




Research Article

Mg-Al-Cr₂O₇ Hydrotalcite-Like Catalysts Synthesized at Different pH Values for Styrene Oxidation

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Abstract: Dichromate anions were intercalated between two consecutive hydroxide layers of $[\text{Mg}_{0.6}\text{Al}_{0.4}(\text{OH})_2]^{0.40+}$ via co-precipitation at different pH conditions. The physico-chemical properties of the obtained solids were examined by physical methods such as X-ray diffraction (XRD), Infrared (IR), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET) and Energy-Dispersive Spectroscopy (EDS). The experimental results indicated that the amount of dichromate anions in the catalysts varies with the pH media. Also, the morphology, structure and chemical composition of the materials depends strongly on the preparation conditions. The Mg-Al-Cr₂O₇ hydrotalcite-like compounds are used as heterogeneous catalysts for the styrene oxidation with H₂O₂ at mild conditions. The styrene conversion is about 20-50% while styrene selectivity remains rather high.

Keywords: Mg-Al-Cr₂O₇, hydrotalcite, interlayer anion, oxidation, styrene

1. Introduction

Partial and selective oxidation of styrene has received great attention from researchers because its products are valuable intermediates used in numerous industrial processes such as manufacture of coloring agents, pharmaceuticals, perfumes and organic synthesis. A conventional procedure is to perform the liquid-phase reaction in homogeneous processes, giving a mixture of unselected products.¹ In the interest of green chemistry, scientists have attempted to develop solid catalysts and utilize eco-friendly oxidizing agents such as hydrogen peroxide, molecular oxygen, and air instead of inorganic oxidizing chemicals.^{2,3} These heterogeneous catalysts were readily removed from the product mixture, easily recycled after reaction. However, the oxidation reactions of unsaturated hydrocarbons with H₂O₂ over solid catalysts usually produce numerous oxygenated products.^{4,5} Therefore, preparation of product-selected catalysts is always an interesting subject.

Hydrotalcite-like compounds have been known as good adsorbents, anion scavengers/exchangers, catalyst supports, and catalysts. The potential applicability of such mineral-structured-like materials comes from their special textural features. The brucite-like sheets are constructed from divalent and trivalent metallic cations in octahedral coordination. These octahedral layers appear positive charges, which are compensated by guest anions. Thus, the general formula for these compounds is expressed as $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where x is the trivalent metal ratio $\text{M}^{\text{III}}/(\text{M}^{\text{II}}$

+ M^{III}) ($0.2 \leq x \leq 0.4$).⁶ Another transition metal may replace a divalent cation.^{5,7,8} For example, chromium(III) ions are already introduced to the hydroxide layers and exploited significant catalytic performance in the oxidation of primary alcohols and aromatic compounds.⁸⁻¹¹ The catalytic activity of the latter materials may involve in the oxidation-reduction cycle between Cr(III) and Cr(VI) ions.¹²⁻¹⁴ The present work reports the role of dichromate moieties in the Mg-Al layered double hydroxides in the oxidation of styrene. Thus a set of dichromate-intercalated Mg-Al hydrotalcites was prepared at different pH media and used as a catalyst for the liquid oxidation of vinyl group.

2. Materials and methods

2.1 Sample preparation

Mg-Al hydroxide layers were built by precipitation of the corresponding nitrate salts in basic solution. Briefly, 150 mL of mixed aqueous solution of magnesium nitrate hexahydrate (99%, Merck) and aluminum nitrate nonahydrate (99.99%, Merck) with a given molar ratio was added dropwise into 25 mL of aqueous solution containing a rational amount of potassium dichromate (or carbonate, 99.5%, Wako) in a 600-mL beaker. During the precipitation, the mixture remained at a nearly fixed pH value (pH = 7, 8, 9, 10 and 11) with slow drops of 1.0 M NaOH solution. The resulting suspension was kept under magnetic stirring at 65°C for 24 h. The obtained mixture was cooled to room temperature, filtrated and washed several times with distilled water, and then left in a drying oven operating at 65°C for another 24 h. In addition, a physical mixture of MgO, Al₂O₃, and K₂Cr₂O₇ blended together with Mg/Al/Cr of 6/4/2 molar ratio was used as reference.

