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Mg-Al-MoO_4 layered double hydroxides used as catalysts for the oxidation of styrene

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Abstract

Mg-Al layered double hydroxides have been prepared by the precipitation method and characterized by the physical methods such as XRD, EDS, SEM. The synthesized solids showed the layered hydroxide structure with molybdate and carbonate anions as interlayer compensating anions in the uniform particles. While Mg-Al-CO_3 is inactive for the liquid oxidation of styrene, Mg-Al-MoO_4–LDH catalyst exhibits a good activity in the conversion of styrene into benzaldehyde and phenyl oxirane. The catalytic activity and product selectivity depend on the reaction conditions and oxidant nature. The styrene conversion is moderate about 10-15 % and the total selectivity to benzaldehyde and styrene oxide reached 99 % as air and *t*-butyl hydrogen peroxide used as milder oxidants.

Keywords. Benzaldehyde, styrene, molybdate, hydrotalcite, oxidation.

1. INTRODUCTION

Layered double hydroxides (LDHs) are composed of an unusual class of layered materials with positively charged hydroxide layers and charge balancing, mobile anions stayed in the interlayer regions. In details, LDHs have a similar structure to brucite-like $Mg(OH)_2$ sheet where an isomorphous substitution of Mg^{2+} by a trivalent element M^{3+} occurs. In brucite, each magnesium cation is octahedrally surrounded by hydroxyl groups [1]. The resulting octahedron shares edges to form infinite sheets. When Mg^{2+} ions are isoamorphously replaced by a trivalent ion, a positive charge is created in the brucite layer. The positive charge is then compensated by foreign anions in the interlayer sheets [1, 2]. The layered hydroxide compounds are generally described by the empirical formula $(Mg_{1-x}{}^{2+}M^{3+}{}_x(OH)_2)^{x+}(A^{z-})_{x/z}\cdot nH_2O$, where M^{2+} and M^{3+} are the metal cations, A^{z-}represents the anion needed to compensate the net positive charge (CO_3^{2-},SO_4^{2-}, MoO_4^{2-}…), and n is the number of interlayer water molecules [3, 4]. Therefore, layered double hydroxides have aroused considerable interest because of the diversity of their chemical compositions that make them have many practical applications, such as catalysts, catalyst supports, ion exchangers, stabilizers, and adsorbents [1, 5, 6]. As a result, layered double hydroxides have been among the most widely investigated catalyst precursors because of the noteworthy properties of the final catalysts such as a large surface area, basic properties, high metal dispersion, and stability against sintering even under extreme conditions for last decades [1, 3-6].

The aim of this work was to report the preparation of Mg-Al layered double hydroxides in which the foreign anions are carbonate or molybdate and to use as catalysts for styrene oxidation under milder conditions. The catalytic performances of the solids were found to be in correlation with the morphology, and structure of the layered double hydroxides, the presence of molybdate ions, and the nature of oxidants.

2. EXPERIMENTAL

2.1. Catalyst preparation and characterization

50 mL of distilled water containing a stoichiometric amount of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$) and 50 mL of NaOH solution were added into 500 mL-beaker and magnetically stirred at 65 °C for 1 h. Then, a quantity of aluminum nitrate nonahydrate and magnesium nitrate hexahydrate dissolved in 150 ml of distilled water was added into the beaker. Aqueous NaOH solution (1.5 M) was used for the pH adjustment of 9.0. The sample was then submitted to an aging treatment at 65 °C for 24 h, followed by filtration, washing with hot distilled water, and drying at 70 °C for 24 h. The obtained solid was ground into powder. In the case

of preparation of the Mg-Al-CO_3 sample, ammonium heptamolybdate was replaced by sodium carbonate.

Powder X-ray diffraction (XRD) patterns were recorded on a D8 Advance-Bruker instrument using CuK_α radiation (λ = 1.59 Å). Scanning Electron Microscopy (SEM) Hitachi S-4500 (Japan) with the magnification of 200,000 times. Energy-dispersive spectroscopy EDS) data were obtained from Varian Vista Ax X-ray energy-dispersive spectroscopy.

2.2. Catalytic performance

The catalytic oxidation of styrene in N,N’-dimethylformamide (DMF) solvent was carried out in a 100 mL three-neck glass flask fitted with a reflux condenser. For a typical run, 17.4 mmol of styrene, 7.0 mL of solvent and 0.2 grams of catalyst were loaded into the flask. After the reaction mixture was magnetically stirred and heated to the desired temperature, then *t*-butyl hydrogen peroxide (TBHP, 70 %, Sigma Aldrich) or hydrogen peroxide solution (H_2O_2, 30 %) was dropped into the flask. As air was used, the flow of air (5 mL/min) was conducted into stirred reaction mixture and the reaction time starts being recorded. After the reaction finished, the mixture was cooled down to room temperature and the catalyst was filtered off. The reaction product mixture was then analyzed by gas chromatography and GC-MS (HP-6890 Plus, capillary column HP-5 MS crosslinked PH 5 % PE Siloxane, 30 m x 1 μm x 0.32 μm).

