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# Selective oxidation of ethylbenzene to acetophenone catalyzed by mixed oxide spinels derived from layered double hydroxides

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**Mixed oxide spinels were prepared by the calcination of corresponding layered double hydroxides. Ethylbenzene was oxidized using *tert*-butyl hydroperoxide and $H_2O_2$. The catalytic activity of mixed oxide spinels increased in the order MgCuMnAl > MgCoMnAl > > MgMnAl > MgCrAl > CoMnAl oxides with high selectivity for acetophenone.**

The oxidation of ethylbenzene is of importance for the production of acetophenone.[1] The liquid-phase oxidation of ethylbenzene to acetophenone with $O_2$ using homogeneous transition metal compounds as catalysts was reported: $Co(OAc)_2$ in the presence of *N*-hydroxyphthalimides as co-catalysts and acetic acid (80–96% conversion and 59–85% selectivity in 24 h at 80 °C);[2] fluorinated metalloporphyrins without any additives (38% conversion and 94% selectivity in 24 h at 100 °C)[3] or $H_2O_2$ as an oxidant, *e.g.*, 8-quinolinolato $Mn^{III}$ complexes and $NH_4OAc$–AcOH additives, the most active dibrominated Mn catalyst gave 56% conversion and 78% selectivity in 7 h at 30 °C[4] or Mn-MCM-41 using TBHP as an oxidant to yield 66% conversion and 43% selectivity in 24 h at 80 °C.[5] The heterogeneous catalysts have also been reported: Cr-containing mesoporous molecular sieve (Cr-MCM-41) catalyst using $O_2$ to provide 66% conversion and 90% selectivity in 24 h at 95 °C;[6] Mn on Schiff base-functionalized $SiO_2$–$Al_2O_3$ mixed oxides using TBHP, affording 67% conversion and 93% selectivity in 24 h at 80 °C;[7] and Co-HMS catalyst yielding 49% conversion and 60% selectivity in 24 h at 80 °C.[8]

Layered double hydroxides (LDHs) have the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A_{n-x/n})^{x-}\cdot mH_2O$, where $M^{II}$ and $M^{III}$ are divalent and trivalent metal cations, respectively, and A is an anion. Co-precipitation is a simple and effective method for the preparation of LDHs. LDHs catalyze the oxidation of ethylbenzene, *e.g.*, $MnO_4^-$-exchanged MgAl-LDH (22% conversion and 98% selectivity),[9] MnAl-LDH (26% conversion and 94% selectivity)[10] and Cu/ZnAl-LDH (8% conversion).[11] Upon calcination, LDHs lose their layer structure and form highly active composite metal oxides with high thermal stability, high surface area, good metal dispersion and possessing synergetic effects between the elements.[12] The oxidation of ethylbenzene with TBHP (EB : TBHP molar ratio of 1:2) over CuNiCr oxide at 70 °C for 8 h showed 60% conversion and 65% selectivity for acetophenone.[13] We reported the order of catalytic activities of mixed metal oxides using TBHP (EB : TBHP molar ratio of 1:2) at 130 °C for 12 h: MgCuAl > > MgNiAl ~ NiAl ~ MgCoAl ~ CoAl > CuAl > MgAl oxides. High conversion (80%) and selectivity (92%) were obtained with the MgCuAl (3:1:1) oxide.[14]

The LDHs were synthesised by co-precipitation from aqueous solutions of suitable metal nitrates according to our previous work[14] and then used as catalysts in oxidation of ethylbenzene.[†]

Metal compositions, BET surface areas and XRD data of as-synthesized LDHs and calcined LDHs are shown in Table 1. The atomic ratios were close to the values of the starting solutions. The calcined samples exhibited higher surface areas. The $N_2$

**Table 1** Composition, surface area and XRD analysis of as-synthesized LDHs and calcined LDHs.

| Catalyst | Atomic ratio | | As-synthesized | | Calcined | |
|---|---|---|---|---|---|---|
| | Starting | Analyzed | $S_{BET}$/m$^2$ g$^{-1}$ | XRD phase | $S_{BET}$/m$^2$ g$^{-1}$ | XRD phase |
| CoMnAl | 3:1:1 | 3.2:0.9:1 | 79 | LDH | 100 | Spinel |
| MgMnAl | 3:1:1 | 2.2:0.9:1 | 90 | LDH, $MnCO_3$ | 110 | Spinel, $Mn_3O_4$ |
| MgCrAl | 3:1:1 | 2.4:0.8:1 | 162 | LDH | 173 | Spinel |
| MgCoMnAl | 2.5:0.5:1:1 | 2.1:0.4:0.9:1 | 124 | LDH, $MnCO_3$ | 160 | Spinel, $Mn_3O_4$ |
| MgCuMnAl | 2.5:0.5:1:1 | 2.2:0.4:0.8:1 | 86 | LDH, $MnCO_3$ | 99 | Spinel, $Mn_3O_4$ |

