal Ru doping is 4 wt%.

Then, in the presence of appropriate amount of RuO_2@ZrO_2 (4 wt%), the effect of various amounts of catalyst (10, 20, 30 mg) was studied in the oxidation of benzyl alcohol. The conversion increased from 80 to 85 % by increasing the catalyst amount from 10 to 30 mg and the best condition was obtained using 20 mg of catalyst.

The catalytic activity of 4 wt% of RuO_2@ZrO_2 as a catalyst was examined in the oxidation of model reaction at reflux condition (80 °C) and room temperature (25 °C). It can be seen that when the temperature was elevated from 25 °C to reflux condition, the benzhydrol conversion increased from 30 to 85 %. Therefore, reflux condition (80 °C) was considered as the optimum reaction temperature.

Another important factor in this oxidation is the effect of oxygen sources on the reaction rate. To evaluate the oxidants effect in the catalytic activity of RuO_2@ZrO_2, oxidation of the benzhydrol was investigated in the presence of tetrabutyl hydroperoxide (TBHP), hydrogen peroxide (H_2O_2) and oxygen (Table 2). According to the results in Table 2, RuO_2@ZrO_2 gave maximum conversion and good reaction time in the presence of TBHP as an oxidant. Actually, when H_2O_2 was utilized for the oxidation of alcohols, most of the H_2O_2 molecules decomposed into O_2 and the reaction time was prolonged [27].

Table 1 Oxidation of benzhydrol in presence of different catalysts under various conditions

Entry	Catalyst	Catalyst amount (mg)	Temp. (°C)	Time (min)	Conversion (%)	GC yield (%)[a]
1	–	–	Reflux	45	5	–
2	ZrO_2	100	Reflux	20	10	5
3	ZrO_2/RuO_2 (1 wt%)	30	Reflux	15	60	50
4	ZrO_2/RuO_2 (2 wt%)	30	Reflux	5	80	75
5	ZrO_2/RuO_2 (4 wt%)	30	Reflux	5	85	80
6	ZrO_2/RuO_2(10 wt%)	30	Reflux	5	85	81
7	ZrO_2/RuO_2 (4 wt%)	20	Reflux	5	85	80
8	ZrO_2/RuO_2 (4 wt%)	10	Reflux	20	70	60
9	ZrO_2/RuO_2 (4 wt%)	20	25	60	30	20

Reaction conditions: benzhydrol (1 mmol), acetonitrile (5 ml), TBHP (0.3 ml)

[a] Isolated yield

Table 2 Optimization of the solvent, oxidant agent in the model oxidation reaction

Entry	Oxidant agent	Solvent	Time (min)	Conversion (%)	GC yield (%)[a]
1	t-BHP	Acetonitrile	5	85	80
2	H_2O_2	Acetonitrile	90	5	–
3	O_2	Acetonitrile	90	10	5
4	t-BHP	Toluene	5	70	60
5	t-BHP	Dichloromethane	5	75	65

Reaction conditions: benzhydrol (1 mmol), RuO_2@ZrO_2 (4 wt%) (20 mg), acetonitrile (5 ml), reflux

[a] Isolated yield

Table 3 Oxidation of benzhydrol using RuO_2@ZrO_2 (4 wt%) at different irradiation

Entry	Irradiation	Time (min)	Conversion (%)	GC yield (%)[a]
1	Ultrasound	15	80	75
2	Microwave	1	85	80
3	UV–vis	25	85	80

Reaction conditions: benzhydrol (1 mmol), ZrO_2/RuO_2 (4 wt%) (20 mg), acetonitrile (5 ml), TBHP (0.3 ml)

[a] Isolated yield

In the following, various solvents were examined in the oxidation of benzhydrol. The results showed that acetonitrile is the best solvent for the model reaction in comparison with the other solvents such as dichloromethane and toluene. It is due to the polarity of acetonitrile that was stronger than the other solvents.

In order to study the influence of the reaction conditions, oxidation experiments were assayed in different irradiation, e.g. ultrasound, microwave and UV–vis (Table 3). Microwave method showed the best results in shorter time. The advantage of microwave-assisted as a novel and cleaner reaction tool has been presented to reduce the reaction times and energy consumption together with an increase in production yields and selectivity [35, 36]. The microwave synthesis is considered as environmental friendly method for organic transformation. For this reason, we investigated the effect of microwave irradiation on the synthesis of the target compounds and the results showed enhancement in the speed and reaction times.

