

Oxidation of 2,3,5-trimethylphenol to 2,3,5-trimethylbenzoquinone with aqueous hydrogen peroxide in the presence of spinel CuCo_2O_4

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Abstract

The catalytic oxidation of 2,3,5-trimethylphenol was carried out with aqueous hydrogen peroxide over spinel CuCo_2O_4 ; under the mild conditions, this study realized 80% selectivity for 2,3,5-trimethylquinone at 100% conversion of 2,3,5-trimethylphenol. The catalyst was investigated by XRD, TEM, UV–vis and FT-IR; and the reaction has been studied by different parameters like performance of different catalysts, effect of aqueous hydrogen peroxide, reaction time, reaction temperature, solvents, catalyst concentration, catalyst separation, and recycling of catalyst. Compared to the conventional methods, this method could be more eco-friendly.

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1. Introduction

Selective oxidation of phenols with hydrogen peroxide is one of the attractive problems from the synthetic viewpoint as well as in biological oxygenation [1], and it is well known that quinones possess pronounced bioactivity, consequently, are important for medicinal applications [2]. 2,3,5-Trimethyl-1,4-benzoquinone (TMQ), as an important intermediate, is used to synthesize Vitamin E, and it stems from the oxidation 2,3,5-trimethylphenol (TMP) or 2,3,6-trimethylphenol (Scheme 1). Several heterogeneous [3–9] and homogenous [10–13] catalysts are extensively used; at the same time, various organic solvents were used in these literatures. Among which CuCl_2 is most favored when it was used as catalyst with equimolar amount of TMP. Takehira [14] and Bodnar et al. [15] reduced the amount of the catalyst by applying nitrogen-containing organic compounds as co-catalysts, but the co-catalysts were partly consumed in the reaction system. Furthermore, the sound control of metal leaching is difficult in the oxidation TMP over heterogeneous catalysts [3–9].

In recent years, studies of various mixed metal oxides with the spinel structure have increased their applicability to serve

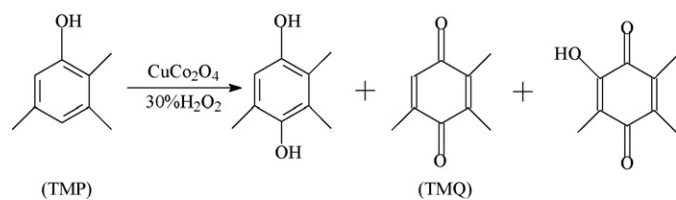
as suitable substitutes for noble metal catalysts in a variety of areas. Thus, they have been extensively proposed as catalysts for many reactions, including hydrocarbon oxidation [16,17], pollution control [18], and water gas shift reaction [19]. Moreover, spinel is highly resistant to dissolution even though in acidic fluids [20–22]. However, to the best of our knowledge, there is no report that CuCo_2O_4 was used for catalytically oxidizing TMP to TMQ. In our study, it was found that TMP would be oxidized high effectively to TMQ under mild conditions over spinel CuCo_2O_4 prepared by the sol–gel technique, both the highest yield for TMQ and conversion of TMP are achieved. And there is no metal leaching of CuCo_2O_4 in this reaction.

2. Experimental

2.1. Catalyst preparation

The CuCo_2O_4 was prepared by sol–gel method using inorganic salts. Aqueous solution of $\text{Cu}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$ and citric acid was prepared separately and then mixed with the molar ratio of citric acid: $\text{Co}(\text{NO}_3)_2$: $\text{Cu}(\text{NO}_3)_2 = 3:2:1$. The pH of the mixture solution was not additionally adjusted. The above solution were first kept in a water bath at 60 °C until gelatin was completed, and then the as-prepared gels was dried at 80 °C for 8 h and calcined at 400 °C for 4 h. The mono-component CuO and Co_3O_4 were prepared by the same procedures.

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2.2. Catalytic oxidation procedure

The catalytic oxidation reactions of TMP were performed in a 100 ml three-necked flask equipped with reflux condenser, magnetic stirrer, super constant temperature oil bath and thermometer. In a typical reaction, TMP (1 mmol) and CuCo_2O_4 were placed in the reactor, and then the 30% H_2O_2 (10 mmol) was added into the acutely stirred mixture at room temperature (25 °C). The selectivities and conversions were determined by gas chromatography.