3. RESULTS AND DISCUSSION

3.1 Textural properties of catalysts

Two layered double hydroxides with nominal composition formula of $Mg_{0.7}Al_{0.3}(OH)_2(CO_3)_{0.15}.xH_2O$ (MgAl-CO_3) and $Mg_{0.7}Al_{0.3}(OH)_2(MoO_4)_{0.15}.xH_2O$ (MgAl-MoO_4) have been prepared at a constant pH conditions. It is noticeable that the purpose of this preparation recipe is to synthesize the same Mg/Al molar ratio, but different anions in the interlayer gallery. The X-ray diffraction patterns of the two samples are displayed in Figure 1. It is observed that the two peaks at low 2-theta of 11.2, 22.5° are essentially ascribed to the reflections of basal planes of (003), (006), respectively. The other broad and asymmetric peaks at 2-theta of 34.2, 38.2, 45.5, 60.2, 61.3° are respectively contributed to the reflection signals of (012), (015), (018), (110), and (113) planes. These reflection peaks are typical characteristics for layered double hydroxide structure in which carbonate and molybdate anions are already inserted into the interlayer region [7, 8]. At the same Mg/Al molar ratio of 7/3, the XRD pattern for MgAl-MoO_4 sample slightly shifted to the lower reflection angles as compared with that for MgAl-CO_3 solid, indicating a larger interlayer distance between layered hydroxide sheets in the LDH-molybdate material [1, 2, 5-8].

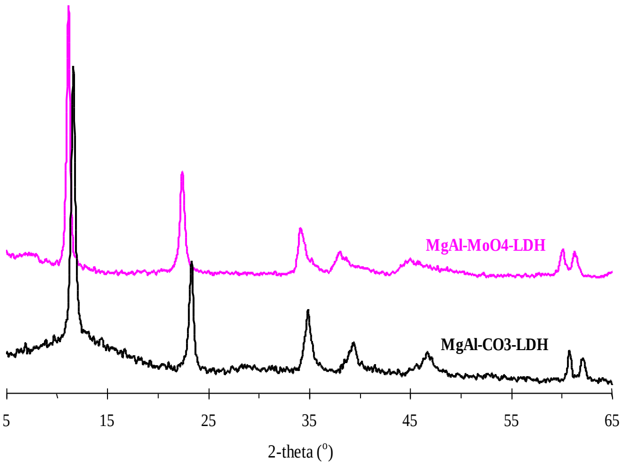
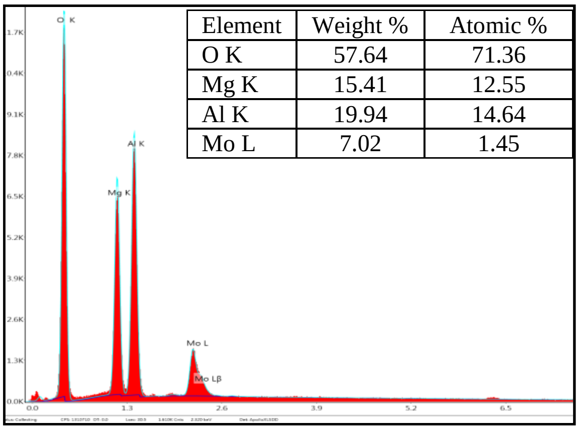


Figure 1: XRD pattern for three solid samples

Since two synthesized samples possess lamellar structure, the presence of all elemental components is screened by EDS technique. Figure 2 elucidated an EDS spectrum for the MgAl-MoO_4 sample.



Element	Weight %	Atomic %
O K	57.64	71.36
Mg K	15.41	12.55
Al K	19.94	14.64
Mo L	7.02	1.45

Figure 2: EDS spectrum for MgAl-MoO_4-LDH sample

Energy-dispersive X-ray spectrometry (EDS) analysis provides local information of the concentrations of different elements in the outermost layers of the catalyst particles. Alumina, magnesium, molybdenum, and oxygen are clearly identified on the solid surface of the sample. Molybdenum metal content is close to the theoretical value, indicating the presence of molybdate as an interlamellar anion in the interlayer regions.

The catalyst morphology is investigated using scanning electron spectroscopy. Both MgAl –LDH samples show uniform plates with the thickness of 20 nm. The particles lay on each other, giving rise to less porosity. However, MgAl-MoO$_4$ sample is likely more compactness and thus is expected the lower external surface area [5-7].