2.2 Catalyst characterization

Powder X-ray diffraction (XRD) patterns of all samples were recorded on a D8 ADVANCE-Bruker instrument with CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$). Fourier-transform Infrared (FT-IR) spectra were obtained in 4000-400 cm⁻¹ range on a FT/IR Spectrometer (Shimadzu 6300, Japan). Energy-dispersive spectroscopy (EDS) data were collected using a JEOL JSM-84A (JEOL, Tokyo, Japan) equipped with an energy-dispersive X-ray (EDS) Oxford ISIS 300 micro-analytical system (Isis Innovation Ltd., University of Oxford, Oxford, UK). The morphology of modified hydrotalcites was observed using scanning electron microscopy (SEM) on a Hitachi S-4800-10W-HI-9057-0006 (Japan). Specific surface area of the materials was determined by Brunauer-Emmett-Teller (BET) method (TriStar 3000 V6.07, USA). Diffuse reflectance spectra of the catalysts were acquired in the 220-800 nm region using a Libra S80 Double Beam Spectrophotometer (Biochrom, UK). Raman spectra of the powder solids were recorded on a LabRAM HR800 spectroscopy (HORIBA, French) in the spectral range of 200-1200 cm⁻¹.

2.3 Styrene oxidation

Liquid oxidation of styrene was carried out in a 50 mL three-neck round bottom flask attached to a reflux condenser. For all experiments conducted in this study, 0.20 g of catalyst, 8.0 mL of N,N'-Dimethylformamide (DMF) solvent and 17.4 mmol of styrene were contained in the flask under magnetic stirring. The mixture was raised to the desired temperature and hydrogen peroxide solution (H₂O₂, 30%, Sigma Aldrich) was dropped into the system. Finally, the mixture cooled down to room temperature and the catalyst was removed. The filtrate was subjected to a quantitative analysis using a GC-MS (HP-6890 Plus).

Table 1. Some physical properties of Mg-Al-Cr₂O₇ layered materials

Sample	Batch No.	pH	S _{BET} (m ² /g)	Lattice parameters (Å) ^a		Molar ratio ^b	
				a	c	Mg/Cr	Al/Cr
Mg-Al-CO ₃	MACa9	9	138	3.03	22.7	-	-
	MACr7	7	-	3.04	-	-	-
	MACr8	8	8.5	3.04	25.5	3.07	2.29
Mg-Al-Cr ₂ O ₇	MACr9	9	-	3.04	25.1	-	-
	MACr10	10	47.7	3.04	23.9	6.02	3.07
	MACr11	11	-	3.03	22.3	-	-

^aLattice parameters: $a = 2 \times d_{110}$; $c = 1.5 \times (d_{003} + 2 \times d_{006})$; ^bEstimated from EDS analysis

3. Results and discussion

3.1 Physico-chemical characterization

X-Ray diffractodiagram for all prepared solids are displayed in Figure 1. First of all, the XRD pattern for the typical Mg-Al hydrotalcite sample (MACa9) shows clear reflection lines with a very high signal-to-noise ratio (SNR). These reflection lines are typical descriptions of a well-ordered hydrotalcite structure—a hexagonal lattice with R3m rhombohedral symmetry.¹²⁻¹⁴ Meanwhile, XRD patterns of dichromate-inserted samples express a lower SNR, indicating a low crystalline degree. Furthermore, the reflection angles of 2-theta of Mg-Al-Cr₂O₇ patterns are somewhat deviated from that of the parent Mg-Al-CO₃ material (MACa9), suggesting a change in interlayer domain and basic spacing. In more detail, a shift in reflection lines at (003) position in XRD patterns is attributed to the presence of Cr₂O₇²⁻ anions between brucite-like layers.^{15,16} Lattice parameters of synthesized catalysts, calculated from X-ray diffraction data, are listed in Table 1. Apparently, no observable change in the lattice parameter (*a*) was noted for Mg-Al-Cr₂O₇ samples prepared at different pH values because the molar ratio of Mg/Al is constant. In contrast, the interlayer gallery height is slightly extended due to the insertion of chromates into interlayer regions. Figure 1 also reveals that the structure of sample MACr9 is close to the one of MACa9. Thus, the appropriate pH value for the synthesis of Mg-Al-Cr₂O₇ is in the range of 8.0-10.0.

