Development of Highly Effective Nanoparticle Spinel Catalysts for Aerobic Oxidation of Benzylic Alcohols

JI, Hong-Bing(纪红兵)   WANG, Le-Fu*(王乐夫)
Chemical Engineering College , South China University of Technology , Guangzhou , Guangdong 510640 , China

Spinel catalyst $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$ with particle size of about 42 nm is an effective heterogeneous catalyst for the oxidation of benzylic alcohols. The substitution of Fe for Cu improves its catalytic activity. Based on the characterization of BET, XPS and EXAFS, two factors influencing the structure and texture of the catalyst caused by the substitution of Cu for Fe may be assumed: physical factor responsible for the increasing of surface area; chemical factor responsible for the transformation of Ru—O bonds to Ru = O bonds. β-Elimination is considered to be an important step in the reaction.

Keywords   spinels, nanoparticle catalyst, benzylic alcohol, XPS, EXAFS

Introduction

Selective oxidation of alcohols has been widely studied due to its importance in many organic syntheses.[1-7] How to make more effective, cheap, easily accessible and environmentally benign catalysts is matter of wide interest.

It is well known that spinel-type (AB_2O_4) of complex oxides can be applied as electronics, magnetic materials and catalysts. However the application of ferrite spinel in catalytic reactions is less studied.[8-13] The purpose of this paper is to report a highly functionalized nanoparticle spinel which can effectively catalyze heterogeneous aerobic oxidation of benzylic alcohols to produce the corresponding carbonyl compounds under mild conditions. To our knowledge, this is the first time that spinels are used as heterogeneous catalysts for the oxidation of benzylic alcohols to aldehydes and ketones.

Experimental

Catalyst preparations

Four methods of catalysts preparation were used.

Coprecipitation process 1: anhydrous $FeCl_3$ (15.6 mmol) and $MnCl_2 \cdot 4H_2O$ (8.0 mmol) were dissolved in 20 mL of deioned water. $RuCl_3$ (0.4 mmol) was added into the solution under stirring. Then the above solution was slowly added into an aqueous solution of NaOH (124.2 mmol, 25 mL). The resulting solution was programmingly heated to 110 ℃ at a rate of 1 ℃/min and kept for two hours. The obtained slurry was naturally cooled to room temperature for overnight, filtered, washed with deioned water and followed by drying at 110 ℃ for 24 h. For the coprecipitation 2, the process was similar with the coprecipitation 1, the difference was that $FeSO_4 \cdot 7H_2O$ (15.6 mmol) was used instead of anhydrous $FeCl_3$. Besides, KNO_3 (8.0 mmol) as an oxidant was simultaneously added into an aqueous NaOH to oxidize Fe^{2+} to Fe^{3+}.[14]

In order to get finer particles, two more catalysts were made according to reference.[15] This nanoparticle spinel catalyst was synthesized through the formation of water-in-toluene reverse micelles with sodium dodecylbenzensulfonate (NaDBS) $[CH_3(CH_2)_{11}(C_6H_4)SO_3]Na$ as surfactant. The synthesis started with $Mn(NO_3)_2$ (2.5 mmol) and $Fe(NO_3)_3$ (4.875 mmol) dissolved in 12.5 mL of deioned water to form a clear solution. $RuCl_3$ (0.125 mmol) was added to the above solution and dark solution was obtained. An aqueous solution of NaDBS (0.2 mol/L, 25 mL) was added into the metal salt solu-

tion and followed by the addition of toluene (250 mL). After stirring overnight, the mixture became a single-phase solution containing reverse micelles. To form colloids in reverse micelles, an aqueous solution of NaOH (1.0 mol/L, 20 mL) was added drop by drop accompanied by vigorous stirring. The solution was stirred for two more hours to complete the formation of colloids. Then, the volume of the solution was reduced by distilling out water and most of the toluene solvent. The concentrated solution with suspended colloids was washed with water and ethanol to remove excess surfactant. The products were collected through centrifugation. After heat treatment for 12 h, the catalyst was formed. The difference between reverse micelle processes 1 and 2 is that the heat treatment temperature of the former was 110 ℃ under air and the heat treatment temperature of the latter was 350 ℃ in Argon.

