

Highly Efficient, Green Oxidation of Alcohols Using Novel Heterogeneous Ruthenium Catalyst

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Abstract: $\text{MnFe}_{1.4}\text{Ru}_{0.45}\text{Cu}_{0.15}\text{O}_4$ was an effective heterogeneous catalyst for the oxidation of various types of alcohols to the corresponding carbonyl compounds using atmospheric pressure of oxygen under mild conditions. Furthermore, this catalyst was also effective towards alcohol oxidation using water as solvent instead of toluene.

Keywords: Alcohol oxidation, ruthenium, heterogeneous reaction, surfactant.

Heterogeneous oxidation of organic compounds using molecular oxygen as oxidant under mild condition is gathering much attentions in synthetic organic chemistry¹. Therefore, the heterogeneous catalysts for alcohol oxidations to the corresponding carbonyl compounds, such as Ru-hydroxycalcite²⁻⁴, Pd-hydroxycalcite^{5,6}, Ni-hydroxycalcite⁷, Ru-hydroxyapatite⁸ and Pd-giant cluster⁹ have been developed. Using partially substituted ferrite spinel by Ru and Cu, $\text{MnFe}_{1.8}\text{Ru}_{0.05}\text{Cu}_{0.15}\text{O}_4$ was proved to be an efficient heterogeneous catalyst¹⁰. In the present paper, we have found that more amount of Ru, *i.e.*, $\text{MnFe}_{1.4}\text{Ru}_{0.45}\text{Cu}_{0.15}\text{O}_4$ catalyst is much more efficient and powerful than other reported solid catalysts for alcohol oxidation. The reaction can be completed in shorter time. Strikingly, this heterogeneous catalyst is also active for alcohol oxidation using water as solvent, which demonstrates that this catalyst is highly environmentally-friendly.

Wet chemical method was used to prepare $\text{MnFe}_{1.4}\text{Ru}_{0.45}\text{Cu}_{0.15}\text{O}_4$ catalyst and the typical example was as follows: 3-neck round bottle flask equipped with a thermometer, reflux condenser and mechanical stirrer were charged with 50 mL deionized water and 372.7 mmol of NaOH pellets. 33.6 mmol of FeCl_3 , 24.0 mmol of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 10.8 mmol of RuCl_3 , 3.6 mmol of $\text{Cu}(\text{NO}_3)_2$, were dissolved in 30 mL of water. The later solution was added dropwise to the first solution while stirring for a period of about 1.5 h. After addition was completed, the resulting solution was programmically heated to 110°C at the rate of 1 °C/min and kept at 110°C for two hours. The cooled mixture was filtered, washed repeatedly with deionized water till neutrality, and dried overnight under air atmosphere at 110°C to afford black powder (7.4 g). [XPS: Mn 2p_{3/2} = 641.2 eV, FWHM = 3.7 eV; Fe 2p_{3/2} = 710.0 eV, FWHM = 4.4 eV; Cu 2p_{3/2} = 932.8 eV, FWHM =

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3.8 eV; Ru 3d_{2/5} = 281.6 eV, FWHM = 2.5 eV.].

A typical procedure for aerobic alcohol oxidation is as follows: into a glass vessel with a reflux condenser were placed MnFe_{1.4}Ru_{0.45}Cu_{0.15}O₄ (0.3 g), cinnamyl alcohol (2.0 mmol), and toluene (5 mL). The resulting mixture was stirred at 60°C for 20 min under atmospheric pressure of O₂. After the reaction, the catalyst was separated by filtration. GC analysis of the filtrate showed a quantitative yield of product. **Table 1** shows a typical result for the oxidation of various alcohols including alkenic alcohols, benzylic alcohols, secondary alcohols and primary alcohol using MnFe_{1.4}Ru_{0.45}Cu_{0.15}O₄ as catalyst at 60°C under atmospheric pressure of O₂. Cinnamyl alcohol and its derivatives can be easily oxidized to give the corresponding α , β -unsaturated aldehydes in high yields with shorter reaction time (entries 1-3). Primary benzylic alcohol was nearly quantitatively converted to the corresponding aldehyde (entries 4-5). Secondary benzylic alcohol was also easily oxidized to the corresponding ketone in high yields (entry 6). This catalyst was also suitable for the oxidation of heterocyclic alcohol such as 2-thiophenemethanol (entry 7). Secondary alcohols including secondary aliphatic and sterically hindered alcohols were also successfully oxidized (entries 8-9). Furthermore, primary alcohol, such as 1-octanol could also be oxidized to octanal in good yield (entry 10). Little conversion of cinnamyl alcohol could be achieved when Ar was used instead of O₂ as oxidative agent.