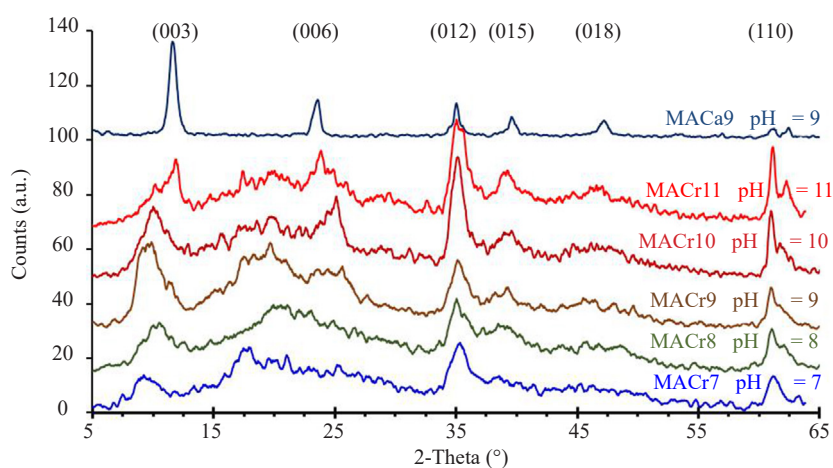


Figure 1. XRD patterns for Mg-Al-CO₃ (MACa9) and Mg-Al-Cr₂O₇ hydrotalcite-like samples (MACr7-11) synthesized at different pH conditions

Since the pH media has a strong effect on the crystalline degree and structure of dichromate-intercalated double hydroxides, the composition of chromium ions may be beyond from theoretical values. Elemental composition of some representative samples determined by the EDS technique reported in Table 1 and Figure 2. Indeed, line intensities of chromium in sample MACr8 are much higher than those in MACr10, which are in good agreement with XRD analysis (Figure 1). At a higher pH, the amphoteric nature of aluminum hydroxides leads to the formation of several hydroxide phases in addition to hydrotalcite component. Lower trivalent metal content results in less significant positive charge in the brucite sheets and followed by declined chromate content.

Infrared (IR) spectra were taken to identify the chemical bonds in Mg-Al-Cr₂O₇ samples. A strong absorption band at 3485 cm⁻¹ is attributed to the stretching mode of hydrogen-bonded hydroxides in brucite-like layers and absorbed water molecules,^{4,17} while the weaker band at 1645 cm⁻¹ is assigned to the bending mode of interlayer water molecules.^{15,16,18} A sharp peak at 1375 cm⁻¹ is firmly ascribed to the vibration of dichromate in the interlayer galleries. The absorption band at 881 cm⁻¹ and a visible shoulder at 910 cm⁻¹ are assigned to terminal (Cr-O) vibration.¹⁹ In the region below 800 cm⁻¹ where metal-oxygen modes are normally found, it is difficult to assign (Cr-O-Cr) vibration mode; however, a broad band at 780 cm⁻¹ and a weak adsorption at 555 cm⁻¹ are ascribed relatively to the asymmetric and symmetric stretch of this bridge.¹⁹

