

CONVERSION OF STYRENE INTO BENZALDEHYDE AND STYRENE EPOXIDE OVER MgCoAl-LDH CATALYSTS

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ABSTRACT

Co-containing hydroxides have been successfully synthesized by the co-precipitation of starting-metal salts. The obtained materials were characterized by some physical means including XRD, EDS, nitrogen physisorption, etc. It was found that Co^{2+} ions were present in the layered double hydroxide (LDH) sheets. The presence of cobalt ions in LDH played as active sites for the oxidation of styrene with air. The catalysts exhibited a very high activity in the conversion of styrene into two main products (benzaldehyde and styrene oxide). The highest styrene conversion was about 90 – 95 % and the total selectivity to benzaldehyde and styrene oxide was in the range of 80 – 85 % under reported experimental conditions.

Keywords: styrene, benzaldehyde, epoxide, LDH, hydrotalcite.

1. INTRODUCTION

The catalytic oxidation of alkenes of great interest since the oxygenated compounds are the most useful synthetic intermediates for a wide variety of products such as pharmaceuticals, polymers, and epoxy paints [1]. For example, benzaldehyde is widely used in many industrial fields like pharmaceuticals, dyes, resin additives, flavors which always required a high purity in order to use in food or medical industries. Nowadays, in the advanced process of styrene oxidation, benzaldehyde requires to produce as an main by-product without halogen and thus has a wider application [1, 2]. Meantime, the conventional methods for the oxidation of unsaturated hydrocarbons in industry are known as the chlorohydrin process or Halcon process which is quite harmful to environment and seriously influences on the quality of products [1, 3]. In other context, this homogeneous process suffers from catalyst recovery and recycling problems that make some researchers also have developed more efficient heterogeneous catalysts [1, 2, 4 - 7]. Recently, many methods have been reported for the epoxidation of styrene by using several milder and greener oxidants such as molecular oxygen [4 - 6], air [3, 7 - 9], hydrogen peroxide [10, 11], tert-butyl hydroperoxide [12, 13] etc. Some of these oxidants are rather active for the oxidation of stable unsaturated hydrocarbons, depending on the nature of transition metal catalysts. In practice, transition metal ions known to be good selective oxidation catalysts using

friendly oxidant agents above include copper [6, 8, 13], titanium [2, 14, 15], molybdenum [16, 17], manganese [11,18] and cobalt [3, 9, 19 - 22]. Among these metals, cobalt is the most efficient once and is widely applied in the field of liquid oxidation. For example, cobalt ions exchanged in zeolites [4, 20], immobilized in polymers [19], and introduced in perovskite framework [21] or CoO_x loaded on silica [3] are reported to be good catalysts for the selective oxidation of styrene.

In this study, cobalt ions are inserted into layered hydroxide sheets for the selective oxidation of styrene to styrene oxide and benzaldehyde in the presence of air as oxidant. The effects of time and temperature on styrene conversion and product selectivity were investigated to control the two main product selectivities.

2. EXPERIMENTAL SECTION

2.1. Preparation and characterization of the catalysts

A stoichiometric amount of sodium carbonate was dissolved in 25 mL of water in a 500 mL-beaker. The solution was heated to 60 - 65 °C. Then, amounts of aluminum nitrate nonahydrate and magnesium nitrate hexahydrate and cobalt nitrate hexahydrate were dissolved in 150 mL of distilled water. The pH of the solution was adjusted to approximately 9.50 using 1.5 M NaOH and was kept for 24 h. The precipitate was filtered, washed and dried at 80 °C.

Powder X-ray diffraction (XRD) patterns were recorded on a D8 Advance-Bruker instrument using CuK_α radiation ($\lambda = 1.59 \text{ \AA}$). Energy-dispersive spectroscopy (EDS or EDX) 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 of styrene in the absence of solvent was carried out in a 100 mL three-neck glass flask fitted with a reflux condenser. For a typical run, 87.28 mmol of styrene and 0.2 grams of catalyst were loaded into the flask unless some particular tests indicated. After the reaction mixture was magnetically stirred and heated to the desired temperature, the flow of air (5 mL/min) was added at once, which initiated the reaction. After the reaction, the mixture was quenched to room temperature and then catalyst was filtered off. The filtrate was quantitatively analyzed by a GC-MS (HP-6890 Plus).

3. RESULTS AND DISCUSSION

3.1. Catalytic Characterization

In the present study, two MgCoAl hydroxides were prepared accordingly with the nominal chemical composition of $\text{Mg}_{0.4}\text{Co}_3\text{Al}_{0.3}(\text{OH})_2(\text{CO}_3)_{0.15}$ and $\text{Mg}_{0.7}\text{Al}_{0.3}(\text{OH})_2(\text{CO}_3)_{0.1}$. In order to confirm the presence of cobalt ions in the former sample, we have used a X-ray energy-dispersive spectroscope to examine the elemental composition on the solid surface. Figure 1 displays an EDS spectrum of a selected area for MgCoAl sample.

