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Oxidation of styrene over molybdenum-containing hydrotalcite catalysts

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Abstract

$Mg_{0.6}Al_{0.4}(OH)_2(MoO_4)_{0.2}.mH_2O$ was prepared via coprecipitation method and characterized by XRD, BET, EDS techniques. The solid has a hydrotalcite-like structure and molybdate anions stayed in the interlayer regions between two brucite sheets. The synthesized material has been used as heterogeneous catalyst for the liquid oxidation of styrene with air. The oxidation reaction was carried out at atmospheric pressure in the temperature range of 60-110 °C. The presence of molybdate anions plays role of active site for the conversion of styrene into benzaldehyde and styrene epoxide with the selectivity of 97-99 %.

Keywords. Benzaldehyde, epoxide, molybdate, LDH, intercalation.

1. INTRODUCTION

The hydrotalcite-like compounds are generally described by the empirical formula $(M_{1-x}^{2+}M_x^{3+}(OH)_2)(X^{z-})_{x/z}.mH_2O$, where M^{2+} and M^{3+} are the metal cations, X^{z-} represents the anions (CO_3^{2-} , SO_4^{2-} , MoO_4^{2-} ...), and m is the number of interlayer water molecules [1]. Thus, they are well known as anionic clays with the structure similar to that of brucite-like $Mg(OH)_2$ where an isomorphous substitution of Mg^{2+} by a trivalent element M^{3+} occurs. In details, each magnesium cation in the brucite is octahedrally surrounded by hydroxyls, resulting octahedron shared edges to form infinite sheets with no net charge. When Mg^{2+} ions are replaced by a trivalent ion, a positive charge is generated in the brucite sheet. The positive charge is compensated by anions (X^{z-}) in the interlayer while water molecules fulfill in the interlayer free spacings [1-4]. Anionic clays based on hydrotalcite like-compounds have been attractive because of the diversity of their chemical compositions. Therefore, they have shown great applicability in heterogeneous catalysts, bifunctional catalysts, ion exchangers, stabilizers, and adsorbents [1, 5, 6]. Recently, we have exploited great ability of Mg-(Co, Cu)-Al hydrotalcite catalysts in the oxidation of styrene. Our catalysts have exhibited a good activity in selective conversion of styrene into desired products [7-11].

The aim of this work is to deal with a representative Mo-modified hydrotalcite-like

catalyst for styrene oxidation with molecular oxygen in air. The activity and selectivity of the catalysts were related to small amounts of molybdate anions compensated the net positive charge. The catalytic performances of the solids were correlated to the morphology, and structure of the layered double hydroxides.

2. EXPERIMENTAL

2.1 Preparation and characterization of the catalysts

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, 150 mL of 0.45M magnesium nitrate and 0.093 M aluminum nitrate solution was added with a constant flow rate of 1mL/min into the beaker and kept stirring for 3 hours. 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 Bruker Avance instrument using CuK_α radiation ($\lambda = 1.59 \text{ \AA}$). Energy-dispersive

spectroscopy (EDS) data were obtained from Varian Vista Ax X-ray energy-dispersive spectroscope. The nitrogen physisorption was measured at 77 K on an Autochem II 2920 (USA).

2.2. Catalytic performance

The catalytic oxidation process of styrene was carried out in a 100 mL three-neck glass flask fitted with a reflux condenser. For a typical run, 100 mmol of styrene, 50 ml of solvent (N,N'-dimethylamide, ethanol) and 0.2 grams of catalyst were loaded into the flask. After the reaction mixture was magnetically stirred and heated to the desired temperature, air was led into stirred reaction mixture and the reaction is initiated. The three-neck glass flask was quenched to room temperature and then catalyst was filtered off after the reaction. The filtrate was quantitatively analyzed by a gas chromatography –mass spectroscopy (GC-MS, HP-6890 Plus).