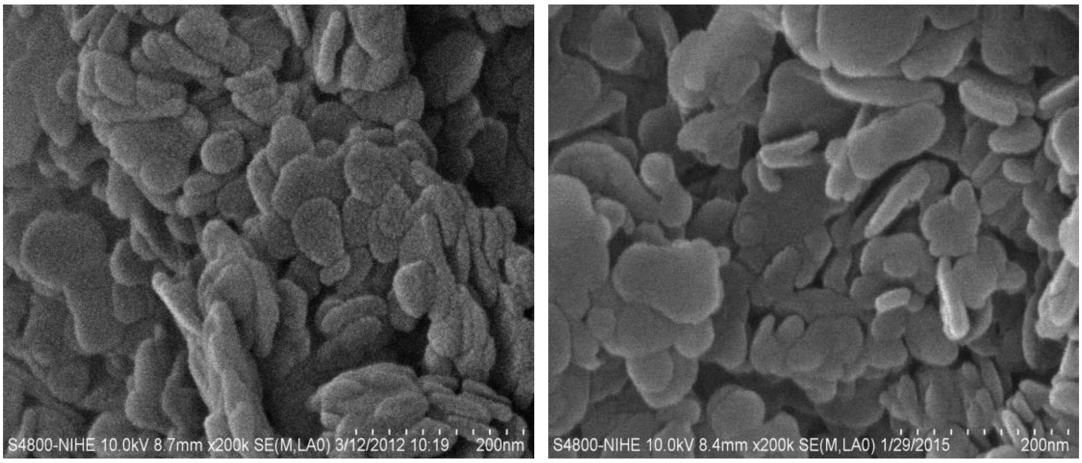


Figure 2: SEM images for MgAl-CO$_3$ (left) and MgAl-MoO$_4$ LDH (right) samples

3.2. Catalytic activity

Both Mg-Al LDHs have been tested for the liquid oxidation of styrene in the presence of air. In comparison, a blank test (no catalyst) shows no conversion of styrene. It is noted that Mo-Al-CO$_3$ LDH catalysts also gives a very low conversion of styrene and only traces of oxygenated products were detected after 4 hours-reaction time, in good consistent with the literature [6-9]. In contrast, MgAl-MoO$_4$ LDH catalyst is added into the reaction mixture flask, the styrene conversion grows significantly up. Indeed, Figure 4 depicted both styrene conversion variation and product distribution of the oxidation at different reaction temperatures. The styrene conversion observably increases with increasing reaction temperature and remains below 20 % at 110 °C (Fig. 4A). Interestingly, both phenyl oxirane and benzaldehyde are produced in parallel in the reaction temperature range of 90-110 °C (Fig. 4B) as the major products [2, 7, 10, 11].

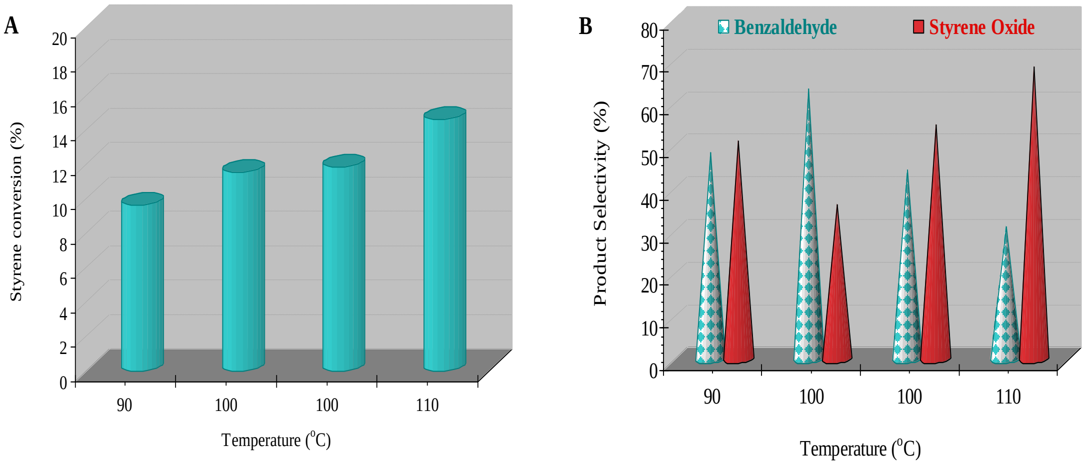


Figure 4: Effect of reaction time on the catalytic activity over MgAl-MoO$_4$-LDH catalyst (DMF solvent, 0.2 grams of catalyst, 4 hours)

