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Mixed metal oxide catalysts for the selective oxidation of ethylbenzene to acetophenone

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Abstract

MgAl and MgMAl oxides (M = Co, Ni and Cu) with a Mg:M:Al molar ratio = 4:1:1 were synthesized from the calcination of their corresponding layered double hydroxide (LDHs) precursors. Their catalytic activities were examined for the oxidation of ethylbenzene using *tert*-butylhydroperoxide (TBHP) as an oxidant. The oxidized product was mainly acetophenone. The catalytic activities were in the order of MgCuAl > MgNiAl ~ NiAl ~ MgCoAl ~ CoAl > CuAl > MgAl oxides. Reusability studies show that the catalysts are stable under the reaction conditions.

Keywords: Ethylbenzene; Oxidation; Mixed metal oxides

Acetophenone is used as a component of perfumes and as an intermediate for the manufacture of pharmaceuticals, resins and alcohols. Its current industrial production is based on the oxidation of ethylbenzene with molecular oxygen in acetic acid using cobalt acetate as the catalyst [1]. However, oxidation of ethylbenzene by homogeneous catalysts gives rise to problems of catalyst recovery and recycling [2,3]. It is therefore of great practical interest to develop a more efficient, reusable, and environmentally friendly catalyst. Toward this end, permanganate or dichromate can be replaced by cleaner oxygen- or peroxide-based oxidants. Indeed, heterogeneous catalysts using O_2 [4–6], H_2O_2 [7] or TBHP [8,9] have been reported. TBHP should be regarded as being preferable to molecular oxygen as molecular oxygen-organic mixtures sometimes ignite [10].

The catalysts to be employed herein involve high surface area mixed transition metal oxides. These may have oxidative or reductive properties, and can be obtained by controlled thermal decomposition of their layered double hydroxides (LDHs), $(M(II)_{1-x}M(III)_x(OH)_2)^{x+}(A_{n-x/n})^{x-}\cdot mH_2O$, for which M(II) and M(III) are divalent and trivalent metal cations, and A is an n-valent anion.

In this work we report the solvent-free, liquid phase oxidation of ethylbenzene catalyzed by the above heterogeneous catalysts using the clean oxidant, TBHP. The activities of the various catalyst systems are compared.

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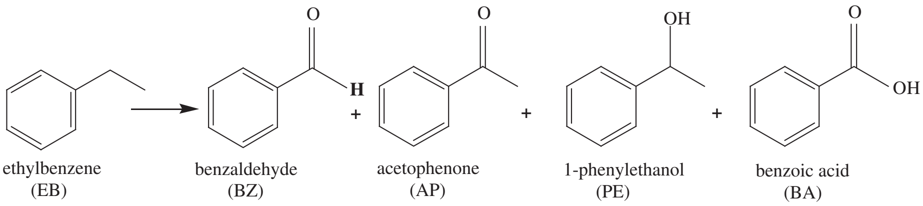
1. Experimental

A mixture consisting of $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and metal nitrate was prepared, having a Mg:M:Al molar ratio of 4:1:1, from their 0.06 mol/L solutions, and the mixture was heated to 65 °C. To this a mixed solution of 0.6 mol/L NaOH and 0.06 mol/L Na_2CO_3 was added dropwise with constant and uniform stirring to maintain a constant pH of 10. The precipitate was maintained at 65 °C for 18 h. The precipitate was then filtered, washed and dried at 110 °C for 12 h and calcined at 500 °C for 5 h.

Catalytic tests were carried out in a magnetically stirred stainless steel reactor. Ethylbenzene (1.2 mL, 10 mmol) and the catalyst (0.2 g) were added, followed by 70% aqueous TBHP as the oxidant in an amount necessary to yield the desired EB/TBHP molar ratio. The reaction times and temperatures were varied. The catalysts were separated by centrifugation and the products were analyzed by GC. For the reusability tests, the catalysts were removed from the reaction mixtures, washed with acetone, and calcined at 500 °C for 5 h. Fresh ethylbenzene was then employed in the repeated testings.

2. Results and discussion

The analyzed Mg:M:Al atomic ratios (by ICP), BET surface areas and phases (by XRD) of the mixed metal oxides are shown in Table 1. LDH precursors were found to have been transformed into their corresponding oxides, or into spinel phases [11] with other metal oxides in some cases [12,13]. The activities of all catalysts were tested under the same reaction conditions and compared to simple metal oxides (MgO, NiO, Co_3O_4 and CuO). The main product from the oxidation of ethylbenzene with TBHP was acetophenone with only small amounts of other products (Eq. (1)). Without the catalyst or the oxidant, no reaction occurred.