All the obtained catalysts were dark powder.

Alcohol oxidation

A typical procedure for aerobic alcohol oxidation is as follows: into a glass vessel with a reflux condenser were placed the catalyst (0.3 g), substrate (2 mmol), and toluene (5 mL). The resulting mixture was stirred at 60 ℃ under atmospheric pressure of O_2. After the reaction, the catalyst was separated by filtration. GC analysis was employed to get the yield of product.

Characterization

X-Ray diffraction patterns (XRD) were measured on an X'pert diffractometer (Phillips Co. Ltd.) using Cu Kα radiation ($\lambda = 0.15405$ nm).

BET surface areas were measured on a BELSORP18PULS-SP.

XPS spectra were recorded on a Shimadzu ESCA-KM using Mg Kα radiation.

Ru K-edge X-ray absorption data were recorded at room temperature in a transmission mode at the EXAFS facilities installed on the BL-10B line of Photon Factory at High Energy Accelerator Research Organization, Tsukuba, Japan, with a ring energy of 2.5 GeV and a storage current of 390—210 mA, using a double-crystal Si(311) monochromator. The sample (about 50 mg) was mixed with boron nitride as a binder and pressed into a 10 mmΦ disk. The EXAFS data were normalized by fitting the

background absorption coefficient around the energy region higher than the edge about 35—50 eV with the smoothed absorption of an isolated atom. Fourier transformation (FT) of k^3-weighted normalized EXAFS data was performed over the 0.35 nm < k < 1.2 nm range to obtain the radial structure function. CN (coordination number of scatterers), R (distance between an absorbing atom and scatterer) and Debye-Waller factor were estimated by curve-fitting analysis with the inverse FT assuming single scattering.

Results and discussion

Optimal preparative conditions

The XRD (SiO_2 was used as standard with particle size of 5.10 μm and lattice constant of 0.5430758 ± 0.0000031 nm) peak positions indicate that the $MnFe_{1.95}Ru_{0.05}O_4$ prepared by coprecipitation processes 1 and 2, and reverse micelle process 2 possesses the structure of spinels, while that prepared by reverse micelle process 1 is amorphous. The average size of the nanoparticles has been calculated according to the peak broadening in X-ray diffraction pattern by using the Debye-Scherrer equation.[16] The particle sizes of catalysts prepared by coprecipitation processes 1 and 2 were 40 nm and 56 nm, respectively, and that of the catalyst made by reverse micelle process 2 was 7 nm. The particle sizes of these catalysts are very near that given in references[14-17] meaning that nanoparticle spinel can be produced by the above mentioned preparation methods.

Catalytic properties test

The oxidation of benzyl alcohol to benzaldehyde was adopted as a probe reaction. Oxidation of benzyl alcohol over the catalysts prepared by the above mentioned methods was carried out at 60 ℃ in oxygen atmosphere and the results are summarized in Table 1.

Table 1 shows that the catalyst with a suitable particle size prepared by coprecipitation process 1 gives the highest yield of benzaldehyde. This is not the case that the smaller the particle size is, the better the yield.

By means of the coprecipitation process 1, partial substitution of Fe ions for transition metals such as Ti, Cr, Co, Ni, Cu, Zn, Zr, La, Ce and Pr in the form of nitrate salts was adopted to improve the catalysts. The re-

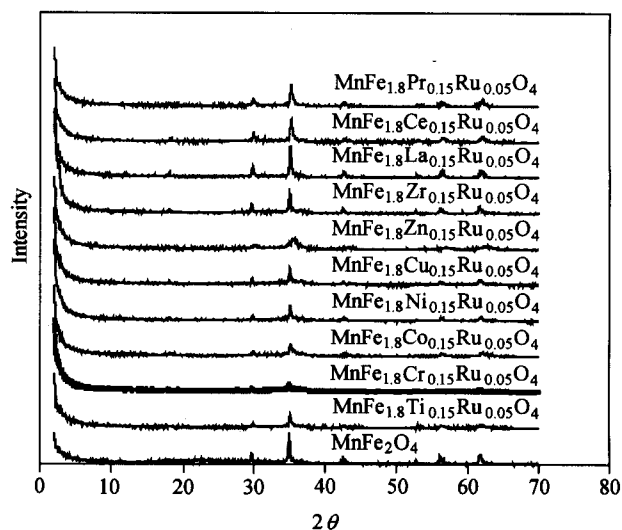**Table 1** Catalytic properties of $MnFe_{1.95}Ru_{0.05}O_4$ catalysts prepared by different methods[a]

