

Heterogeneous catalysis in the liquid phase oxidation of alcohols by Cu(II) complexes immobilized between silicate layers of bentonite

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Abstract

Immobilized Cu(II) complexes with ligands of 2,2'-bipyridine (bpy), ethylenediamine (en), *N,N'*-ethylenebis (salicylideneamine) (salen) and acetylacetonate (acac), were used for oxidation of alcohols such as cyclohexanol, hexanol, benzyl alcohol and trans-2-hexene-1-ol with *tert*-butylhydroperoxide (TBHP) as oxidant. The high conversion percentage of cyclohexanol about 98% with 100% selectivity toward the formation of cyclohexanone with [Cu(bpy)₂]⁺²/bentonite is remarkable.

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1. Introduction

The search for new catalysts is one of the most important topics connected with both industrial and academic research. The oxidation of alcohols to aldehydes or ketones is a vital reaction in synthetic organic chemistry. In this way chemists have used different kinds of metals salts and oxides in the form of homogeneous catalysts [1–5] or supported metal ions [6–10] and supporting oxometal catalysts [11,12] as heterogeneous systems. Supported metal ions and their complexes in zeolites or layered silicates such as bentonite and montmorillonite are significantly important due to

drastic change in the reactivity and specially selectivity toward a desirable product [13,14]. For example, the K10 clay supported iron(II) nitrate (clayfen) or potassium ferrate and Cu(II) nitrate (claycop) have been used as catalyst in the oxidation of alcohols [15,16] and oxidative coupling of thiols [17], respectively. Zeolite encapsulated metal ion complexes are also active for oxidation of alcohols [18]. In general, there have been many attempts to carrying out the reactions with high yield and selectivity. Since we realized that it is possible to obtain a rather simple oxidation catalyst by immobilization of some Cu(II) complexes on bentonite, we decided to investigate the oxidation of some alcohols to their corresponding carbonyls with *tert*-butylhydroperoxide (TBHP) under the effect of these catalysts.

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2. Experimental

2.1. Materials

All materials were of commercial reagent grade. Bentonite (Fluka) was activated with 1 M solution of sodium nitrate before using.

2.2. Preparation of catalysts

2.2.1. Preparation of Cu^{2+} -bentonite catalysts

Six grams of Na-bentonite was slowly added to 100 ml of 0.1 M solution of Cu(II) chloride in methanol. The suspension was then stirred for 24 h at room temperature. The colored solid was filtered, washed with methanol and dried at 50 °C under vacuum.

2.2.2. Preparation of Cu(II) complexes included in bentonite: general procedure

These catalysts were prepared according to the procedure described previously [19]. To prepare the catalyst, 1 g of Cu/bentonite was added to a solution of 2.176 mmol of ligands 2,2'-bipyridine (bpy) or ethylenediamine (en) in 100 ml methanol. To prepare the catalyst with ligands *N,N'*-ethylenebis (salicylideneamine)(salen) and acetylacetonate (acac), 1 g of Cu/bentonite was added to a solution of 1.088 mmol of salen or 2.176 mmol of acac and 2.176 mmol NaOH in 100 ml methanol. The suspension was then heated under reflux condition for 24 h. The solid was separated, washed with methanol and then Soxhlet extracted with a mixture of 1:1 methanol and chloroform in order to remove unreacted ligands. It was then dried at 125 °C under nitrogen atmosphere for several hours.

2.3. Oxidation of alcohols: general procedure

A mixture of 0.5 g catalysts and 30 mmol of cyclohexanol was stirred under nitrogen at 50 °C for 30 min. Then 14 mmol of TBHP solution in di-*tert*-butylperoxide was added. The resulting mixture was then refluxed for 8 h under nitrogen atmosphere. After filtration, the solid was washed with methylene chloride. The products then subjected to GC and GC-mass analysis using a Philips pu-4400 chromatograph (1.5 m, 3% OV-17 column), varian

Table 1

Oxidation of cyclohexanol with TBHP in the presence of Cu complexes immobilized in bentonite^a

Catalyst	Conversion (%) ^b	Selectivity (%) ^c
Bentonite	27.5	100
Cu/bentonite	41.5	100
[Cu(salen)]/bentonite	48	100
[Cu(acac) ₂]/bentonite	55	100
[Cu(en) ₂] ²⁺ /bentonite	85	100
[Cu(bpy) ₂] ²⁺ /bentonite	>98	100

^a Time: 8 h, amount of Cu: 65 mg/g bentonite.