2.3. Physical measurements

The crystalline structure of the catalyst was analyzed by using a DMAX-2500 Diffractometer with $\text{Cu K}\alpha$ radiation. The working voltage and current of the X-ray tube were 40 kV and 100 mA. Low temperature (−196 °C) absorption of nitrogen was performed by a sorptometer ASAP 2010 made by Micromeritics. The surface area was established by the BET method. The UV–vis spectra of CuO , Co_3O_4 and CuCo_2O_4 were performed with a TU-1901 UV–vis spectrophotometer using a quartz cell. IR studies were carried out on a Perkin-Elmer system 2000 FT-IR spectrophotometer with a resolution of 2 cm^{-1} . GC analyses were performed using a gas chromatograph (GC-2010, Shimadzu) equipped with a flame ionization detector and quartz capillary column ($25\text{ m} \times 0.3\text{ mm}$) filled with Carbowax 20M. GC–MS analyses of organic products were conducted using a HP 5973/6890 system (electron impact ionization at 70 eV, He carrier gas, $30\text{ m} \times 0.25\text{ mm}$ cross-linked 5% PHME siloxane ($0.25\text{ }\mu\text{m}$ coating) capillary column; HP-5MS) or a VG-7070 instrument.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the powders obtained after calcining the CuCo_2O_4 gel precursor in air at 400 °C for 4 h are shown in Fig. 1 in 2θ range of 10–90°. From the Fig. 1, we can see that the XRD pattern of CuCo_2O_4 shows the typical spinel structure [23], X-ray diffraction studies showed that the sample had a very pure cubic spinel structure and did not contain CuO . The BET surface of CuCo_2O_4 is $67.5\text{ m}^2\text{ g}^{-1}$. The microstructure examinations were obtained by transmission electron microscopy (TEM), Fig. 2 indicated the size of CuCo_2O_4 is the range of 40–80 nm. And Fig. 3 shows the UV–vis absorption spectra of CuCo_2O_4 , CuO and Co_3O_4 . From the Fig. 3, we can see that both CuCo_2O_4 and Co_3O_4 have an absorption peak

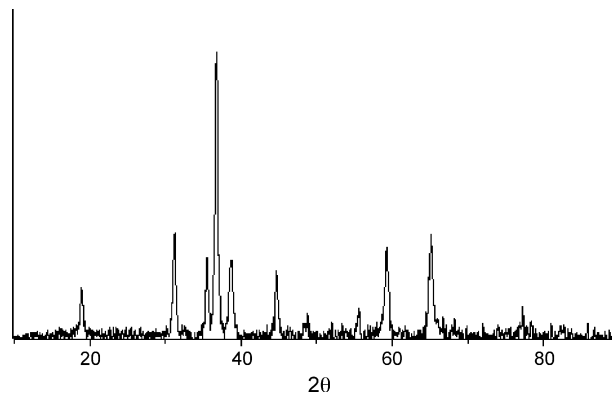


Fig. 1. XRD of CuCo_2O_4 .

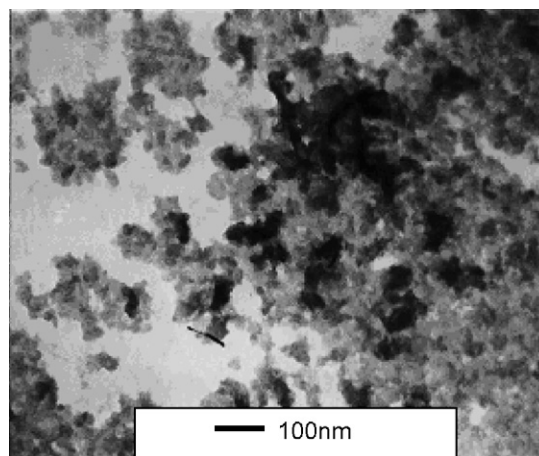


Fig. 2. TEM of CuCo_2O_4 .