Preparation method	Conv. of benzyl alcohol (%)	Yield of benzaldehyde (%)	TN[b]	Particle size (nm)
Coprecipitation 1	56	49	45	40
Coprecipitation 2	27	25	23	56
Reverse micelle 1	16	13	13	/
Reverse micelle 2	8	4	3	7

[a] Benzyl alcohol: 2 mmol; weight of catalyst: 0.1 g; toluene: 5 mL; reaction temperature: 60 ℃; reaction time: 1 h; oxygen atmosphere. [b] TN was definated as ratio of molar product and molar Ru.

sults of XRD show the retention of spinel structure of the samples doped with different transition metals (Fig. 1). As can be seen from Table 2, most of these catalysts have nanoparticle structures.

From Table 2, it can be seen that the catalysts doped with Cr, Ni, Cu, Zn, Zr, La or Ce show better catalytic properties, while the others give nearly the same or less conversion and yield. Copper salt was employed in our further research because it can be easily accessible and cost-effective. Due to the existence of synergism effect between Ru and Cu in the catalytic oxidation of benzyl alcohol[18,19] (as opposed to the case of $MnFe_{1.95}Ru_{0.05}O_4$), which will be discussed below, the precursor and amounts of Cu salt were changed to search for the suitable copper salt and copper amount (Table 3 and Table 4). The results show that the catalytic properties of catalysts are insensitive to the precursor and the amount of copper. Mn:Fe:Cu:Ru with ratio of 1:1.8:0.15:0.05 (molar ratio) is the optimal ratio of the compounds in the catalyst for the topic reaction. Experiments on the solvent dependence of the reaction show that toluene, bromobenzene and trifluorotoluene are suitable solvents for the reaction.

Aging temperature dependence of the catalysts was also studied. The results of benzyl alcohol oxidation show that aging temperature does not influence the catalytic properties of the catalysts (Table 5).

Fig. 1 XRD spectra of $MnFe_{1.95}Ru_{0.05}O_4$ partially substituted of Fe with different transition metals.

Table 2 Catalytic properties of catalysts doped with different transition metals[a]

Catalyst	Conv. of benzyl alcohol (%)	Yield of benzaldehyde (%)	TN[b]	Particle size (nm)
$MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$	60	59	56	42
$MnFe_{1.8}Ce_{0.15}Ru_{0.05}O_4$	60	59	55	25
$MnFe_{1.8}Ni_{0.15}Ru_{0.05}O_4$	59	58	55	40
$MnFe_{1.8}Zr_{0.15}Ru_{0.05}O_4$	58	57	54	110
$MnFe_{1.8}La_{0.15}Ru_{0.05}O_4$	58	57	54	47
$MnFe_{1.8}Cr_{0.15}Ru_{0.05}O_4$	57	56	53	23
$MnFe_{1.8}Zn_{0.15}Ru_{0.05}O_4$	55	53	51	7
$MnFe_{1.8}Co_{0.15}Ru_{0.05}O_4$	50	47	45	22
$MnFe_{1.8}Ti_{0.15}Ru_{0.05}O_4$	48	47	45	21
$MnFe_{1.8}Pr_{0.15}Ru_{0.05}O_4$	45	44	44	35

[a] Benzyl alcohol: 2 mmol; weight of catalyst: 0.1 g; toluene: 5 mL; reaction temperature: 60 ℃; reaction time: 1 h; oxygen atmosphere. [b] TN was definated as a ratio of molar product and molar Ru.

Table 3 Influence of copper precursors on reaction properties[a]

Copper precursor	Conv. of benzyl alcohol (%)	Yield of benzaldehyde (%)	TN[b]
$Cu(NO_3)_2$	60	59	56
$Cu(OH)_2$	59	57	54
CuC_2O_4	57	56	52
$CuCl_2$	53	52	49
$CuSO_4$	49	48	46
$CuBr_2$	48	45	43

[a] Benzyl alcohol: 2 mmol; weight of catalyst: 0.1 g; toluene: 5 mL; reaction temperature: 60 ℃; reaction time: 1 h; oxygen atmosphere. [b] TN was definated as a ratio of molar product and molar Ru.

