



## Catalytic oxidation of styrene over Cu-doped hydrotalcites



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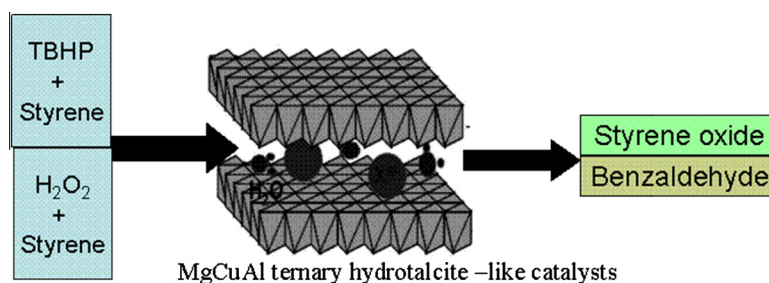
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## HIGHLIGHTS

- The successful substitution of  $Mg^{2+}$  by  $Cu^{2+}$  in Mg/Al hydrotalcite.
- $Cu^{2+}$  in octahedral sites of hydrotalcite is prerequisite for the oxidation of styrene.
- Styrene conversion depends on the copper content.
- Selectivity to products is dependant on the nature of oxidants.

## GRAPHICAL ABSTRACT

$Cu^{2+}$  ions in the brucite-like sheet play a crucial role in the oxidation of styrene at 60–90 °C. The catalytic activity is related to the overall amount of  $Cu^{2+}$  ions and the nature of oxidants.



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## ABSTRACT

A set of Mg–Cu–Al hydrotalcite-like materials with different Mg/Cu/Al ratios were synthesized by the co-precipitation technique. The prepared samples were characterized by physical techniques of XRD, FT-IR, Raman, N<sub>2</sub> physisorption, SEM, TEM, XPS, and UV prior to use as catalysts for the liquid oxidation of styrene. All synthesized samples possess a well crystallized hydrotalcite structure, medium surface, and uniform particles.  $Cu^{2+}$  ions at octahedral sites stably in the brucite-like sheets catalyze the epoxidation of styrene with *tert*-butyl hydrogen peroxide oxidant. The catalytic activity is related to the amount of copper content and oxidant behavior. The Cu-doped hydrotalcite catalysts show a rather good activity and high selectivity to styrene oxide (80–90%) at a high styrene conversion level.

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## 1. Introduction

Oxidation of styrene is a very important reaction because its products, mainly benzaldehyde and styrene epoxide, are widely used in many application fields [1]. Certainly, benzaldehyde is a very valuable chemical that has widespread application in perfumery, pharmaceuticals, dyestuffs, and agrochemicals. Styrene oxide is industrially used for the production of epoxy resin diluting agents, ultraviolet absorbents, flavoring agents... [1]. It is also a

fine chemical for organic synthesis, pharmacology and perfumery. However, the oxidation of styrene is somewhat difficult because it is a terminal olefin. Thus, many attempts have been developed to increase in the controllable conversion of styrene to oxygenated products [2–4]. First all, different homogeneous catalysts have been used for styrene oxidation using various oxidants, but these reaction systems face a huge challenge of removal of catalyst from the reaction mixture and some cases show rather poor catalytic activity [1,2]. Therefore, heterogeneous catalysts are considered as more efficient and environment friendly systems for the greener chemistry principles and thus many new catalysts in this trend have been recently developed [3–10]. Indeed, Table 1 summarized a series of typical performances established