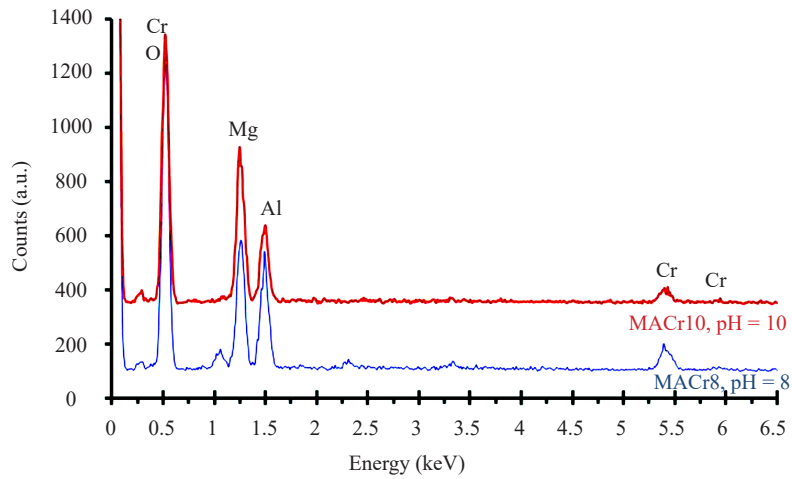


Figure 2. EDS spectra for Mg-Al-Cr₂O₇ layered double hydroxides (pH = 8, 10)

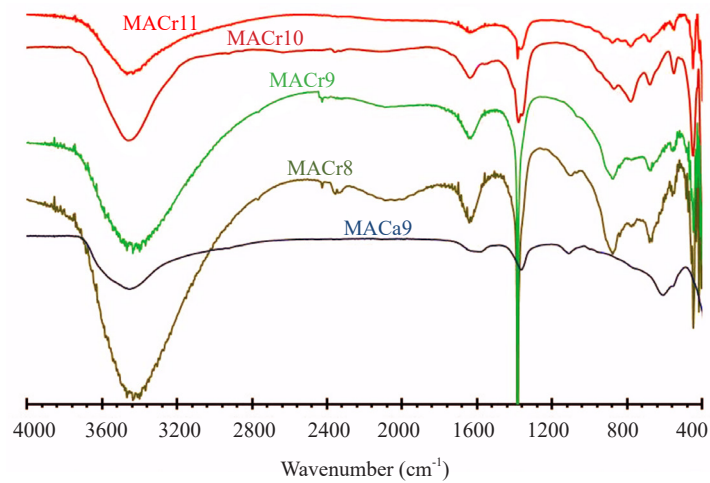


Figure 3. IR spectra of Mg-Al-CO₃ and Mg-Al-Cr₂O₇ hydrotalcite-like compounds synthesized at different pH = 8-11

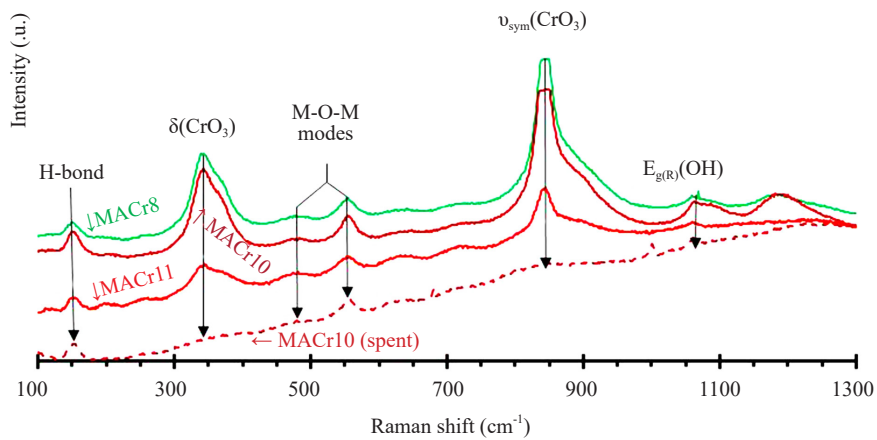


Figure 4. Raman spectra of Mg-Al-Cr₂O₇ materials before and after oxidation reaction