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[†] An aqueous solution containing appropriate amounts of metal nitrates (0.06 mol dm$^{-3}$, with the M:Al atomic ratio of 4:1) was heated to 65 °C, and a slight excess of $Na_2CO_3$ (0.06 mol dm$^{-3}$) was added dropwise with stirring. The pH 10 was maintained by the addition of NaOH (0.6 mol dm$^{-3}$). The precipitate was maintained at 65 °C for 18 h, then filtered off, washed thoroughly with distilled water (until the total absence of nitrates and sodium), dried at 110 °C for 12 h and calcined at 500 °C for 5 h to obtain the corresponding mixed oxides.

The atomic ratios of metals were determined by inductive coupled plasma emission spectroscopy (ICP, Perkin Elmer model PLASMA-1000). Specific surface areas were measured using the BET method on a BELSORP-mini instrument. XRD measurements were performed on a Rigaku DMAX 2002/Ultima Plus powder X-ray diffractometer. Temperature programmed reduction (TPR) measurements were carried out on a TPR MODEL BEL-CAT instrument equipped with a thermal conductivity detector (TCD).

The catalytic oxidation of ethylbenzene over mixed oxides in the absence of solvent was carried out in a magnetically stirred stainless steel reactor. Ethylbenzene (1.2 ml, 10 mmol), 10 wt% catalyst and aqueous TBHP (70%) or $H_2O_2$ (30%) solutions were added successively (EB : oxidant molar ratio of 1:3). The reaction mixture was stirred and heated in an oil bath for 12 h. The catalyst was filtered off, and the products were analyzed by GC (Agilent Technologies 6890N Network GC System with FID, a DB-1 capillary column). The conversion and selectivity presented here are based on the GC calculations using standard reference compounds. The oxidation was also performed in the presence of solvents (MeCN, $CH_2Cl_2$ and MeOH). The spent catalysts were washed with acetone, and calcined at 500 °C for 5 h.

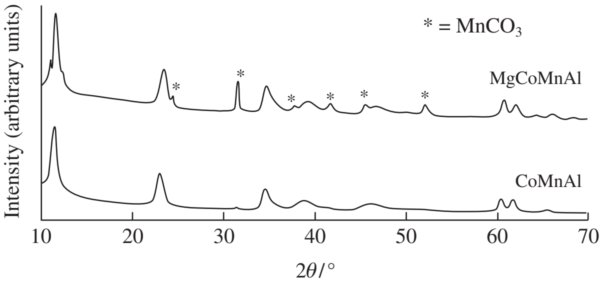

**Figure 1** XRD patterns of the MgCoMnAl and CoMnAl-LDHs.

adsorption/desorption results indicated that all LDHs and mixed oxides presented IUPAC type IV isotherms.

In the powder XRD patterns of all as-synthesized samples, an LDH-like phase was detected.[15] Representative XRD patterns of the MgCoMnAl and CoMnAl-LDHs are shown in Figure 1. The $MnCO_3$ phase (JCPDS: 44-1472) was also observed in the MgMnAl, MgCoMnAl and MgCuMnAl samples and their crystallinity was low.[16] Upon calcination at 500 °C, the absence of diffraction peaks corresponding to an LDH phase reveals that the layer structure was completely destroyed and the spinel phase was formed. In the MgMnAl, MgCoMnAl and MgCuMnAl samples, $MnCO_3$ was converted into an $Mn_3O_4$ phase (JCPDS 24-0734).

The reducibility of the mixed oxides was studied by TPR experiments (Figure 2). For the CoMnAl oxide, there were two main temperature regions. The first was ascribed to the reduction of Co and the second represented the reduction of Mn in the spinel.[17] In the MgCoMnAl oxide, three regions were observed, the first at 310 °C attributed to the reduction of $Co^{2+}/Co^{3+}$ to $Co^0$. The second region at 345 °C possibly corresponded to the reduction of spinel $CoAl_2O_4$[18] and the last peak centered at 418 °C represented the reduction of spinel $Co(Mn)Al_2O_4$. The MgCuMnAl oxide showed two peaks, one at 300 °C related to the reduction of $Mn^{4+}$ to $Mn^{3+}$, the peaks around 380 °C corresponded to the conversion of $Cu^{2+}$ into $Cu^0$.[19] For the MgMnAl oxide, reduction temperatures were higher than that of the MgCuMnAl or MgCoMnAl oxide. It was reported that reduction temperature decreased after the incorporation of Cu or Co into the Mn oxide.[20] The two peaks in the MgMnAl oxide corresponded to the reduction of Mn ions in different environments, $Mn_3O_4$ and the spinel. In the MgCrAl oxide, three reduction peaks appeared, attributed to the reduction of Cr ions in various oxidation states, formed as a solid solution in the MgAl oxide matrix.