MnFe_{1.4}Ru_{0.45}Cu_{0.15}O₄ catalyst was easily separated from the reaction mixture and can be reused without loss of activity (entries 1-2 and entries 4-5). Regenerating process is simple. The used catalyst was washed with aqueous 10% Na₂CO₃ and water, drying at 50°C for 12 hours.

Table 1 Aerobic oxidation of various alcohols using MnFe_{1.4}Cu_{0.15}Ru_{0.45}O₄^a

Entry	Substrate	Product	Time (min)	Conv. (%)	Yield (%) ^b
1	cinnamyl alcohol	cinnamaldehyde	20	98	98
2 (reuse)	cinnamyl alcohol	cinnamaldehyde	20	97	97
3	geraniol	citral	60	95	94
4	benzyl alcohol	benzaldehyde	40	95	95
5 (reuse)	benzyl alcohol	benzaldehyde	40	93	93
6	benzhydrol	benzophenone	40	100	100
7	2-thiophenemethanol	2-thiophene-carbaldehyde	40	100	>99
8	2-octanol	2-octanone	120	97	96
9	2-adamantanol	2-adamantanone	90	100	100
10 ^c	1-octanol	octanal	150	84	84

^a Reaction conditions: substrate (2.0 mmol), MnFe_{1.4}Cu_{0.15}Ru_{0.45}O₄ (0.3 g), toluene (5 mL), 60°C, O₂ atmosphere; ^b Yields of aldehydes and ketones were determined by GC analysis using internal standards, based on alcohols; ^c 1-octanol (1 mmol).

Water can be used as solvent, alleviating the pollution by organic solvents. However there are few reports on use of water as solvents in oxidation of alcohol with palladium(II) bathophenanthroline complex as catalyst¹¹. In some cases, surfactants were used to enhance the solubility. In the present study, four types of surfactants, hexadecylpyridium chloride monohydrate (cationic), sodium *n*-dodecylbenzene- sulfonate (anionic), *n*-dodecyltrimethyl(3-sulfopropyl)-ammonium hydroxide (ampho- teric) and

Highly Efficient, Green Oxidation of Alcohols Using Novel Heterogeneous Ruthenium Catalyst 617

Tween #60 (polyoxyethylene sorbitan monostearate) (nonionic) were adopted to increase solubility of benzyl alcohol in water. The decreasing reactive sequence is hexadecylpyridium chloride monohydrate (cationic), Tween #60 (nonionic), *n*-dodecyl-dimethyl (3-sulfopropyl)-ammonium hydroxide (amphoteric), sodium *n*-dodecyl-benzenesulfonate (anionic) and no surfactant. Using hexadecyl-pyridium chloride monohydrate as surfactant, **Table 2** gives the results of the oxidation of various alcohols including alkenic alcohols, benzylic alcohols and secondary alcohols using water as solvent. The reactions proceeded smoothly despite that the reaction time was longer, comparing with using organic solvents as a reaction medium.

Table 2 Aerobic oxidation of various alcohols using deionized water as solvent^a

Entry	Substrate	Product	Time (hr)	Conv. (%)	Yield (%) ^b
1	cinnamyl alcohol	cinnamaldehyde	3	100	>99
2	geraniol	citral	10	94	92
3	benzyl alcohol	benzaldehyde	10	95	94
4 ^c	benzhydrol	benzophenone	3.5	100	99
5	2-thiophenemethanol	2-thiophene-carbaldehyde	2	100	99
6	2-octanol	2-octanone	19	73	70

^a Reaction conditions: substrate (2.0 mmol), MnFe_{1.4}Cu_{0.15}Ru_{0.45}O₄ (0.3 g), surfactant (1.0 mmol), deionized water (5 mL), 60°C, O₂ atmosphere; ^b Yields of aldehydes and ketones were determined by GC analysis using internal standards, based on alcohols; ^c Reaction temperature: 70°C.

The addition of Ru is indispensable. Ru-free catalyst, *i.e.*, MnFe_{1.85}Cu_{0.15}O₄ was prepared to test the catalytic activity for cinnamyl alcohol oxidation. Little conversion of cinnamyl alcohol could be achieved, which showed that Ru is of great importance for the reaction. The activity of MnFe_{1.55}Ru_{0.45}O₄ was also tested. The result showed it was less effective than the catalyst MnFe_{1.4}Ru_{0.45}Cu_{0.15}O₄. It means Cu also played role in this catalyst system.

Considering the reaction mechanism, oxidative dehydrogenation of alcohols *via* Ru-alcoholate species, which undergo β-elimination to afford aldehydes was proposed¹².

In a word, the water suspension of MnFe_{1.4}Ru_{0.45}Cu_{0.15}O₄ is an effective, green catalytic system for alcohol oxidation.

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