^b The concentrations were determined using internal standard procedure.

^c The concentrations were determined using internal standard procedure.

Table 2

Effect of the amount of Cu in the oxidation of cyclohexanol^a

Catalyst	Amount of Cu (mg/g bentonite)	Conversion (%)	Selectivity (%)
Cu/bentonite	65	41.5	100
[Cu(bpy) ₂] ²⁺ /bentonite	65	>98	100
Cu/bentonite	95	90	100
[Cu(bpy) ₂] ²⁺ /bentonite	95	>98	100

^a Time: 8 h.

3400 chromatograph (2.5 m, DB-5 column) coupled with a QP finnigan MATINCOF 50, 19 ev., respectively.

3. Results and discussion

In the preliminary phases, the reactivity of a model compound, the secondary cyclohexanol was examined under a variety of experimental conditions, Tables 1–3. Table 1 shows the results of the oxidation of cy-

Table 3

Effect of the time in the oxidation of cyclohexanol^a

Catalyst	Time (h)	Conversion (%)	Selectivity (%)
Cu/bentonite	2	16	100
[Cu(bpy) ₂] ²⁺ /bentonite	2	80	100
Cu/bentonite	8	90	100
[Cu(bpy) ₂] ²⁺ /bentonite	8	>98	100

^a Amount of Cu: 95 mg/g bentonite.

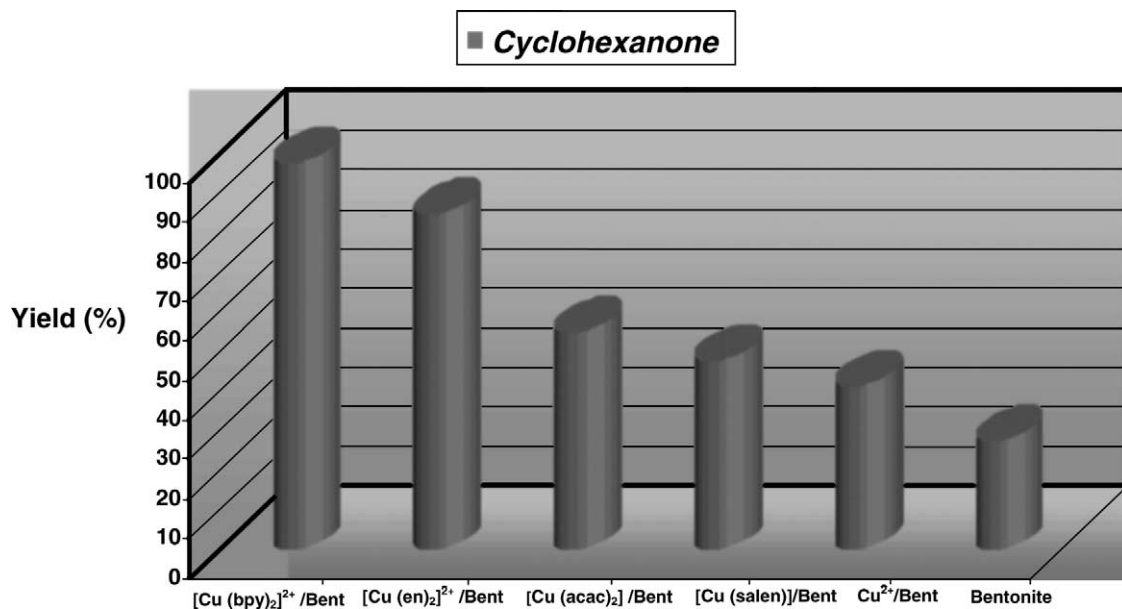


Fig. 1. Oxidation of cyclohexanol with TBHP in the presence of Cu complexes immobilized in bentonite.

clohexanol with TBHP in the presence of bentonite with or without immobilized Cu²⁺ complexes. The determining role played by the immobilized Cu²⁺ or its complexes in bentonite is seen in Table 1 which shows the conversion percentages enhancement from 27.5 to more than 98 in the presence of bentonite and [Cu(bpy)₂]²⁺/bentonite, respectively (Fig. 1). The formation percentage of cyclohexanone is 100% no matter what kind of catalysis system is used.