As seen in Figure 4, Raman spectra appear a sharp band at 1061 cm^{-1} , with a broader and much weaker overlapping band around 1053 cm^{-1} , which is assigned as $E_{g(R)}(\text{OH})$.¹⁵ The two bands around 476 and 552 cm^{-1} correspond to hydroxyl groups mainly associated with Al^{3+} ions, which are probably influenced by the Mg^{2+} cations. The sharp peak in the region below 200 cm^{-1} is assigned to hydrogen bonding. The only visible absorption peaks of $\text{Cr}_2\text{O}_7^{2-}$, centered at 379 cm^{-1} and 883 cm^{-1} , are assigned to bending mode $\delta(\text{CrO}_3)$ and CrO_3 -symmetric stretch.²⁰ The significant shift of these bands towards lower frequencies due to a weakening of the Cr-O bond results from an interaction via hydrogen bonds, either with the water molecules present in the interlamellar space or with the OH groups from the brucite-like sheets. In the spent sample, the weak signals are due to chromate ions being leached out of the interlayer domains.

SEM micrographs (Figure 5) are obtained to study the influence of pH on the catalyst morphology. The decreased average diameter of Mg-Al- Cr_2O_7 particles at high pH value is smaller than that at low pH preparation. Overall, the synthesized solids have uniform particles and high density, which results in less porosity and a low specific surface area.

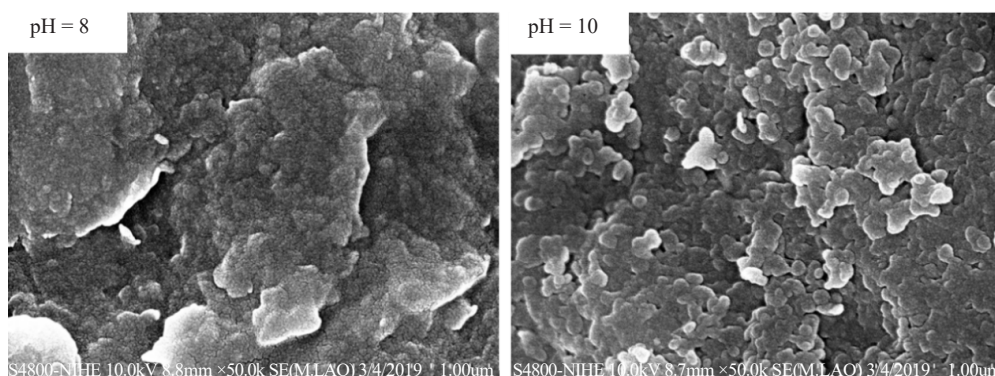


Figure 5. SEM micrographs of Mg-Al- Cr_2O_7 samples

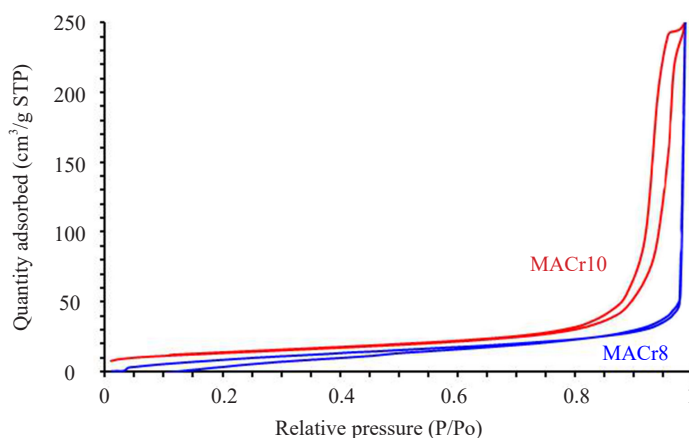


Figure 6. Nitrogen adsorption-desorption isotherms of Mg-Al- Cr_2O_7 hydrotalcite-like catalysts (pH = 8, 10)

The porosity of Mg-Al- Cr_2O_7 samples is characterized by the nitrogen physical sorption method. The isotherm curves of the two samples are quite similar in the relative pressure of 0-0.80 (Figure 6). The isotherm of MACr10 has a H3 hysteresis loop in the relative pressure range 0.80-1.0, indicating the presence of mesopores and micropores in the solids.^{15,18} Meanwhile, both desorption and adsorption curves are not well separated from each other for sample MACr8, inferring the absence of mesopores-like spaces between particles. As a consequence, the specific surface area of MACr8 is smaller than that of MACr10, in good harmony with the observation from SEM image.