The selectivity to benzaldehyde reaches the highest value at 100 °C and then slightly decreases at the higher temperature while that to styrene epoxide likely increases with the reaction temperature (Fig. 4B). Although the product distribution changes in the reaction temperature, but total selectivity to both benzaldehyde and styrene oxide is almost constant under reported experiments. Thus, it is suggested that Mg-Al-MoO_4 is a very selective catalyst for the liquid oxidation of styrene into valuable oxygenated compounds. Furthermore, figure 4 also reveals that benzaldehyde is produced at a lower temperature while styrene oxide is more favorably yielded at a higher temperature. This is explained by the thermodynamics of the oxidation that the free energy of benzaldehyde ($\Delta_fG^0_{benzaldehyde}$ = 61.2 kJ/mol, $\Delta_fH^0_{benzaldehyde}$ = -36.8 kJ/mol) is lower than that of styrene epoxide ($\Delta_fG^0_{styrene\ oxide}$ = 103.5 kJ/mol, $\Delta_fH^0_{styrene\ oxide}$ = -31.1 kJ/mol) [12, 13].

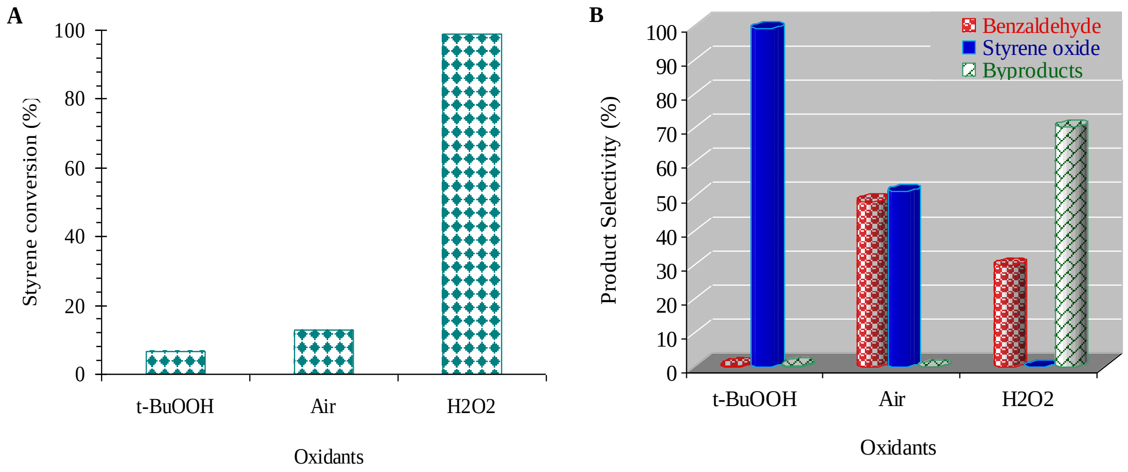


Figure 5: Effects of oxidant nature on catalytic activity over sample MgAl-MoO_4-LDH catalyst at 90 °C, 4 hours, air oxidant, DMF solvent, 0.2 grams of catalyst

Moreover, the catalytic activity does not only vary with the reaction temperatures but also depends on the oxidant nature. In practice, Figure 5A presents the different catalytic activity as different oxidants are introduced into the styrene reactant. It is worthily noted that three examined oxidants all express the good ability to oxidize styrene over Mg-Al-MoO_4 catalyst, but the styrene conversion decreases as follows of H_2O_2 > air > t-BuOOH under the same experimental conditions. Hydrogen peroxide may convert styrene up to 95 %, but only a trace of styrene oxide was detected in the product mixture. In this case, benzoic acid and phenyl acetaldehyde, styrene glycol… are mainly formed in addition to 28 % selectivity of benzaldehyde [10, 12, 14, 15]. Thus, it is suggested that oxidation of styrene with H_2O_2 is not selective process in spite of very high activity. Meanwhile, t-BuOOH has displayed a great potential to convert styrene into phenyl oxirane only (Fig. 5B) while air presents the equivalent ability to oxide vinyl benzene into benzaldehyde and styrene epoxide [10, 15-17]. The high activity with H_2O_2 oxidant may be related to the formation of HO• radicals [14].

4. CONCLUSIONS

Mg-Al LDH catalysts are successfully prepared by the precipitation method. The synthesized solids showed a good lamellar structure which molybdate and carbonate anions are introduced into the interlayer domains. The catalysts have uniform particle. It was found that only Mg-Al-MoO_4–LDH catalyst is active for the oxidation of styrene and the main products are benzaldehyde and styrene epoxide. The product distribution depends on the reaction conditions and oxidant nature. Air and *t*-butyl hydrogen peroxide are selective oxidants to convert styrene into two valuable products (benzaldehyde and styrene oxide). The styrene conversion is about 10-15 % and the selectivity to the main products of 99 % at 90 °C.

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