at approximately 210 nm which agrees with the structure of nano-spinel, but the UV–vis spectra of CuO had not absorbed at the same regions. Fig. 4 presents FT-IR spectra of CuO , Co_3O_4 and CuCo_2O_4 . In the investigated region ($4000\text{--}500\text{ cm}^{-1}$), it is believed the broad peaks at 3455, 3448, 3429, 1634 and 1633 cm^{-1} can be attributed to the surface-adsorbed water and

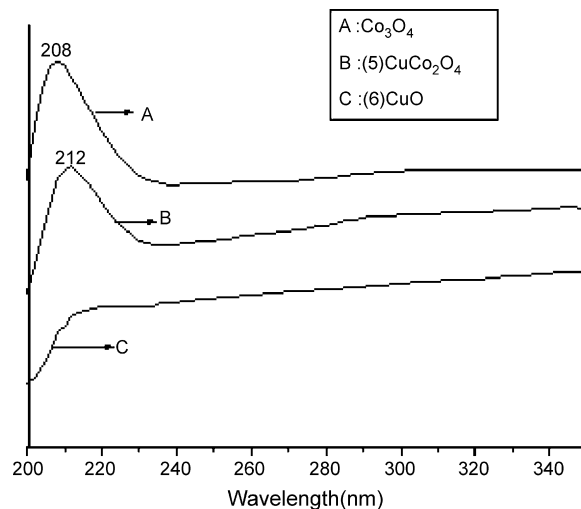


Fig. 3. UV–vis absorption spectra of CuCo_2O_4 , CuO , and Co_3O_4 .

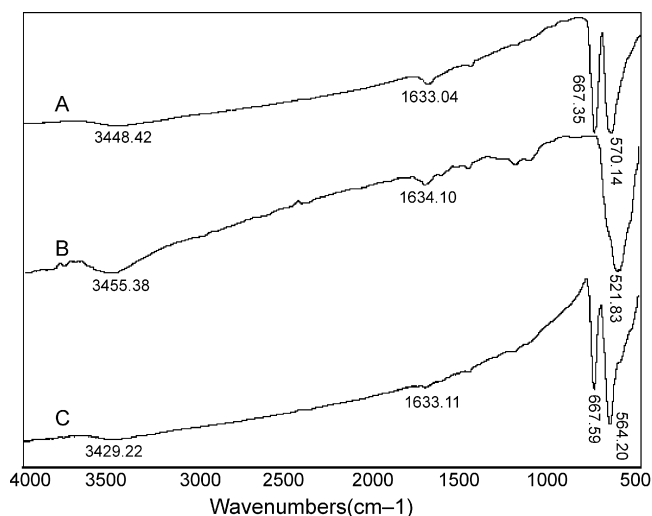


Fig. 4. FT-IR spectra of CuCo_2O_4 , CuO and Co_3O_4 (A: Co_3O_4 ; B: CuO ; C: CuCo_2O_4).

hydroxyl groups [24–26]. Furthermore, the FT-IR spectra of CuCo_2O_4 , and Co_3O_4 reveal two remarkable keen-edge peaks in the range of $1000\text{--}500\text{ cm}^{-1}$, these are contribution from the spinel phase [27], but CuO had only one. From the spectroscopic experiments, we can conclude that CuCo_2O_4 is a typical nano-spinel, and these spectroscopic data indicates CuCo_2O_4 is not a mixture of CuO and Co_3O_4 or CuO and Co_2O_3 but a complexity.

3.2. Catalytic oxidation of 2,3,5-trimethylphenol

3.2.1. Performance of different catalysts

The catalytic performance of different catalysts for the oxidation of TMP by H_2O_2 was compared under the same conditions in Table 1. A blank run without catalyst gave no products. Single component catalysts exhibit lower activity and selectivity than bimetallic catalyst; in the single component catalysts, Co_3O_4 showed the highest conversion while CuO exhibited the highest selectivity. However, not only the conversion of TMP but also the selectivity of TMQ remarkably improved when the CuCo_2O_4 was acted as the catalyst under the same conditions. Interestingly, the mono-component of CuO or Co_3O_4 did not exhibit any meaningful activity, but the CuCo_2O_4 showed extremely high conversion and good selectivity of 2,3,5-trimethylbenzoquinone at room temperature ($25\text{ }^\circ\text{C}$). Variations in performance are partly due to the difference in the activation energies of exchange in active oxygen which roots in $30\% \text{H}_2\text{O}_2$. Low activation ener-