Table 4 Influence of copper amount on reaction properties[a]

Catalyst	Conv. of benzyl alcohol (%)	Yield of benzaldehyde (%)	TN[b]
$MnFe_{1.7}Cu_{0.25}Ru_{0.05}O_4$	57	56	53
$MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$	60	59	56
$MnFe_{1.9}Cu_{0.05}Ru_{0.05}O_4$	57	55	52

[a] Benzyl alcohol: 2 mmol; weight of catalyst: 0.1 g; toluene: 5 mL; reaction temperature: 60 ℃; reaction time: 1 h; oxygen atmosphere. [b] TN was definated as a ratio of molar product and molar Ru.

Table 5 Influence of aging temperature of catalysts on reaction properties[a]

Temperature (℃)	Conv. of benzyl alcohol (%)	Yield of benzaldehyde (%)	TN[b]
90	60	59	56
100	60	59	56
110	60	59	56
120	61	60	56
130	60	59	56
140	60	59	56

[a] Benzyl alcohol: 2 mmol; weight of catalyst: 0.1 g; toluene: 5 mL; reaction temperature: 60 ℃; reaction time: 1 h; oxygen atmosphere. [b] TN was definated as a ratio of molar product and molar Ru.

Oxidation of various benzylic alcohols

Oxidation of several kinds of benzylic alcohols over $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$ in a toluene solvent was carried out at 60 ℃ in an oxygen atmosphere. As shown in Table 6, the catalyst $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$ shows high activity

for benzylic alcohol oxidation with higher TN than other heterogeneous catalysts.[5,19-22] Furthermore, this catalyst was applicable for the oxidation of heterocyclic alcohols including nitrogen and sulfur atoms. 2-Pyridinemethanol and 2-thiophenemethanol were smoothly oxidized to the corresponding aldehydes with high conversions and yields (Entries 5 and 6). Secondary benzylic alcohols were also completely converted into the corresponding ketones (Entries 7—9). It should be noted that this catalyst could oxidize cyclopropylphenyl carbinol to cyclopropyl phenyl ketone without breaking triatomic ring group (Entry 9). Besides, this catalyst could be reused after regeneration (Entries 1a and 1b).

Investigation of active site

The addition of Ru is very important. Ruthenium-free catalyst as $MnFe_{1.85}Cu_{0.15}O_4$ was prepared to test catalytic properties for the benzyl alcohol oxidation. Little conversion of benzyl alcohol appeared. The typical result of benzyl alcohol using $MnFe_{1.85}Cu_{0.15}O_4$ is that the conversion of benzyl alcohol is only 6%, which means that Ru is an active component for this type of reaction.
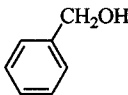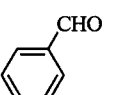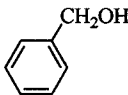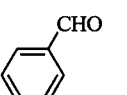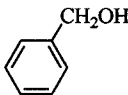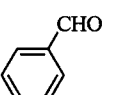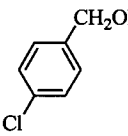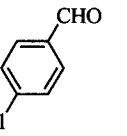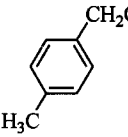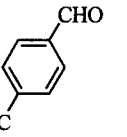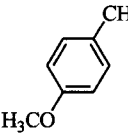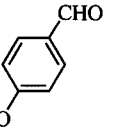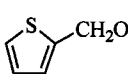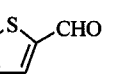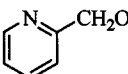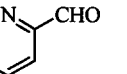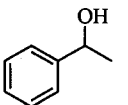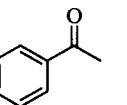
The influence of the substitution of Fe for Cu was investigated by means of BET, XPS and EXAFS.

The BET surface areas of $MnFe_{1.95}Ru_{0.05}O_4$ and $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$ were 205 and 248 m^2/g, respectively. After the substitution of Fe for Cu, the surface area increased about 20%. This is the physically structural factor of enhancement of the catalytic activity.