Since SEM and EDX analyses were carried out on the sample to observe microstructural and composition inhomogeneity, it was observed all components (Mg, Al, Co, C, O), especially

cobalt species in the solid. The ratio of Mg^{2+} to Co^{2+} was atomically analyzed to be close to the nominal values of the starting chemical ratio.

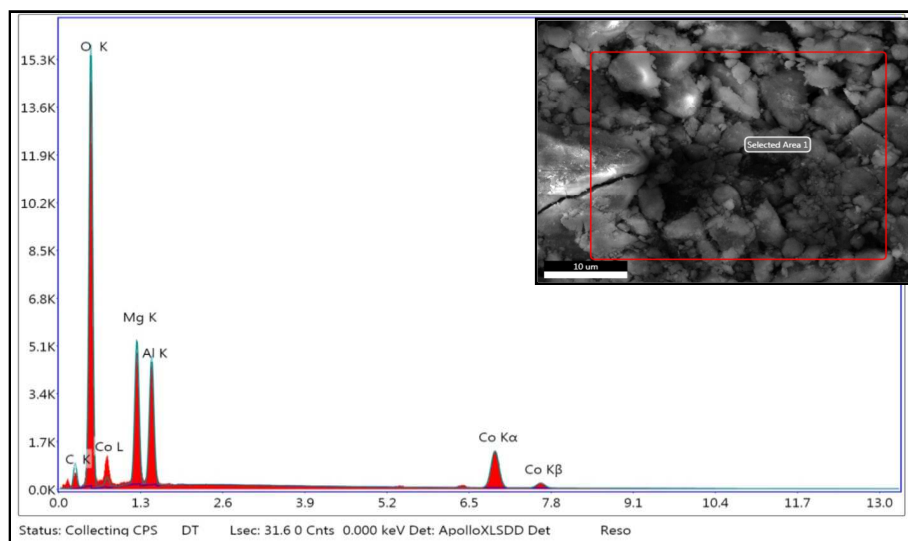


Figure 1. EDS spectrum and SEM image of Mg Co Al -LDH sample.

The phase structure of the synthesized samples was investigated by X-ray diffraction method. XRD patterns for the synthesized samples (Fig. 2) presented mainly characteristic features of typical layered double hydroxide (LDH). In details, symmetric and high intensities at low reflection angles (23.6°) and weak signals, asymmetric lines were observed at higher 2-theta values of $34.6, 39.4, 46.7, 61.1,$ and 62.1° [8-10,16,23]. The signals were respectively attributed to the reflection planes of (006), (009), (015), (018), (110) and (113), in good agreement with the literature [5, 10, 23, 24].

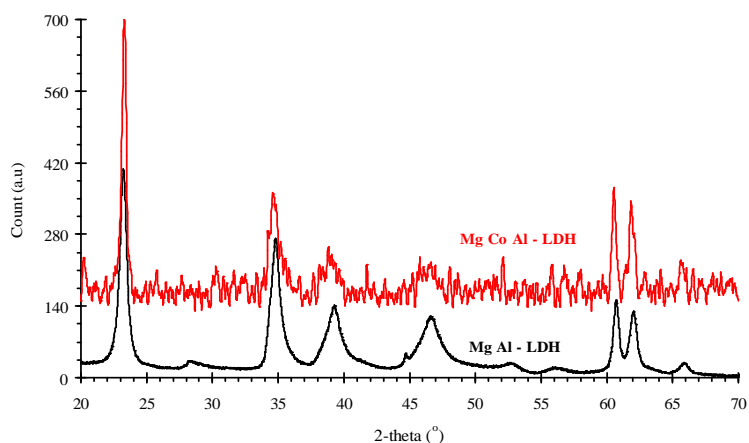


Figure 2. X-ray diffraction patterns of Mg(Co)Al - LDH catalysts.

By comparison, Figure 2 also revealed that the reflection lines of the MgCoAl patterns were essentially matched with those of MgAl sample, indicating the successful incorporation of Co into the Mg-Al LDH structure [9, 10, 23]. However, the signal-to-noise ratio of the former

pattern was much higher than that of the latter one, implying a slightly poorer crystallinity compared with the Co-free (Mg, Al) hydroxide layered-sample.

The catalyst morphology was roughly screened by EDS-SEM microscope (Fig. 1). It was irregular shaped particles for Mg-Co-Al sample. In some regions, aggregates of small particles are observed. The agglomeration of the primary particles led to the formation of empty spaces. These voids led to the appearance of the hysteresis during physical adsorption/desorption of nitrogen as shown in Fig. 3 [10, 23, 24].