UV-Vis spectra were recorded to examine the presence of dichromate moieties in the samples before and after a

2-hour reaction. UV-Vis spectra of such solids show two strong absorption peaks at 275 and 375 nm. The first band is ascribed to the charge transfer transition between oxygen and chromium(VI) ions and the other one is ascribed to the chromate ions.^{19,21-23} It is noted that the intensity of maximal absorption of chromate centered at 375 nm increases in the range of pH from 8 to 11, reflecting the presence of chromate anions on the external surface. Indeed, a sharper absorption band on the spent MACr10 is interpreted by the fact that chromate anions are out of the interlayer regions after catalytic oxidation reaction.

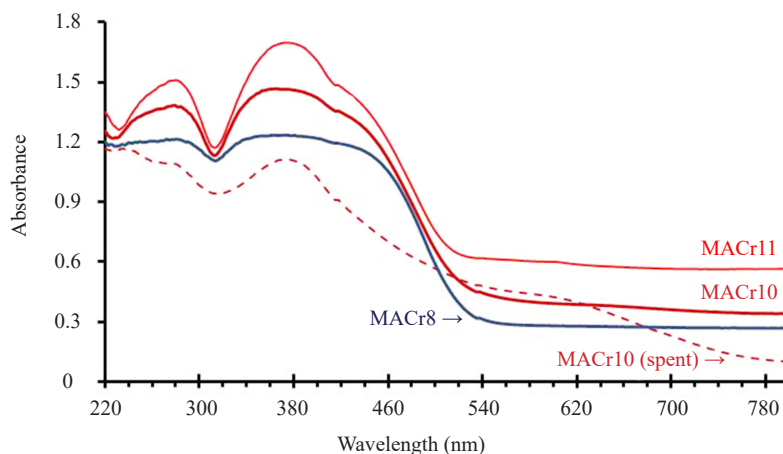


Figure 7. UV-Vis data of Mg-Al-Cr₂O₇ samples (pH = 8, 10, 11)

3.2 Catalytic activity

Mg-Al-Cr₂O₇ layered double hydroxides were used as catalysts in the liquid oxidation of styrene with H₂O₂ in DMF solvent at 40°C for 2 h. In reference, a blank test (without catalyst) and a mixture of MgO/Al₂O₃/K₂Cr₂O₇ were carried out under similar conditions. The blank test shows a trace of products. In all cases, the main products are benzaldehyde and styrene oxide in addition to a small amount of benzoic acid.