By means of XPS, the chemical shift of the binding energy of Ru $3d_{5/2}$ was found for $MnFe_{1.95}Ru_{0.05}O_4$ and $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$. Binding energy of Ru^0 $3d_{5/2}$ is 279.9 eV, and those of Ru $3d_{5/2}$ in $MnFe_{1.95}Ru_{0.05}O_4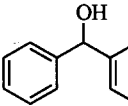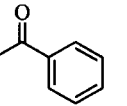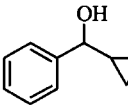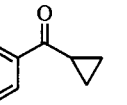$ and $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$ are 281.5 and 282.0 eV, respectively. That the chemical shifts were 1.6 and 2.1 eV for $3d_{5/2}$ in $MnFe_{1.95}Ru_{0.05}O_4$ and $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$ means that Ru valence in $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$ is a little higher than that in $MnFe_{1.95}Ru_{0.05}O_4$. The verification of this conclusion is further supported by Ru K-edge EXAFS characterization.

Fig. 2 shows the EXAFS profiles and Table 7 gives the curve-fitting parameters. As shown in Fig. 2(a), the absence of 0.35 nm peak means that no Ru—Ru bond in $MnFe_{1.95}Ru_{0.05}O_4$ and $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$ exists. From Table 7, we can assume that isolated Ru—O species

Table 6   Oxidation of various benzylic alcohols over $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4{}^a$

Entry	Substrate	Product	Reaction time	Conv. of alcohol (%)	Yield (%)	TN[b]
1			80 min	95	94	30
1a	(benzyl alcohol, CH_2OH)	(benzaldehyde, CHO)	80 min	93	92	29
1b			80 min	90	90	27
2	4-Cl benzyl alcohol (CH_2OH, Cl)	4-Cl benzaldehyde (CHO, Cl)	80 min	94	93	29
3	4-CH_3 benzyl alcohol (CH_2OH, H_3C)	4-CH_3 benzaldehyde (CHO, H_3C)	80 min	100	>99	31
4	4-CH_3O benzyl alcohol (CH_2OH, H_3CO)	4-CH_3O benzaldehyde (CHO, H_3CO)	40 min	100	>99	32
5	2-thiophene methanol (S, CH_2OH)	2-thiophene carbaldehyde (S, CHO)	80 min	99	98	31
6	2-pyridine methanol (N, CH_2OH)	2-pyridine carbaldehyde (N, CHO)	6 h	95	94	28
7	1-phenylethanol (OH)	acetophenone (O)	70 min	100	>99	32
8	benzhydrol (OH)	benzophenone (O)	1 h	100	>99	31
9	cyclopropyl phenyl carbinol (OH)	cyclopropyl phenyl ketone (O)	2 h	100	>99	31

^{a} Substrate: 2 mmol; weight of catalyst: 0.3 g; toluene: 5 mL; reaction temperature: 60 °C; oxygen atmosphere. ^{b} TN was definated as a ratio of molar product and molar Ru.

exist and the Ru cations are located at an octahedral coordination site. The existence of the monomeric Ru could be verified by the competitive oxidation of 1-octanol and 4-octanol. When an equimolar mixture of 1-octanol and 4-octanol was used as substrate, 95% 1-octanol and 30%

4-octanol were selectively converted to octanal and 4-octanone (as shown in Fig. 3). The above high chemoselectivity of the Ru doped spinel samples for primary hydroxyl functions is similar to that of monomeric $RuCl_2$-$(PPh_3)_3$ complex[23] and Ru-hydroxyapatites.[22] The coordi-

Table 7   Result of curve-fitting analyses

Catalyst	Shell	Coordination number	Interatomic distance (nm)	$\Delta\sigma^2$ $(nm^2)^a$
$MnFe_{1.95}Ru_{0.05}O_4$	Ru—O	5.12	0.1989	0.00002
$MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$	Ru—O(1)	0.98	0.1879	0.000009
$MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$	Ru—O(2)	4.99	0.2000	0.000027
$RuO_2{}^b$	Ru—O	6.0	0.196	0