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experimentally for selected representative catalysts. This selection of literature data was made for experiments conducted in conditions close to the ones in this work in order to allow some comparisons with our proposed catalyst. Among these heterogeneous systems, titanium-containing catalysts are the most available systems reported in literature, but their activity is rather fluctuation and strongly dependent upon the preparation routes, chemical precursors, and laboratory skills (Table 1, Entry # 2–6) [4–8]. Hence, many other transition metals have been recently tried in variable ways for the preparation of catalysts, including in the form of oxide film [7,8], nanoxides [9], metals supported catalysts [4,10,17], immobilized systems [2,18–20]. The product selectivity is strongly dependent on the catalyst nature, oxidant behavior, solvent... (Table 1). For example, TS-1 film showed a good activity in conversion of styrene into phenylacetaldehyde [7,8] while TiO<sub>2</sub>/SiO<sub>2</sub> produces mainly benzaldehyde from styrene [6]. In the case of anhydrous urea-hydrogen peroxide used as oxidizing agent, titanium silicate converted styrene to styrene oxide [4,5]. For group VIII elements-containing catalysts, either benzaldehyde or styrene oxide can be a major product; the catalytic activity in the latter case is related the oxidation state and the coordination geometry of transition metal ions, catalyst morphology [7,11,16,27]. Following this trend; we are in an endeavor to design an efficient catalyst based on hydrotalcites for the liquid oxidation of styrene. It is well known that hydrotalcite-like compounds are a two-dimensional material and sometimes show good ability to the oxidation reactions [21–29]. In essence, isomorphous substitution of transition metal ions in a brucite-like lattice leads to the appearance of oxidation–reduction centers in the sheets which may acts as active sites for the catalytic oxidation reaction [16,25–28]. In earlier work, we have successfully modified the hydrotalcite composition as well as hydrotalcite-derived oxides as catalysts for the catalytic applications [16,30,31]. A synergetic interaction between transition metal-doped element and the hosting cations in the hydrotalcite lattice gives a great catalytic property in the oxidation and combination reaction [7,16,24,28,32]. Hence, this article reports the characteristics and catalytic activity of Mg–Cu–Al hydrotalcite-like materials in the liquid oxidation of styrene. The present work also reports the correlation between copper geometry and the product selectivity in the styrene oxidation reaction.

## 2. Experimental

### 2.1. Preparation and characterization of the catalysts

Mg–Cu–Al–CO<sub>3</sub> double layered hydroxides were prepared by the coprecipitation method. The detailed procedure was described in our previous publications [16,29]. In brief, a 150 mL-mixed aqueous solution of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99%), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (98%) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (>98%) with different molar ratios of Mg<sup>2+</sup>/Cu<sup>2+</sup>/Al<sup>3+</sup> was added dropwise to 25 mL of 0.60 M Na<sub>2</sub>CO<sub>3</sub> under vigorous stirring (see Table 1S in Supplementary Materials). The solution pH was adjusted to 9.50 using 1.5 M NaOH and was kept for 24 h. Then, the resulting gel-like material was aged at 60–65 °C for 24 h. The resultant slurry was then cooled to room temperature and separated by filtration, washed with hot distilled water several times, and then dried at 80 °C for 24 h in air. For the sake of brevity, the prepared catalysts are denoted as TH00–TH05 and the expected formula compositions are reported in Table 2.

The metal composition (Mg, Cu, Al) of catalyst was measured using an ICP-MS Elan 9000 (Perkin Elmer, USA). Powder X-ray diffraction (XRD) patterns were recorded on a D8 Advance-Bruker instrument using CuK<sub>α</sub> radiation ( $\lambda = 0.1549$  nm). Fourier transform infrared (FT-IR) spectra were obtained in 4000–400 cm<sup>-1</sup> range on a FT/IR spectrometer (DX-Perkin Elmer, USA). The Raman spectra of samples were analyzed by a LabRAM HR800 spectroscopy (HORIBA, French). The recorded spectral range was 100–2500 cm<sup>-1</sup> and scanned 3 times with the wavelength of laser beam of 632 nm. Energy-dispersive spectroscopy (EDS) data were obtained from Varian Vista Ax X-ray energy-dispersive spectroscope. The scanning electron microscopy (SEM) microphotographs were obtained with a JEOS JSM-5410 LV. TEM images were collected on a Japan Jeol. Jem. 1010. The nitrogen physisorption was run on an Autochem II 2920 (USA). The XPS analysis was made on a photoelectron spectrometer (KRATOS Axis 165, Shimadzu, Japan) with Mg K<sub>α</sub> radiation (1253.6 eV). Deconvolution of the experimental photopeaks was carried out using a Lorentzian peak fit procedure. UV–vis spectra were collected with UV–visible spectrophotometer, JASCO V-670. BaSO<sub>4</sub> was used as a reference material. The spectra were recorded at room temperature in the wavelength range of 200–800 nm.