Table 1
Oxidation of TMP over various catalysts

Catalyst	Conversion of TMP (mol%)	Selectivity of TMQ (mol%)
–	0.0	0.0
CuO	1.7	24.0
CuCl_2	2.4	21.1
Co_3O_4	4.6	10.5
CuCo_2O_4	32.9	87.6

Reaction conditions: 1 mmol TMP, 0.01 mmol catalyst, 10 mmol $30\% \text{H}_2\text{O}_2$, reaction time: 6 h, reaction temperature: room temperature ($25\text{ }^\circ\text{C}$).

Table 2
Oxidation of TMP under the various pattern of added hydrogen peroxide

Addition pattern of H_2O_2	Conversion of TMP (mol%)	Selectivity of TMQ (mol%)	Other products (mol%) ^a
One-off	32.9	87.6	12.4
Two times ^b	64.7	85.4	14.6
Three times ^c	95.0	83.3	16.7
Dope wise	100.0	80.0	20.0

Reaction conditions: 1 mmol TMP, 0.01 mmol CuCo_2O_4 , 10 mmol $30\% \text{H}_2\text{O}_2$, reaction time: 6 h, reaction temperature: room temperature ($25\text{ }^\circ\text{C}$).

^a Other products: 2,3,5-trimethyl-hydroquinone and 2-hydroxyl-3,5,6-trimethyl-1,4-benzoquinone.

^b $30\% \text{H}_2\text{O}_2$ was added every 2 h.

^c $30\% \text{H}_2\text{O}_2$ was added every 1 h.

gies result in a high oxygen supply ability. The literature data [28] on oxygen isotopic exchange give the sequence of oxygen supply ability as $\text{Co}_3\text{O}_4 > \text{MnO}_2 > \text{CuO}$. The oxidation reaction requires a reasonable activation match of the C–H and C–H of TMP and oxygen *via* interaction with the catalyst active site. The electrophilic oxygen tend to accumulate on the surface of cobalt ion of the CuCo_2O_4 catalyst, which enhances the probability of electrophilic attack on the C–OH bond of 2,3,5-trimethyl-hydroquinone. And cobalt as an assistant to copper improves the oxygen exchange between bulk phase and the catalyst surface by accelerating the valence transformation of copper. Furthermore highly activity of CuCo_2O_4 is possibly related to special $\text{Cu}_{2p}\text{--Co}_{2p}$ structure [29–31].

3.2.2. Effect of aqueous hydrogen peroxide

During the oxidation of TMP, it was found that the added mode of aqueous hydrogen peroxide would be effected seriously the conversion of TMP and the selectivity of TMQ (Table 2). When aqueous hydrogen peroxide was added to the reactant system one-off, the conversion of TMP was lower than others, although the selectivity of TMQ was most; while H_2O_2 (30%) was doped wise, the conversion of TMP added up to 100% and the selectivity of TMQ also arrived at 80.0% . This is due to the high catalytic activity of CuCo_2O_4 , the aqueous hydrogen peroxide was quickly decomposed when it was added one-off. The density of H_2O_2 was lower than others while it was doped wise, so the decomposition rate of H_2O_2 would be minished and the utilization of it was remarkably improved. Compared to RuCl_3 , the CuCo_2O_4 catalyst is more inexpensive, and suitable for large-scale production under the same conditions; at the same time, the selectivity of TMQ is more remarkable than Cu, Fe or Mo salts [13].