The liquid-phase oxidation of ethylbenzene with TBHP over all the mixed oxides was carried out under the same reaction conditions (Table 2). Blank experiment performed without an oxidant or catalyst gave no ethylbenzene conversion. Catalytic results show the formation of mainly acetophenone with a small amount of 1-phenylethanol.

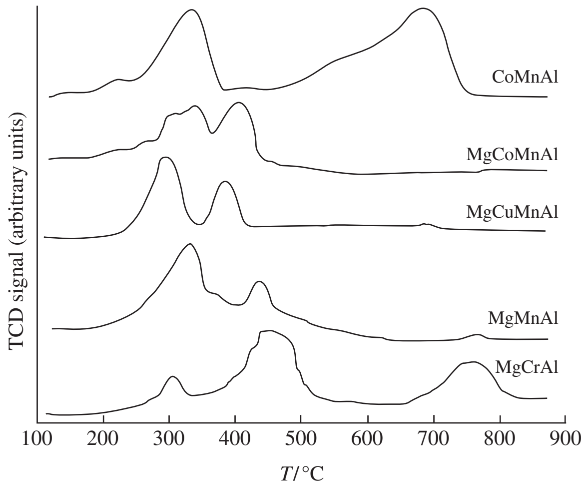

**Figure 2** Temperature-programmed reduction of the mixed oxides.

**Table 2** Oxidation of ethylbenzene with TBHP (120 °C) and $H_2O_2$ (70 °C) (10 wt% catalyst, ethylbenzene : oxidant molar ratio of 1:3, 12 h).

| Catalyst | TBHP | | $H_2O_2$ | |
|---|---|---|---|---|
| | Conversion (%) | Selectivity (%) | Conversion (%) | Selectivity (%) |
| CoMnAl | 58 | 90 | 22 | 90 |
| MgCoMnAl | 70 | 93 | 31 | 94 |
| MgCuMnAl | 74 | 92 | 39 | 92 |
| MgMnAl | 65 | 93 | 27 | 92 |
| MgCrAl | 67 | 92 | 28 | 92 |

Under the same conditions, the ethylbenzene conversion followed the order MgCuMnAl > MgCoMnAl > MgMnAl > MgCrAl > > CoMnAl oxides. Quaternary spinels showed higher activity than ternary spinels. The results clearly suggest that redox metal species present in the structure were responsible for the activity in the oxidation process. The phase composition of the catalyst also affected the activity rather than surface area. The highest conversion of the MgCuMnAl was 74%. The Mg-containing oxide catalysts showed higher selectivity for acetophenone due to their higher basicity.[21] When the reaction was carried out using $H_2O_2$ as an oxidant, the observed conversion and selectivity were much lower. This could be owing to the fast decomposition of $H_2O_2$ (without being involved in the oxidation). Unused or residual $H_2O_2$ was quantified by titration with 0.1 M $Ce(SO_4)_2$ using ferroin as an indicator.[22] It was found in the range of 20–26%. The use of $H_2O_2$ as an oxidant did not change the product selectivity.

When solvents were used in the oxidation of ethylbenzene over the MgCuMnAl, the conversion was lower and followed the order MeCN (55%) > $CH_2Cl_2$ (43%) > MeOH (15%). This is in good agreement with reported data, which is explained by the blocking of active sites with the solvent molecules.[8,13] Besides the coordinating of solvent on the surface of the mixed oxide catalyst, this decrease in conversion can also be due to the dilution of catalyst and substrate concentrations by the addition of the solvent.

The catalyst was filtered off from the hot liquid reaction mixture after reaction, and the resulting filtrate was analyzed by ICP AES. The result showed the absence of metal ions leach-out. The spent catalyst was washed several times with acetone, dried and calcined for 8 h at 500 °C. The structure of the mixed oxide remained unchanged, as revealed by its XRD pattern. The recovered catalysts can be reused three times with a little drop in activity (2–4%).

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