3. RESULTS AND DISCUSSION

3.1. Textural properties of catalysts

X-ray diffraction patterns of two hydrotalcite-like compounds are presented in Figure 1. For the comparison, XRD spectrum of a reference salt, Na_2MoO_4 (Sigma Aldrich) is recorded. It is clearly observed that reflections indexed to molybdate anions are detected for Mg-Al-MoO₄ hydrotalcite-like samples, indicating various molybdate anionic species were inserted into the interlamellar space. Furthermore, all reflection signals for $\text{Mg}_{0.6}\text{Al}_{0.4}(\text{OH})_2(\text{MoO}_4)_{0.2}\cdot\text{mH}_2\text{O}$ are typically matched with those for the corresponding hydrotalcite sample of $\text{Mg}_{0.6}\text{Al}_{0.4}(\text{OH})_2(\text{CO}_3)_{0.2}\cdot\text{mH}_2\text{O}$ (Fig. 1).

Indeed, the two peaks at low 2-theta of 11.20, 22.49° are essentially assigned to the reflections by the basal planes of (003), (006), respectively. The other broad and asymmetric peaks at 2-theta of 34.25, 38.24, 45.53, 60.23, 61.37° are respectively contributed to the reflections by the basal planes of (012), (015), (018), (110), and (113), confirming the formation of a crystallized layered double hydroxide structure [1, 2, 5, 7, 8]. Thus, molybdate anions located in the interlayer region [4, 12-14]. However, X-ray diffraction pattern for molybdenum-containing hydrotalcite sample shows a high signal-to-noise ratio, implying the formation of poorer crystalline structure and inhomogeneous particles as compared with the results of Mg-Al-CO₃ sample [1,7,15]. This may be related to a minor change in

the gallery height due to the presence of molybdate anions [12, 14].

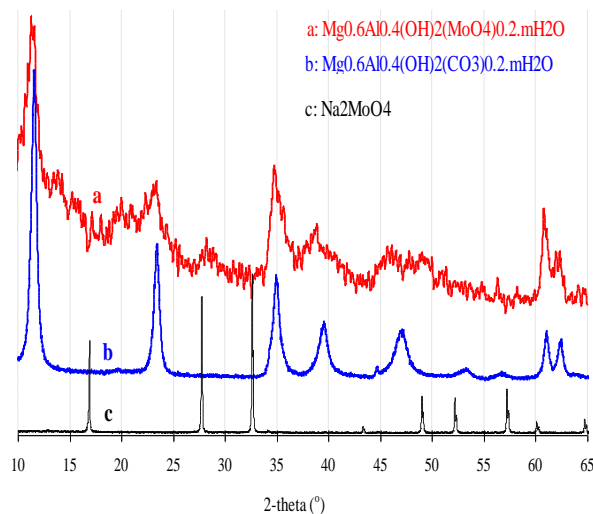


Figure 1: XRD pattern for three solid samples

Nitrogen adsorption/desorption measurement for two hydrotalcite like-samples shows a small change in isothermal –shaped curve. While the nitrogen adsorption/desorption isotherm of Mg-Al-MoO₄ sample appears a plateau from 0 to 0.45 along with a hysteresis loop in the broad range of 0.52 – 0.95, that of Mg-Al-CO₃ exhibits a wider plateau from 0 to 0.80 and a narrow hysteresis loop of 0.85 – 0.95 (Fig. 2) [5,15].

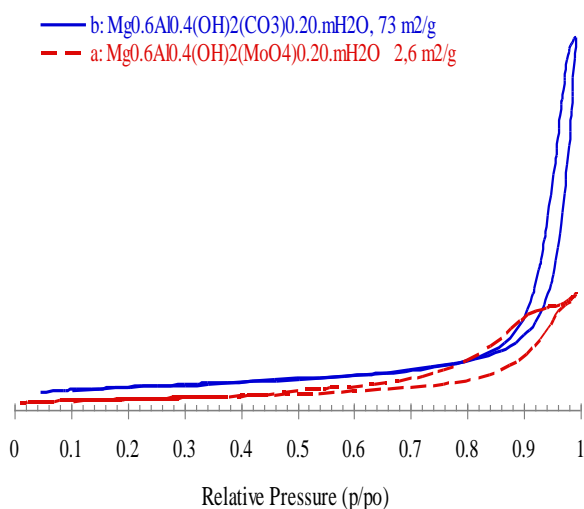


Figure 2: Nitrogen absorption-desorption isotherms of two representative Mg-Al-Molybdate hydrotalcite –like compounds