3.2.3. Influence of solvents

The influence of solvent is summarized in Table 3. When no organic solvent was added, the conversion of TMP and the selectivity of TMQ added up to 100% and 80.0% ; and the selectivity of TMQ increased to 87.4% while the conversion of TMP was not obviously dropped when acetic acid was added in the reaction system, but the catalyst was partly dissolved; while acetonitrile and ethanol was added in the same reaction system, not only the conversion of TMP but also the selectivity TMQ were reduced. However, the selectivity of TMQ increased

Table 3
Influence of solvents

Solvent (ml)	Conversion of TMP (mol%)	Selectivity of TMQ (mol%)
–	100.0	80.0
CH ₃ COOH (0.5)	99.5	87.3
CH ₃ COOH (1.0)	99.6	87.4
CH ₃ COOH (2.0)	99.8	87.2
CH ₃ COOH (5.0)	99.5	87.3
CH ₃ CN (0.5)	10.7	78.7
CH ₃ CN (1.0)	5.9	77.5
CH ₃ CN (2.0)	1.2	74.6
CH ₃ CH ₂ OH (0.5)	100.0	81.8
CH ₃ CH ₂ OH (1.0)	100.0	85.0
CH ₃ CH ₂ OH (2.0)	77.0	80.0
CH ₃ CH ₂ OH (5.0)	22.5	57.1
CH ₃ COCH ₃ (0.5)	6.9	60.5
CH ₃ COCH ₃ (1.0)	2.8	61.3
CH ₃ COCH ₃ (1.0)	<0.1	67.4

Reaction conditions: 1 mmol TMP, 0.01 mmol catalyst, 10 mmol 30% H₂O₂, reaction time: 6 h, reaction temperature: room temperature (25 °C).

to 85.0% when ethanol was acceded to the reaction system. But the catalytic activity of CuCo₂O₄ reduced when ethanol was added excessively, the conversion of TMP and the selectivity TMQ also reduced because of increasing the amount of ethanol blocked the oxidation reaction. Moreover, acetone was found less effective and only 6.9 mol% conversion of TMP was obtained. The observed differences from acetic acid to acetone may be attributed to the difference in polarities of the solvent [32]. These also indicate the CuCo₂O₄ is more inhydrophobicer than other heterogeneous [3–9] catalysts. So organic-solvent-free would be optimum considering economy factor and environments.

3.2.4. Influence of reaction time

Fig. 5 displays the effect of reaction time on TMP reaction over CuCo₂O₄ at room temperature (25 °C). It is seen that the

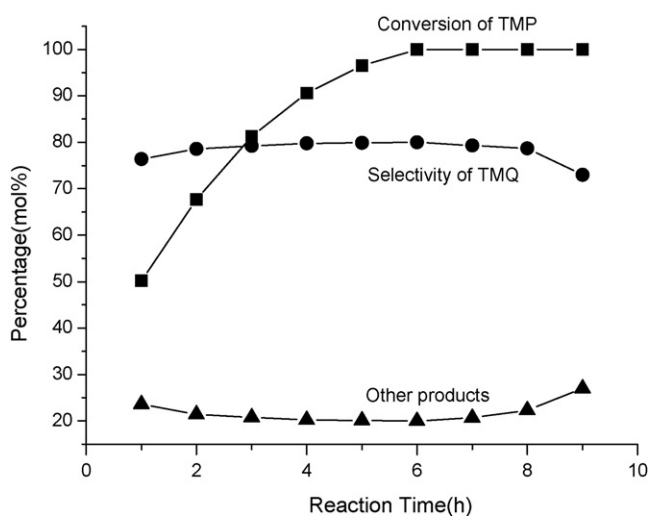


Fig. 5. Effect of reaction time on the conversion and selectivity over CuCo₂O₄ (reaction conditions: 1 mmol TMP, 0.01 mmol CuCo₂O₄, 10 mmol 30% H₂O₂, reaction temperature: room temperature (25 °C)).

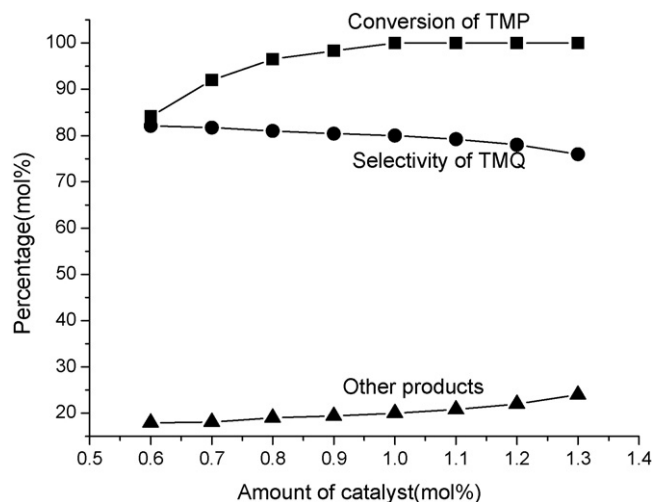


Fig. 6. Effect of catalyst concentration on the conversion and selectivity over CuCo₂O₄ (reaction conditions: 1 mmol TMP, 10 mmol 30% H₂O₂, reaction time: 6 h, reaction temperature: room temperature (25 °C)).