To study the effect of the amount of Cu²⁺ complexes and the reaction time, we examined the catalysis systems with the least and the most activities. It can be seen that if one chooses the same amount of 95 mg Cu²⁺ per each gram of bentonite for either system, cyclohexanone is formed with about 8% difference in these cases (Table 2). Therefore, the observation of indistinguishable conversion percentages in other cases is not unexpected. When the upper limit of the amount of Cu²⁺ with different reaction times were performed, it became clear that the discriminating results would be obtained if the reaction time is 2 h (Table 3).

The oxidation of three other primary alcohols of the type of aliphatic, allylic and benzylic with TBHP was

investigated under the best conditions (Table 4 and Fig. 2). With the exception of trans-2-hexene-1-ol, which partly undergoes further oxidation, the performance of the methodology to these alcohols has afforded satisfactory results. The further oxidation of allylic aldehyde system to the carboxylic acid and the formation of ester under the reaction conditions might have arisen from the existence of the trace amount of water molecules left inside the bentonite, even though it was dried in oven at 50 °C for 24 h. Water is a necessary reactant for at least one of the mechanistic

Table 4
Effect of the [Cu(bpy)₂]²⁺/bentonite catalyst in the oxidation of other alcohols^a

Alcohol	Conversion (%)	Product	Selectivity (%)
Hexanol	42	Hexanal	100
Benzyl alcohol	55	Benzaldehyde	100
		Trans-2-hexenal	67
Trans-2-hexene-1-ol	57	2-Hexenyl-2-hexenoate	33

^a Alcohol = 30 mmol, TBHP = 14 mmol, reflux temperature.

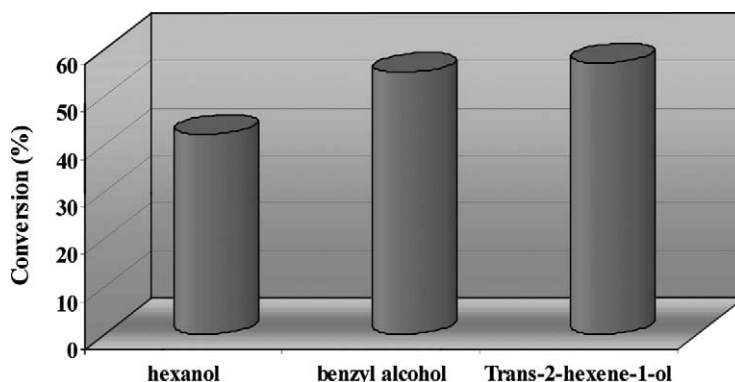


Fig. 2. Oxidation of alcohols with TBHP in the presence of $[\text{Cu}(\text{bpy})_2]^{2+}/\text{bentonite}$.

pathways for the conversion of an aldehyde to an acid [20].

Comparison of our results with those obtained on the oxidation of the secondary benzylic alcohols with TBHP either in the presence of K10-montmorillonite or 4A molecular sieves clearly indicate that our system is more efficient because of the presence of transition metal complexes immobilized between silicate layers. In the absence of metal complexes, the reaction suffers from the disadvantage of higher reaction time [21]. The more activity of our catalysis system has clearly arisen from the existence of electron donating ligands which facilitate the electron transfer rate, a process that has previously observed by us in other oxidation reactions [22,23]. This effect is increased in the case of aromatic bipyridin ligand, which leads to the highest oxidation conversion percentages.

4. Conclusion

In summary, we have shown that copper bipyridin complex exchanged with bentonite coupled with TBHP, as oxidant is a very active catalyst for the oxidation of alcohols. The high conversion percentage of about 98% with 100% selectivity toward the formation of cyclohexanone, which is the precursor of caprolactam, an important raw material for the production of synthetic fibers is remarkable. Finally, The mild conditions, easy working up and the successful accuracy of one stage oxidation in primary alcohol systems are promising.

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