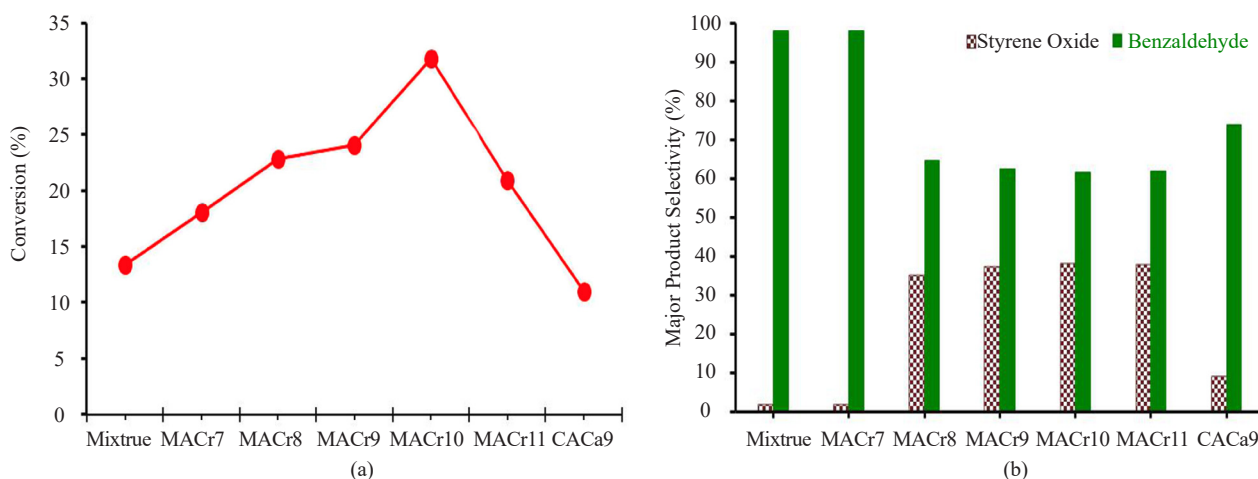


Figure 8. Conversion (a) and product (b) in the oxidation of styrene with H₂O₂ on layered double hydroxides and MgO/Al₂O₃/K₂Cr₂O₇ mixture (H₂O₂/styrene = 1/2, DMF solvent, 40°C, 2 h)

As seen in Figure 8, Mg-Al-CO₃ hydrotalcite catalyst gives the lowest conversion of styrene while the mixture of

MgO/Al₂O₃/K₂Cr₂O₇ shows a small conversion degree. For a set of Mg-Al-Cr₂O₇ hydroxalite-like catalysts, the volcano-shaped curve of styrene conversion was observed in Figure 8a, inferring a relationship between styrene conversion and chromate-inserted amount. A maximal conversion reached on sample MACr10 substantiates an appropriate pH value for the preparation of active Mg-Al-Cr₂O₇ layered double hydroxide catalysts. Essentially, at this pH value, most chromate anions stayed in the interlayer regions as indicated by XRD, Raman and UV-Vis techniques. Moreover, chromate-intercalated species undergo the oxidation of styrene to both styrene oxide and benzaldehyde product (Figure 8b) while chromium(VI)-free ions perform the conversion of substrate to benzaldehyde (sample MgO/Al₂O₃/K₂Cr₂O₇).¹⁵ At a higher pH, other hydroxide phases are present in the solid, resulting in some side reactions.^{24,25}

The influence of reaction temperature on the styrene oxidation was carried out to demonstrate the role of chromate ions. It is observed in Figure 9 that increasing reaction temperature would be beneficial to the partial oxidation of styrene, but not favorable for the formation of benzaldehyde. In detail, styrene conversion increases from 18 to 41.5% as reaction temperature rises from 30 to 60°C (Figure 9a). On the contrary, benzaldehyde selectivity profile (BzH Sel) gradually decreases with increasing temperature. Simultaneously, styrene oxide becomes a major product at higher reaction temperatures (Figure 9). This phenomenon is explained by kinetic chemistry; the activation energy of styrene oxide is higher than that of benzaldehyde as reported in the literature.^{21,22,25} A similar observation was observed on sample MACr10 (Figure 9b).