rate of TMP conversion steeply increases with increase in reaction time up to 6 h and the selectivity of TMQ also slightly increases. The reaction time is longer than 6 h, the conversion of TMP was add up to 100% whereas the selectivity of TMQ decreased a little, which suggests that more 2-hydroxyl-3,5,6-trimethyl-1,4-benzoquinone would be produced. So we suggest that 6 h is suitable reaction time.

3.2.5. Effect of catalyst concentration

The effect of catalyst concentration on TMP reaction over CuCo₂O₄ was also investigated and depicted in Fig. 6. The different ratios of catalyst to TMP were obtained by varying the amount of the catalyst and keeping the concentration of TMP constant. An increase in conversion of TMP was observed when the amount of the catalyst was increased up to 1 mol%, beyond this amount, the conversion of TMP levelled off in the reaction system (up to 100%). While the selectivity of TMQ was obviously reduced when the amount of catalyst was exceeded 1 mol%. In most literatures [3–15], however, the used amount of catalysts is excesser than 1 mol%. Therefore, 1 mol% would be the optimum catalyst amount used for the selectively producing TMQ.

3.2.6. Effect of reaction temperature

The catalytic activity of CuCo₂O₄ on the reaction temperature was investigated in the temperature range 5–65 °C (Fig. 7). The conversion of TMP was found to increase with increase in reaction temperature and passes through a maximum at 25 °C. A further increase in the reaction temperature caused decreases in the conversion of TMP, probably owing to a greater decomposition of H₂O₂ under the CuCo₂O₄ as catalyst at higher temperature. Moreover, at a temperature lower than 25 °C, the selectivity for the desired product, 2,3,5-trimethyl-1,4-benzoquinone, was lowered due to the more formation of 2,3,5-trimethyl-hydroquinone. On the other hand, at a temperature higher than 25 °C, formation of 2-hydroxyl-3,5,6-trimethyl-1,4-benzoquinone became

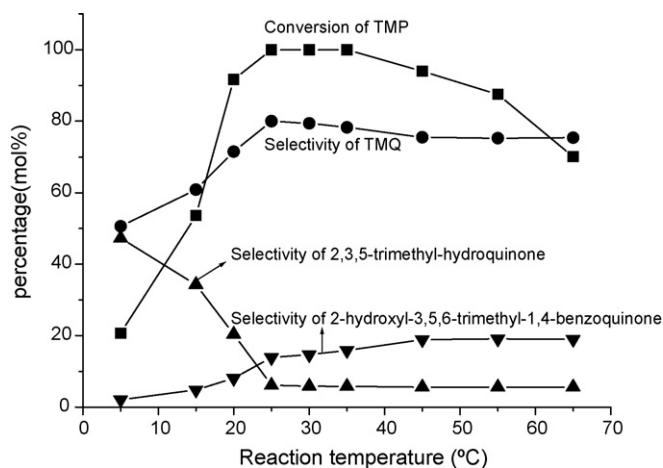


Fig. 7. Effect of reaction temperature on the conversion and selectivity over CuCo_2O_4 (reaction conditions: 1 mmol TMP, 10 mmol 30% H_2O_2 , reaction time: 6 h).

remarkable. These results may suggest the consecutive oxidation of 2,3,5-trimethylphenol via 2,3,5-trimethyl-hydroquinone, 2,3,5-trimethyl-1,4-benzoquinone and finally 2-hydroxyl-3,5,6-trimethyl-1,4-benzoquinone. Therefore the temperature of 25 °C has been demonstrated to be satisfactory.