However, both these patterns are likely classified to the II type and the hysteresis loops are closely to

the H3-classification, suggesting that these solids are either mesopores or nonporous materials [7,14]. Because the distance between layers is in the range of micro-porosity so nitrogen molecules are unable physically to penetrate the interlayer spaces of hydrotalcites, the H3-like hysteresis loop in these cases is essentially attributed to the nitrogen condensation/evaporation phenomena between voids generated by the agglomeration of inhomogeneous particles [1,2,8,15]. The specific surface area of molybdenum containing –sample is much lower than that of Mg-Al-CO₃ samples (Fig. 2). A significantly decreased surface of the Mg-Al-MoO₄ sample is probably associated with the less homogeneous particles because of the precipitation at strong basic condition [1, 4, 12-15].

Table 1: EDS results of sample

Mg_{0.6}Al_{0.4}(OH)₂(MoO₄)_{0.2}.mH₂O before and after reaction of liquid oxidation of styrene at 90 °C, 4 h

Element	Atomic percent (%)	
	Fresh catalyst	Used sample
O	75.17	74.64
Mg	15.49	15.02
Al	7.99	8.96
Mo	1.12	1.06
Fe	0.23	0.32

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 platelet surface of all samples as collected in Table 1. Molybdenum metal content is close to the theoretical value, but observably minor changes after used as a catalyst for the liquid oxidation of styrene.

3.2. Catalytic activity

The catalytic activity of Mg/Al-molybdates hydrotalcite-like catalysts in the liquid oxidation has been carried out with air under atmospheric pressure. For the purpose of comparison, a test without catalyst has been also performed, giving no conversion of styrene. In the case of Mg-Al-CO₃ catalyst used, only traces of products were detected after 4 hours-reaction time at a negligible conversion of styrene, in good agreement with our previous investigations [7-11, 15]. As CO₃²⁻ anions were replaced by MoO₄²⁻ moieties in the interlayer region,

Mg-Al-MoO₄ hydrotalcite-like catalyst exhibits a good catalytic activity in the oxidation. Indeed, Figure 3 clearly shows a gradual increase in styrene conversion with reaction time over Mg_{0.6}Al_{0.4}(OH)₂(MoO₄)_{0.2}.mH₂O catalyst. The styrene conversion almost reaches about 22.5 % after 10-hours-reaction and only two desired products, benzaldehyde and styrene oxide, are produced. Under reported conditions, the selectivity to benzaldehyde is almost 42.3 % while that to styrene oxide is 51.8 %. This indicates that the reaction is very selective for the production of styrene oxide and benzaldehyde, evidenced by a high selectivity to desired products at various conversion levels during the change in reaction time (Fig. 3) [7, 14, 16].

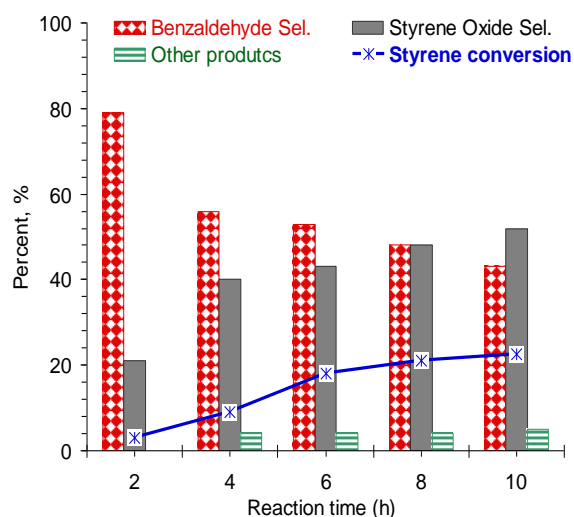


Figure 3: Effect of reaction time on the catalytic activity over Mg_{0.6}Al_{0.4}(OH)₂(MoO₄)_{0.2}.mH₂O at 80 °C, DMF solvent, 0.2 grams of catalyst, DMF solvent (Others: benzoic acid, and styrene glycol)

In order to throw light on the high selectivity of Mg-Al-MoO₄ catalyst, we have carried out a set of styrene oxidation reactions in the reaction temperature range of 80-100 °C.