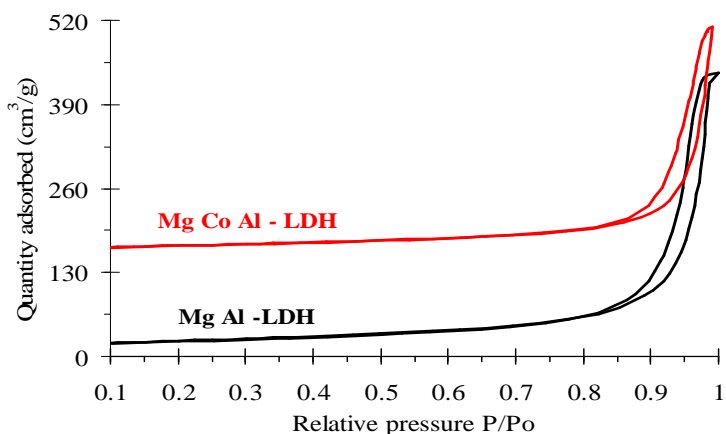


Figure 3. Nitrogen adsorption/desorption isotherms over hydrotalcite catalysts.

Indeed, Figure 3 indicated that the adsorption/desorption isotherms of LDHs were classified in to type of IV with Type H3 hysteresis loop. This is characteristic of a material, which is possibly porous, and has a high energy of adsorption. Slit-like pores are resulted from the agglomeration of interpartilces as seen in Fig. 1 [9, 10, 23, 24]. The BET surface area of MgAl and MgCoAl-LDHs is 83.4 and 74.5 m²/g, respectively.

3.2. Catalytic oxidation of styrene

The oxidation of styrene over two LDHs has been carried out in a batch reactor under atmospheric pressure. A couple of experiments were carried out under the same conditions, but the Co-free LDH exhibits very low conversion of styrene (approximately 1.0 %). Thus, it was suggested that MgAl-LDH catalyst was likely inactive for the oxidation of styrene with air. Therefore, the liquid oxidation reaction of styrene with air was concentrated mainly on Mg_{0.4}Co_{0.3}Al_{0.3}(OH)₂(CO₃)_{0.15}.xH₂O catalyst.

A set of experiments has been carried out in the range of temperatures of 60 – 100 °C. The main products were aldehyde, styrene oxide in addition to a small amount of byproducts including benzoic acid, styrene glycol, phenyl acetaldehyde was also observed, demonstrating the role of cobalt ions in the oxidation of styrene with air [1, 4, 9, 20]. A variation of product selectivity and vinyl benzene conversion with reaction temperatures was drawn in Figure 4. Under our experimental conditions, the reaction temperature was not only affected upon the conversion of styrene, but also influenced on the distribution of the products. In this scenario, the conversion of styrene linearly increased with increasing reaction temperatures. Meanwhile, benzaldehyde selectivity exhibited an opposite trend to the styrene conversion profile. The

temperature at 65 °C could initiate reaction with 18 % of styrene converted into benzaldehyde (99 % of selectivity) only. Along with increasing the reaction temperature to 75 °C, the conversion of styrene quickly increased to 46 %, simultaneously the selectivity to epoxide gradually reached to 30 % while that to benzaldehyde decreased monotonically to 64 %. The observed results let us suggest benzaldehyde likely being produced at lower temperatures. In contrast, selectivity to styrene epoxide reached a maximal value around 85 °C and decreased slightly with increasing reaction temperature as seen in Fig. 4B [2, 10, 22]. This observation was explained by the fact that both styrene oxide and benzoic aldehyde were not thermally stable at a high temperature and probably converted to the oxygen-rich compounds. Another reason was possibility that at higher temperatures the reactions became more complicated. Some side reactions like isomerization, overoxidation and even polymerization may happen simultaneously [2, 20].