3.2.7. Influence of catalyst separation

In order to check whether the TMP conversion proceeds through heterogeneous or homogeneous catalysis, the reaction was carried out for 2 h using CuCo_2O_4 catalyst. The results and reaction conditions are listed in Fig. 8. The catalyst was separated from the reaction mixture after 3 h, copper and cobalt contents of the solution were estimated by AAS. Further the reaction was carried out using the separated reaction mixture without the solid catalyst and compared with a reaction mixture containing the CuCo_2O_4 catalyst. The results of catalyst separation experiment revealed that no conversion of TMP was observed when the catalyst was separated from the reaction mix-

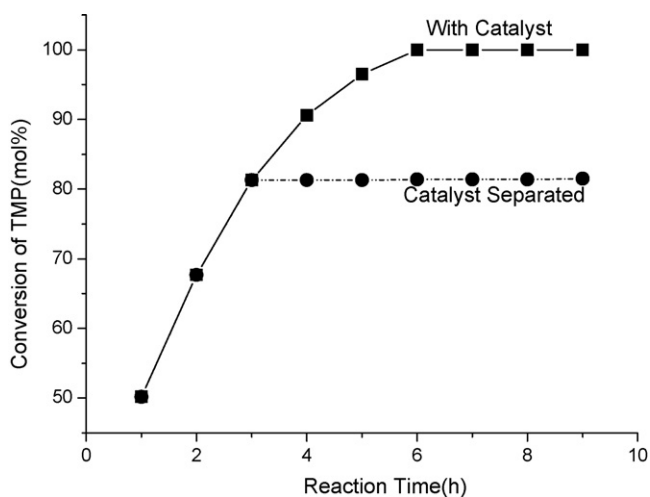


Fig. 8. Effect of CuCo_2O_4 separation on the conversion of TMP (reaction conditions: 1 mmol TMP, 0.01 mmol CuCo_2O_4 , 10 mmol 30% H_2O_2 , reaction temperature: room temperature (25 °C)).

Table 4
Recycling of CuCo_2O_4

Run	Conversion of TMP (mol%)	Selectivity of TMQ (mol%)	Others
1	100.0	80.0	20.0
2	99.7	80.6	19.4
3	99.8	80.4	19.6
4	100.0	80.1	19.9
5	99.8	80.5	19.5

Reaction conditions: 1 mmol TMP, 0.01 mmol catalyst, 10 mmol 30% H_2O_2 , reaction time: 6 h, reaction temperature: room temperature (25 °C).

ture. Therefore, copper and cobalt were not found leaching out from CuCo_2O_4 during 3 h of run by AAS measurements. The results obtained in the experiments suggest that CuCo_2O_4 act as a heterogeneous catalyst in the reaction.

3.2.8. Recycling of the catalyst

CuCo_2O_4 sample used in the oxidation of TMP was recycled five times in order to check the activity and stability of the catalyst. After reaction of each cycle, the catalyst was filtered off, washed with ethanol and dried at 120 °C in the presence of air for 2 h. The reaction was then carried out on the activated recycled catalyst at room temperature (25 °C) under the optimum condition. Table 4 lists the results of these experiments. It was found that CuCo_2O_4 shows a steady activity after successive cycling (runs 2–5). In order to check the structure of the catalyst after each reaction, XRD patterns were recorded and indicated that the catalyst retains the spinel structure; and copper and cobalt metal of the CuCo_2O_4 estimated by AAS were not leached. The present study indicates the catalyst can be recycled a number of times without losing its activity to a greater extent.

4. Conclusions

In conclusion, CuCo_2O_4 synthesized by sol–gel method using inorganic salts presented highly conversion (100%) and reasonable selectivity (80%) of catalytic oxidation of TMP to TMQ using aqueous hydrogen peroxide as oxidant for the first time. The rate of TMP conversion and the yield of the products largely depend on the experimental conditions. The catalyst separation experiments confirm that CuCo_2O_4 acts as a heterogeneous catalyst in the reaction. Recycling of the catalyst indicates that catalyst is stable after some cycles and can be used as a number of times without losing its activity to a greater extent. Compared to the conventional methods, this method could be more eco-friendly, and its applications in the selective oxidation of other similar compounds are underway.

Acknowledgements

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