Figure 4 shows a variation of catalytic activity with elevating reaction temperatures. The styrene conversion increases monotonically with increasing temperature and the product distribution is strongly affected by temperature. It is noted that no byproducts are detected in the temperature range of 80-90 °C although styrene conversion observably increases from 38 to 57 %. At a higher reaction temperature, the styrene conversion may approach 83 %, but the total selectivity to benzaldehyde and styrene oxide decreases to 74 %. This is explained by the fact that unselective cleavage of C=C considerably happens at high temperatures although

the over-reaction of two main products are not phased out under such conditions [7, 13, 17, 18]. Thus, the total selectivity to benzaldehyde and styrene oxide has decreased by 26 %. The selectivity to byproduct keeps increasing at higher temperatures because of secondary conversion of main products. Combination of the catalytic activity is shown in Fig. 3 and 4. It is suggested that the selective oxidation of styrene into benzaldehyde and styrene oxide happens at lower temperature, below 90 °C. An increased reaction time may augment the styrene conversion while the selectivity to benzaldehyde and styrene oxide is still unchanged [8, 15, 19, 20].

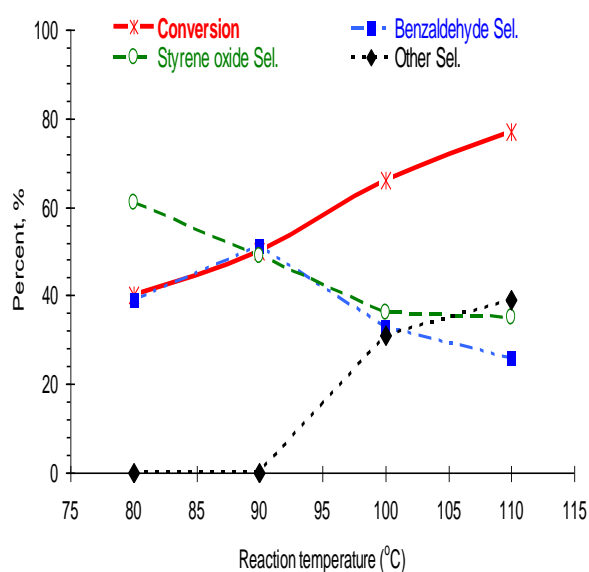


Figure 4: Effects of reaction temperature on catalytic activity over sample $\text{Mg}_{0.6}\text{Al}_{0.4}(\text{OH})_2(\text{MoO}_4)_{0.2} \cdot n\text{H}_2\text{O}$ at 90 °C, 12 h, air oxidant, DMF solvent, 0.2 grams of catalyst.

4. CONCLUSIONS

Molybdenum-containing hydrotalcite catalyst is successfully prepared by the precipitation method at pH of 9.0. The prepared solid samples exhibit hydrotalcite structure and medium surface area, but MoO_4^{2-} moieties were firmly inserted into the interlayer regions. Such anions were found to act as active species for the oxidation of styrene. Under reported experimental conditions, styrene was oxidized selectively into benzaldehyde and styrene as air was used as an oxidant. The catalytic activity was dependant on the reaction temperature and time. The good styrene conversion values and high desired product selectivity were obtained at lower temperatures and longer reaction time. An increased

reaction temperature leads to an observable change in product distribution. The highest styrene conversion (83 %) was obtained at 110 °C and total selectivity to benzaldehyde and styrene oxide is about 74 %.

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