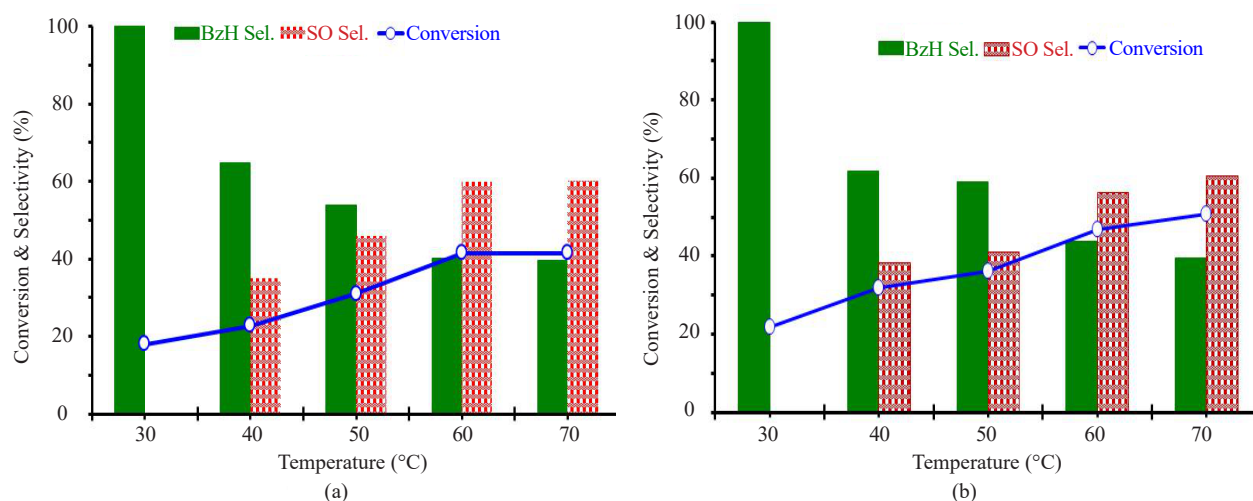


Figure 9. Influence of temperature on catalytic activity of MACr8 (a) and MACr10 (b) in the styrene oxidation with H₂O₂ (oxidant/substrate = 1½, 2 h, DMF solvent)

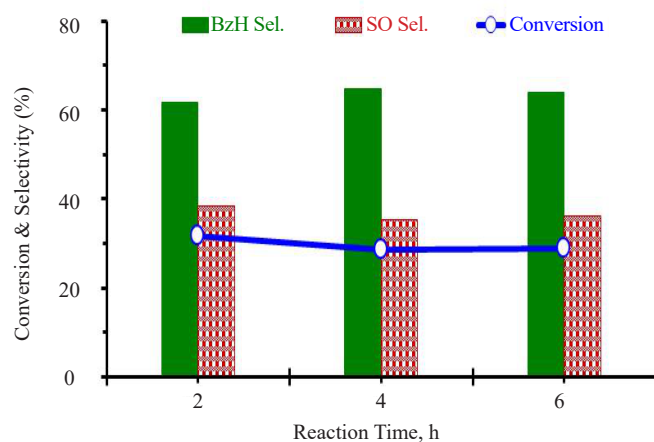


Figure 10. Effect of reaction time on styrene oxidation over MACr10 sample (oxidant/substrate = 1½, 2 h)

Further experiments will investigate the effects of reaction time on the product distribution. Figure 10 exhibits experimental data for the oxidation of styrene over sample MACr10 lasted from 2 to 6 hours. It is observed only a minor change in styrene conversion and product distribution within reaction time window. Chromate moieties confined in the interlayer galleries become less mobile and perform the selective oxidation of styrene with hydrogen peroxide to styrene oxide evidenced by the formation of a high amount of epoxide in the product mixture.^{18,23,24} In practical, the catalyst turned to bluish-green color after 2 hours, suggesting an occurrence of reduction-oxidation interconversion between Cr(VI) to Cr(III) ions.²⁴⁻²⁶

4. Conclusions

Mg-Al-Cr₂O₇ layered double hydroxide was prepared at different pH values to intercalate chromate anions into the interlayer spaces. Under similar synthetic conditions, the pH environment has a significant impact on morphology, structure and chemical composition of the as-synthesized materials. Mg-Al-Cr₂O₇ hydrotalcite-like compounds showed good crystallinity, uniform particles, and high specific surface area as precipitated at pH of 8-10.

The catalyst was subjected to study the liquid phase oxidation of styrene by H₂O₂ and the catalytic activity of Mg-Al-Cr₂O₇ layered double hydroxide depends on the pH preparation, the amount and location of chromate anion, temperature, reaction time. The experimental results indicated that dichromate-intercalated hydrotalcites exhibited good catalytic activity for the oxidation of styrene into benzaldehyde and styrene oxide. The redox properties of Cr₂O₇²⁻ in interlayer domain of hydrotalcite played as active sites for the formation of styrene oxide and benzaldehyde while chromate-free ions are active for the production of benzaldehyde. Styrene conversion reached about 20-50% with excellent selectivity towards benzaldehyde and styrene oxide.

Conflict of interest

The authors declare no competing financial interest.

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