$^a\Delta\sigma^2$ is the difference between the Debye-Waller factors of catalysts and RuO_2. ^{b} From the crystallographic data.
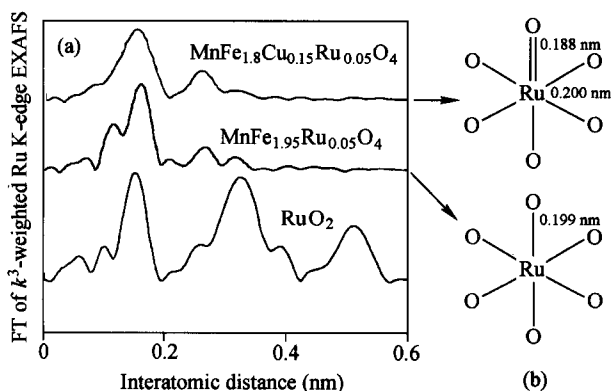

Fig. 2   (a) FT magnitude of k^3-weighted EXAFS of RuO_2, $MnFe_{1.95}Ru_{0.05}O_4$ and $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$; (b) Local environment of Ru.
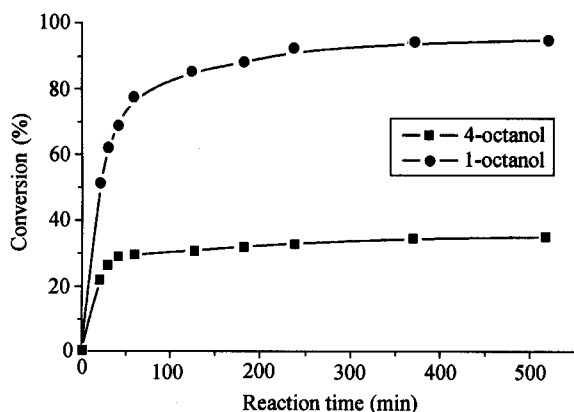

Fig. 3   Competitive oxidation of 1-octanol and 4-octanol over $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$. 1-octanol/4-octanol: 0.50 mmol/0.51 mmol, $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$: 0.5 g, toluene: 5 mL, reaction temperature: 60 ℃, oxygen atmosphere.

nation environment of Ru is shown in Fig. 2(b). It can be seen that the addition of Cu changes one Ru—O to Ru = O. Just the Ru = O bond is selectively active for the alcohols oxidation.[19,24]

From the results of XPS and EXAFS, the chemical factor of enhancement of catalytic activity for the alcohol oxidation is caused by the substitution of Fe for Cu which leads to the transformation of a part of Ru—O bonds to Ru = O bonds.

Reaction mechanism

As to the reaction mechanism, it is assumed that in the *para*-substituted benzyl alcohols, the Hammett ρ value is around -0.9, the oxidation of which likely proceeds through a charge-transfer mechanism.[25] The process of β-elimination is considered to provide the corresponding carbonyl compounds. The reaction mechanism is shown in Fig. 4.
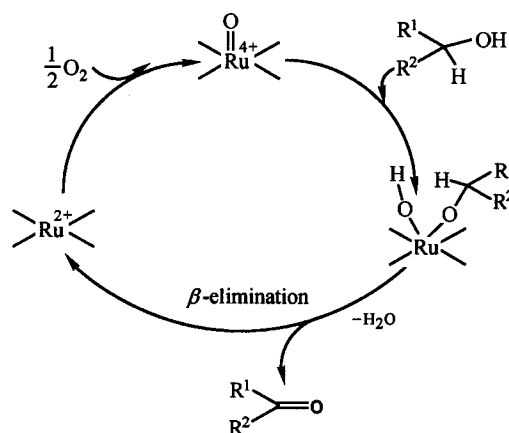

Fig. 4   Reaction mechanism of benzylic alcohol oxidation over $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$.

Conclusions

Spinel catalyst $MnFe_{1.8}Cu_{0.15}Ru_{0.05}O_4$ is an effective heterogeneous catalyst for the oxidation of benzylic alcohols. Ruthenium is an active component for this type of reaction and the importance of the catalyst is due to the transformation of Ru—O bonds to Ru = O bonds caused by the partial substitution of Fe ion for Cu ion.

Acknowledgements

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