**Table 1**  
Comparison of catalytic activity of different catalysts in the oxidation of styrene.

| No. | Catalyst                                | Reaction conditions |                               |          |                   | Styrene conversion (%) | Product selectivity (%) |               |        | Ref. |
|-----|---|---------------------|-------------------------------|----------|-------------------|------------------------|-------------------------|---------------|--------|------|
|     |   | Temperature (°C)    | Oxidant                       | Time (h) | Solvent           |                        | Benzaldehyde            | Styrene oxide | Others |      |
| 1   | Cr-Silica                               | 80                  | H <sub>2</sub> O <sub>2</sub> | 6        | Acetonitrile      | 99.9                   | 62.5                    | 0             | 37.5   | [3]  |
| 2   | TS-1                                    | 60                  | H <sub>2</sub> O <sub>2</sub> | 10       | Dimethylformamide | 53.6                   | 19.2                    | 61.7          | 19.1   | [4]  |
| 3   | TS-1                                    | 40                  | H <sub>2</sub> O <sub>2</sub> | 12       | Acetonitrile      | 51                     | 6                       | 82            | 12     | [5]  |
| 4   | TiO <sub>2</sub> /SiO <sub>2</sub>      | 100                 | O <sub>2</sub>                | 4        | None              | 51.7                   | 93.5                    | 0.2           | 6.5    | [6]  |
| 5   | TS-1 film                               | 80                  | H <sub>2</sub> O <sub>2</sub> | 5        | Acetone           | 16                     | 9.0                     | 0.4           | 90.6   | [7]  |
| 6   | TS-1 zeolite                            | 70                  | H <sub>2</sub> O <sub>2</sub> | 5        | Acetone           | 23                     | 16                      | -             | 84     | [8]  |
| 7   | CuNiCoAl                                | 55                  | TBHP                          | 9        | Acetonitrile      | 81.0                   | 39.0                    | 16.0          | 45.0   | [9]  |
| 8   | 3%V <sub>2</sub> O <sub>5</sub> /SBA-15 | 25                  | H <sub>2</sub> O <sub>2</sub> | 3        | Acetone           | 55.5                   | 38.6                    | 8.9           |        | [10] |
| 9   | Fe-ZSM-5                                | 73                  | H <sub>2</sub> O <sub>2</sub> | 2        | Dimethylformamide | 5.0                    | 63.1                    | 36.9          | -      | [11] |
| 10  | Fe-MCM-41                               | 73                  | H <sub>2</sub> O <sub>2</sub> | 2        | Dimethylformamide | 13.8                   | 37.3                    | 41.8          | 20.9   | [11] |
| 11  | Mn-MCM-48                               | 80                  | TBHP                          | 24       | Acetonitrile      | 58                     | 59                      | 31            | 10     | [12] |
| 12  | V-MCM-48                                | 80                  | TBHP                          | 24       | Acetonitrile      | 84                     | 81                      | 4             | 15     | [12] |
| 13  | Cr-MCM-48                               | 80                  | TBHP                          | 24       | Acetonitrile      | 98                     | 47                      | 24            | 29     | [12] |
| 14  | Au/LDH                                  | 80                  | THBP                          | 8        | Benzene           | 79.4                   | 24.3                    | 74.4          | 1.3    | [13] |
| 15  | Au/MgO                                  | 80                  | TBHP                          | 3        | None              | 62                     | 14                      | 52            | 34     | [14] |
| 16  | W-Silica                                | 80                  | H <sub>2</sub> O <sub>2</sub> | 6        | Acetonitrile      | 79.7                   | 84.4                    | -             | 15.6   | [15] |
| 17  | MgCoAl-LDH                              | 85                  | Air                           | 4        | None              | 52.6                   | 55                      | 38            | 7      | [16] |

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