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

Nguyen Tien Thao *, Dang Van Long, Dinh Minh Hoan

Faculty of Chemistry, VNU University of Science, Vietnam National University Hanoi,
19 Le Thanh Tong ST, Hoan Kiem, Hanoi, 10000, VIETNAM

*Email: ntthao@vnu.edu.vn, nguyentienthao@gmail.com

Received: 13 July 2016; Accepted for publication: 13 March 2017

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\textsubscript{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 benzoic acid 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\textsubscript{α} radiation (\(\lambda = 1.59 \text{ Å}\)). Energy-dispersive spectroscopy (EDS or EDX) data were obtained from Varian Vista Ax X-ray energy-dispersive spectroscopy. 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 Mg\textsubscript{0.4}Co\textsubscript{3.2}Al\textsubscript{0.3}(OH)\textsubscript{2}CO\textsubscript{3}\textsubscript{0.15} and Mg\textsubscript{0.7}Al\textsubscript{0.3}(OH)\textsubscript{2}CO\textsubscript{3}CO\textsubscript{3}0.11. In order to confirm the presence of cobalt ions in the former sample, we have used a X-ray energy-dispersive spectroscopy 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
Conversion of styrene into benzaldehyde and styrene epoxide over MgCoAl-LDH catalysts

cobalt species in the solid. The ratio of $\text{Mg}^{2+}$ to $\text{Co}^{2+}$ 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.](image)

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 ($23.6^\circ$) and weak signals, asymmetric lines were observed at higher 2-theta values of 34.6, 39.4, 46.7, 61.1, and 62.1$^\circ$ [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.](image)

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].

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 interparticiles as seen in Fig. 1 [9, 10, 23, 24]. The BET surface area of MgAl and MgCoAl-LDHs is 83.4 and 74.5 m\(^2\)/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)\(_2\)(CO\(_3\))\(_{0.15}\)-xH\(_2\)O 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-richer 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.](image)

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.

Acknowledgment. This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.05-2017.04.

REFERENCES

1. Marco Dusi, Tamas Mallat, and Alfons Baiker - Epoxidation of Functionalized olefins over solid catalysts, Catal. Rev. – Sci. Eng. 42 (1&2) (2000) 213-278.
2. Stan M. Robert and Geraldine Poignant - Catalysts for Fine Chemical Synthesis, John Wiley & Sons, Ltd, Vol. 1 (2002)
3. Zhan H. J., Xia Q. H., Lu X. H., Zhang Q., Yuan H. X., Su K. X., Ma X. T. - Selective epoxidation of styrene with air catalyzed by CoOx and CoOx/SiO\(_2\) without any reductant, Catalysis Communications 8 (2007) 1472–1478.
4. Tang Q., Zhang Q., Wu H., Wang Y. - Epoxidation of styrene with molecular oxygen catalyzed by cobalt(II)-containing molecular sieves, J. Catal. 230 (2005) 384-397.
5. Beena Tyagi, Ulka Sharma1, Raksh Vir Jasra - Epoxidation of styrene with molecular oxygen over binary layered double hydroxide catalysts, Appl. Catal. A 408 (2011) pp. 171-177.
6. Wenming Zhu, Qinghong Zhang, and Ye Wang - Cu(I)-Catalyzed Epoxidation of Propylene by Molecular Oxygen, J. Phys. Chem. C 112 (2008) 7731–7734.
7. Guangjian Wang, Shuai Zhang, Yanhong Huang, Fangfang Kang, Zhenxing Yang, Yajie Guo - Styrene epoxidation over V-SBA-15 with alkaline-earth metal ion promotion under photo-assisted conditions, Appl. Catal. A 413-414 (2012) 52-61.
8. Nguyen Tien Thao, Le Thi Kim Huyen - Catalytic oxidation of styrene over Cu-doped hydrotalcites, Chemical Engineering Journal 279 (2015) 840-850.
9. Nguyen Tien Thao, Ho Huu Trung - Selective oxidation of styrene over Mg-Co-Al hydrotalcite like-catalysts using air as oxidant, Catalysis Communication 45 (2014) 153-157.
10. Kirm I., Medina F., Rodriguez X., Cesteros Y., Salagre P., Sueiras J. - Epoxidation of styrene with hydrogen peroxide using hydrotalcites as heterogeneous catalysts, Appl. Catal. A 272 (2004) 175–185.
11. Laura Espinal, Steven L. Suib, and James F. Rusling - Electrochemical Catalysis of Styrene Epoxidation with Films of MnO2 Nanoparticles and H2O2, J. Am. Chem. Soc. 126 (2004) 7676-7682.
12. Sweta Sharma, Shishir Sinha, and Shri Chand - Polymer Anchored Catalysts for Oxidation of Styrene Using TBHP and Molecular Oxygen, Ind. Eng. Chem. Res. 51 (2012) 8806-8814.
13. Choudhary V.R., Jha R., Chaudhari N.K., Jana P. - Supported copper oxide as a highly active/selective catalyst for the epoxidation of styrene by TBHP to styrene oxide, Catal. Commun. 8 (2007) 1556-1560.
14. Liang Nie, Ke Ke Xin, Wen Sheng Li, Xiao Ping Zhou - Benzaldehyde synthesis via styrene oxidation by O2 over TiO2 and TiO2/SiO2, Catal. Commun. 8 (2007) 488–492.
15. Nguyen Tien Thao, Nguyen Thi Ngoan, Dang Van Long - Study on catalytic activity of TiO2/SiO2 in the oxidation of styrene, Science & Technology Development-VNUHCM, 12 (3) (2009) 77-86.
16. Choudhary V. R., Indurkar J.R., Narkhede V.S. - MoO4 exchanged Mg–Al hydrotalcite: a stable and reusable/environmental-friendly catalyst for selective oxidation by oxygen of ethylbenzene to acetonophene and diphenylmethane to benzophenone, J. Catal. 227 (2004) 257.
17. Nguyen Tien Thao, Nguyen Duc Trung, Dang Van Long - Activity of molybdate-intercalated layered double hydroxides in the oxidation of styrene with air, Catalysis Letters 146 (3) (2016) 918-928.
18. Zhang S. Q., Wang Y., Itsuki S., Shishido T., and Tekechira K. - Manganese-containing MCM-41 for epoxidation of styrene and stilbene, J. Mol. Catal. A 188 (2002) 189-200.
19. Das B. K., Clark J. H. - A novel immobilised cobalt(III) oxidation catalyst, Chem. Commun. (2000) 605.
20. Sebastian J., Jinka K. M., Vir Jasra R. - Effect of alkali and alkaline earth metal ions on the catalytic epoxidation of styrene with molecular oxygen using cobalt(II)-exchanged zeolite X, J. Catal. 244 (2006) 208-218.

21. Nguyen Tien Thao, Nguyen Anh Tuan - Characteristics and Reactivity of La-Co-Cu based perovskites for the liquid oxidation of styrene, VN Journal of Chemistry 52 (2) (2014) 234-239.

22. Nguyen Tien Thao, Nguyen Van Tien, Dang Van Long, Le Thi Kim Huyen - Catalytic activity of cobalt oxides/bentonite in the conversion of styrene, VNU J. Sci. Technol. 30 6S (2014) 263-268.

23. Williams G.R. and O’Hare D. - Towards understanding, control and application of layered double hydroxide chemistry, J. Mater. Chem. 16 (2006) 3065-3074.

24. Di Cosimo J.I., Diez V. K., Xu M., Iglesia E., and Apestegui C. R. - Structure and surface and catalytic properties of Mg-Al basic oxides, J. Catal. 178 (1998) 499-510.