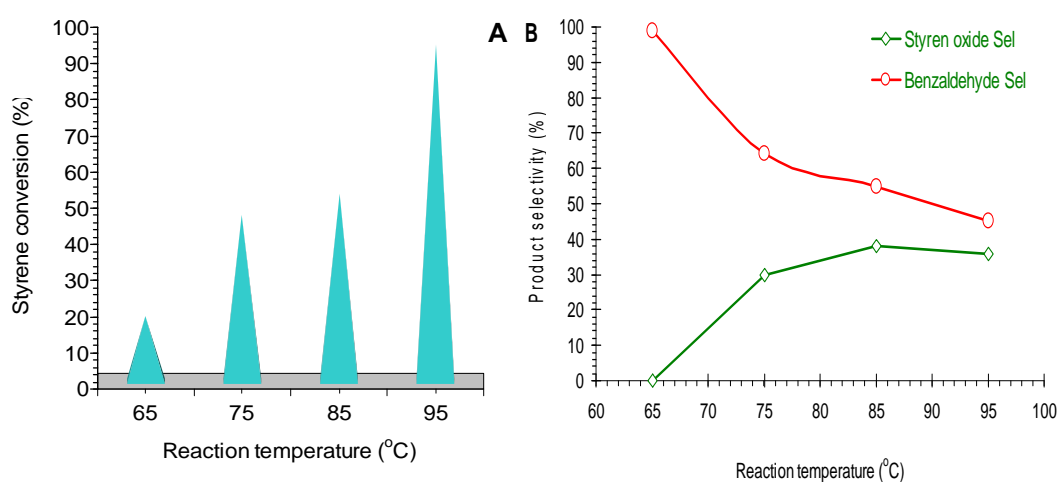


Figure 4. Effect of reaction temperature on styrene conversion (A) and product selectivity (B) over MgCoAl-LDH catalyst, 4 h, 200 mg of catalyst, 85 °C, air oxidant.

In order to elucidate the effect of reaction variables on the product distribution, the oxidation reaction has been carried out for a long period of time at a constant reaction temperature. Figure 5A displayed the conversion of styrene versus reaction time. It was noted that styrene conversion increases as the styrene was kept for a longer time in a batch reactor while larger amount of oxidant added continuously. Moreover, the analysis of product selectivity would provide more interesting information. The trends to benzaldehyde and to styrene oxide selectivity have been switched each other as the reaction time increases. Decreased benzaldehyde selectivity may be related to the secondary reactions in the batch reactor. Benzaldehyde may be further oxidized into other oxygenated compounds such as benzoic acid [1, 2, 20, 21]. Meanwhile, the selectivity to styrene epoxide reached a maximal value after 6 hours and the slightly decreased after a longer reaction time. An observable change in the selectivity to both main products at longer reaction time may be related to the side reactions and the overoxidation of styrene. Indeed, the product mixture was not only consisted of benzaldehyde and styrene oxide in these cases, but also composed of several other products such as diol, carboxylic, phenyl acetaldehyde... and some unidentified polymers. These products were produced from both secondary reactions and primary polymerization. This is in good

agreement with the results reported in our previous publications and literature [3, 8, 9, 17, 18, 20 - 22].

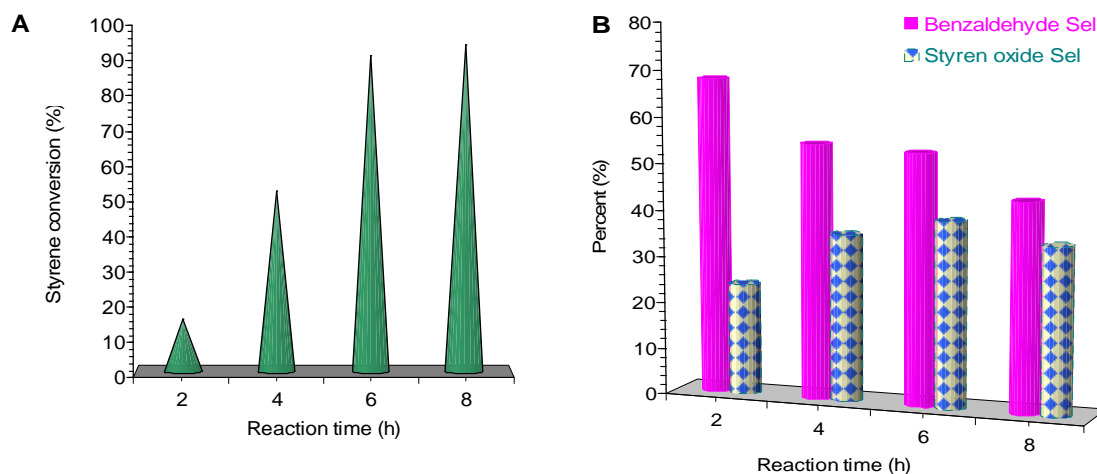


Figure 5. Effect of reaction time on styrene conversion (A) and product selectivity (B) over MgCoAl-LDH catalyst, 4 h, 200 mg of catalyst, 85 °C, air oxidant.

4. CONCLUSIONS

Mg(Co)Al-hydroxide materials had been prepared by the precipitation method. The solid had layered structure and Co^{2+} ions were present in the layered double hydroxide framework. The solids had a medium surface and good porosity. The presence of cobalt ions in LDH played as active sites for the conversion of styrene into benzaldehyde and styrene oxide in the presence of air. The conversion of styrene reached 90 – 95 % with the total selectivity to benzaldehyde and styrene oxide of 80 – 85 % at 85 °C and 6 hours. The preliminary catalytic performance indicated that MgCoAl-LDHs were active and selective in the oxidation of vinyl benzene with a friendly oxidant agent into valuable oxygenate products. The styrene conversion and product distribution were significantly affected by the reaction variables.

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