(1)

In Table 1 the mixed oxides obtained from this work (entries 1–7) show higher activities than those of the simple metal oxides (entries 8–11). The catalytic activities of the oxides were found to follow the order MgCuAl > MgNiAl ~ NiAl ~ MgCoAl ~ CoAl > CuAl > MgAl. The enhanced activity of the MgCuAl oxide relative to the CuAl or MgAl oxides indicated a synergistic effect in the former metal combination. A similar result was reported in the oxidation of 1-phenylethanol [14]. In addition, the presence of Mg has been found to contribute to improved dispersion of Cu at the surface of the catalyst [15,16].

Table 1
Oxidation of ethylbenzene (catalyst 0.2 g, EB:TBHP molar ratio = 1:2, 130 °C, 12 h).

Entry	Catalyst	Mg:M:Al analyzed	BET surface area (m^2/g)	XRD phase	Conversion (%)	Selectivity to acetophenone (%)
1	MgAl	4.3:1	306	Spinel	50	98
2	NiAl	4.8:1	114	Spinel	75	98
3	CoAl	4.6:1	105	Spinel, Co_3O_4	74	98
4	CuAl	4.9:1	90	Spinel, CuO	66	95
5	MgNiAl	2.4:1:1	130	Spinel	74	92
6	MgCoAl	2.1:0.8:1	174	Spinel	73	92
7	MgCuAl	3:1:1	150	Spinel, CuO	80	92
8	MgO	–	–	–	15	98
9	NiO	–	–	–	38	98
10	Co_3O_4	–	–	–	40	98
11	CuO	–	–	–	43	95

Other products detected: 1-phenylethanol, benzaldehyde (and benzoic acid for MgMAl oxides).

Table 2
Oxidation of ethylbenzene over MgCuAl oxide catalysts (0.2 g) at various conditions.

Entry	EB:TBHP	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)			
					Acetophenone	a	b	c
1	1:2	80	12	64	91	5	3	1
2	1:2	100	12	71	91	3	3	3
3	1:2	130	12	80	92	3	2	3
4	1:2	150	12	77	89	3	3	5
5	1:1	130	12	73	91	5	3	1
6	1:3	130	12	87	92	4	1	3
7	1:3	130	18	90	89	2	3	6

a = phenylethanol, b = benzaldehyde, c = benzoic acid.

The effects of the quantities of TBHP, and the reaction temperatures and times on the efficiency of the ethylbenzene oxidation were investigated over the most active MgCuAl oxide catalyst. The results are shown in Table 2. In entries 1–4, ethylbenzene conversion can be seen to increase with an increase in temperature from 80 to 130 °C, though a decrease is observed afterwards. This could be ascribed to competitive thermal decomposition of TBHP, preventing its subsequent involvement in the desired reaction. The selectivity for acetophenone showed a similar trend. In entries 3, 5 and 6, an increase in conversion from 73% to 87% was observed on increasing the ethylbenzene:TBHP ratio from 1:1 to 1:3. However, the selectivity towards acetophenone was not affected (91–92%). At a 1:1 ethylbenzene:TBHP ratio the ethylbenzene conversion was 73% and the selectivity was 91%, both being higher than found for Mn/MCM-41 (57.7% conversion and 82.2% selectivity) [16]. It was also found that an increase in time led to an enhancement of the conversion to 90%, but with a decrease in acetophenone selectivity to 89% (entry 7). This is due to further oxidation of acetophenone to other products [17].

With regards to reusability, it was found that the MgCuAl oxide catalyst showed a slight drop in activity (from 90% to 89%) after the third run, with similar acetophenone selectivity (89%). The decrease in activity could be possibly due to the decrease in active base sites from their coverage by polar products on the catalyst surface. After regeneration, the structure of the mixed oxide catalyst remained unchanged, as revealed by its XRD pattern. For other catalysts, the reusability tests also revealed only a 2–4% drop in activity.

In order to check whether the mechanism of the oxidation occurs *via* free-radicals, a free-radical scavenger (hydroquinone) was added to the reaction. The experiments with hydroquinone addition showed a decrease of ethylbenzene conversion by about half for all mixed oxides, indicating that the oxidation occurs partly *via* a free-radical pathway. Another pathway might involve activation of TBHP by coordination to the active site of the oxide catalyst. Insertion of activated oxygen of co-coordinated TBHP into a C–H bond of the methylene group in ethylbenzene would produce 1-phenylethanol. Subsequent abstraction of alcoholic OH hydrogen and the CH hydrogen of 1-phenylethanol would yield acetophenone or benzaldehyde. Both of these can be oxidized further to benzoic acid.

3. Conclusions

The mixed metal oxides can effectively catalyze the oxidation of ethylbenzene with TBHP under solvent-free conditions. The MgCuAl oxide exhibits the highest catalytic activity. At 130 °C, 12 h and with a ethylbenzene:TBHP ratio of 1:3, the conversion of ethylbenzene is 87% with 92% selectivity to acetophenone. The catalyst can be reused.

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