For establishing this protocol in the oxidation reaction of various alcohols, we studied the oxidation of different types of alcohols, including primary and secondary benzylic alcohols in the presence of RuO_2@ZrO_2 4 wt%. They were efficiently oxidized to their corresponding carbonyl compounds. The model reaction was carried out at both reflux condition and microwave irradiation and their results are listed in Table 4. As shown in this table, benzyl alcohol and its derivatives substituted by –Cl, –Br, $–NO_2$, and $–CH(OH)C_2H_5$ groups were converted to corresponding aldehydes with different conversions and yields. Alcohols with electron withdrawing groups in *para*-positions gave higher yields comparatively than alcohols with electron

Table 4 Oxidation of benzylic alcohols using RuO_2@ZrO_2 (4 wt%) as the catalyst

Entry	Substrate	Product	M.W.			Reflux		
			Time (min)	Conversion (%)	GC yield (%)[a]	Time (min)	Conversion (%)	GC yield (%)[a]
1	Benzylalcohol	Benzaldehyde	4	89	85	15	80	70
2	Benzhydrol	Benzophenone	1	85	80	5	85	80
3	4-Chloro benzylalcohol	4-Chloro benzaldehyde	1	97	90	5	90	85
4	2-Bromo benzylalcohol	2-Bromo benzaldehyde	3	95	90	15	92	85
5	4-Chloro benzhydrol	4-Chloro benzophenone	1	95	90	5	95	90
6	2-Nitro benzylalcohol	2-Nitro benzaldehyde	10	55	50	50	45	34
7	α-Ethyl benzylalcohol	α-Ethyl benzaldehyde	7	80	75	30	70	65

Reaction conditions: substrate (1 mmol), RuO_2@ZrO_2 (4 wt%) (20 mg), acetonitrile (5 ml), TBHP (0.3 ml)

[a] Isolated yield

Table 5 Comparison of the result obtained for the synthesis of benzaldehyde using RuO_2@ZrO_2 (4 wt%) with other catalysts reported in literature

Entry	Catalyst	Solvent	Temp (°C)	Time (min)	Conversion (%)	Ref.
1	MOF-supported Au NPs	$C_6H_5CH_3$	80	60	100	[37]
2	Nano-γ-Fe_2O_3	H_2O_2	75	300	19	[38]
3	Au-doped TiO_2	Solvent-free	100	300	77	[39]
4	Au-doped ZnO	Solvent-free	100	300	38	[39]
5	RuO_2@ZrO_2 (4 wt%)	CH_3CN	Ref	15	80	This work

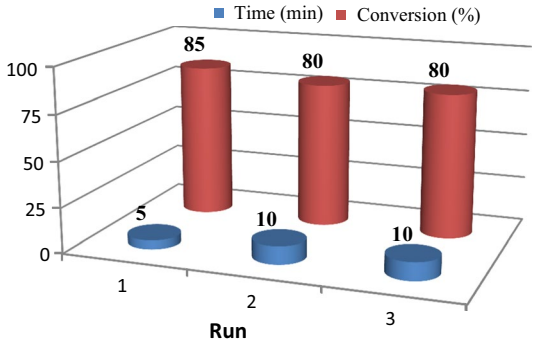

Fig. 3 Reusability of RuO_2@ZrO_2 (4 wt%) in the model reaction (Table 4, entry 1)

withdrawing groups in *ortho*- and *meta*-positions. Similar reactivity was observed for the oxidation of alcohols to the corresponding aldehydes under microwave irradiation.

Furthermore, in order to show the excellent catalytic activity of this catalyst in comparison with the previously reported heterogeneous systems, we compared the results of the oxidation of benzylic alcohols in the presence of RuO_2@ZrO_2 (4 wt%) and other reagents (Table 5). The obtained results indicate the superiority of RuO_2@ZrO_2 (4 wt%) in terms of catalyst, temperature, conversion and reaction times.

The reusability of the synthesized catalysts is a significant factor from environmental and economic points of view. In heterogeneous catalysts, the leaching of metal is a main problem which leads to loss of catalyst activity on subsequent uses. In order to investigate the stability of the catalytic systems, recycling experiments were performed. After completion of the reaction, the catalyst was recovered by centrifugation and washed with deionized water and chloroform, then dried and reused in the subsequent runs. The conversion result showed that RuO_2@ZrO_2 4 wt% can be reused three times without significant loss of activity (Fig. 3).

Conclusion

In conclusion, we attempted to synthesize RuO_2@ZrO_2 core–shell. The catalyst has been characterized by XRD and HR-TEM techniques. Also, we have developed a simple and highly efficient protocol for the oxidation of benzylic alcohols to the corresponding aldehydes or ketones using nano structured RuO_2@ZrO_2 as heterogeneous catalyst under reflux condition and microwave irradiation in acetonitrile. It is worthy to mention that the synthesis catalyst along with the reaction media can be reused for further reactions. Environmentally benign, easy work-up procedure, saving energy and mild reaction conditions are some advantages of this work.

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