

Layered double hydroxides: Novel nanocatalysts for combustion of gaseous toluene from polluted air

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ABSTRACT

The catalytic performance of Ni-Al, Mg-Al, and Co-Ni LDHs as novel nanocatalysts was evaluated in the oxidation of toluene. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). The XRD and FTIR approved the structure and functional groups of the LDH, respectively. Also, the presence of cations with different oxidation state confirmed by XRD. According to this result, Mars Van Krevelen (MVK) mechanism was suggested for the combustion of toluene over the LDH nanocatalysts. The SEM results indicated that the nanostructure and layered morphology of the catalysts. All LDHs exhibited catalytic activity for toluene oxidation. T₈₀ (temperature for 80% conversion for toluene) for Co-Ni, Ni-Al and Mg-Al LDH catalysts were 225, 277 and 350 °C, respectively. So, the Co-Ni LDH showed the highest activity. Furthermore, Ni-Al LDH exhibited the highest thermal stability. So, we concluded that Ni-Al LDH is a superior catalyst for toluene oxidation in the studied series.

Keywords: Air pollution, Toluene, Nanocatalyst, Layered double hydroxides, Catalytic oxidation.

1. Introduction

Large compounds that have the primary role in air pollutions are Volatile Organic Compounds (VOCs). These compounds are the most abundant air pollutants, as a result of industrial activities in the chemical, petrochemical, and related industries. The compounds are not only harmful to the environment but human health even at low concentrations. These days, job contact with volatile organic compounds has become more important. The studies have shown that contact with VOCs has various effects, such as inflammation of the eyes, effects on the nervous system, liver toxicity, and cancers [1-3]. The most common volatile organic compounds in industrial environments are toluene, benzene, Xylene, and ethylbenzene [4]. Toluene, as a representative of VOCs, is commonly used in many industries and environments that deal with paint and painting. The toluene odour threshold is in the range of 3-5.1 ppm, which is hardly detectable by humans in this concentration range.

It is dangerous for jobs that are at risk of long-term exposure, and it has a lot of health effects on the central nervous system [5]. There are a lot of ways for controlling Volatile organic compounds such as Adsorption, thermal and catalytic oxidation, photocatalytic oxidation, and plasma. In the meantime, catalytic or thermal oxidation is a method used by some researchers to remove volatile organic compounds [6-8]. In the catalytic processes, the catalyst plays the main role and determines the selectivity toward the products. Numerous papers have been reporting the application of different catalysts in the combustion of VOCs [1-10].

The hydroxalite-like materials or layered double hydroxides (LDHs) have numerous applications such as ionic conductors, ion exchangers, adsorbents, catalysts, supports, pharmaceuticals and so on [9]. The general chemical formula of materials can be written as $[M^{2+}_{1-x}M^{3+}_x(OH)_2(A^{n-})_{x/n} \cdot mH_2O]$. In the formula, M^{2+} and M^{3+} are divalent and trivalent cations occupying the center of $M(OH)_6$ octahedral units, and A^{n-} is a compensation anion [10].

Numerous cation pairs and interlayer anions have been used in LDHs [11]. However, LDHs replacing the Mg^{2+}

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for transition metals in the brucite-like layer are scarce due to the difficulty in obtaining a pure hydrotalcite phase. Thermal treatment decomposes the LDH and causes to form a mixed oxide which has high surface area [12].

The substitution of trivalent metal instead of divalent cation causes a positive charge, which was further compensated by the exchangeable interlayer anions. Thus, LDHs are considered as anionic clays due to their ability to exchange the anion [9]. The hydrotalcite with the formula of $(\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)_4\cdot 4\text{H}_2\text{O}\text{-LDH})$ was discovered in 1842, and other compounds with LDH structure such as $\text{Mg}_6\text{Cr}_2(\text{OH})_{16}\text{CO}_3\cdot 4\text{H}_2\text{O}$ (stichtite), $\text{Mg}_4\text{Fe}(\text{OH})_{10}\text{Cl}\cdot 3\text{H}_2\text{O}$ (iowaite), $\text{Mg}_6\text{Fe}_2(\text{OH})_{16}\text{CO}_3\cdot 4.5\text{H}_2\text{O}$ (pyroaurite) and $\text{Ni}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\text{OH}\cdot 4\text{H}_2\text{O}$ (takovite) have been found later [13-14]. Also, some synthetic LDHs were prepared with various metal and anionic composition. Recently, hydrotalcite-type LDHs, represented by Mg-Al LDHs, have been studied for different applications [15-16]. These LDHs can be oxidized at a moderate temperature and can be used as an acidic catalyst at hydrogenation or steam reforming process [17-18]. The LDH has also been studied for drug delivery applications [19-21]. It is possible to fabricate LDH-based films by delaminating and reassembling of LDH layers [22] or catalytic materials [23]. The results of the catalytic studies have shown that the entry of hydroxide catalysts in the gas phase to remove toluene has increased the catalytic activity of the new catalyst and increased catalyst selection relative to carbon dioxide [24]. LDHs show good catalytic activity because of important advantages, such as suitable basicity, high surface area and the improved selectivity under mild conditions [25]. Besides, the surface/interface defect structures (e.g., oxygen vacancy defects or metal defects), type, quantity and strength of surface acid/base sites, the geometric and electronic structure can be strategically engineered to give a catalyst with high activity and excellent selectivity for a specific target reaction [26].

Many efforts have been done to tailor the physical and chemical properties of LDHs by changing the nature of metal cations, the molar ratio of $\text{M}^{2+}/\text{M}^{3+}$, the type of interlayer anions. In this work, we focus on changing the type of metal cations and evaluating their catalytic activity in the combustion of toluene. The LDHs, i.e. Mg-Al LDHs, Ni-Al LDH, and Co-Ni LDHs were prepared. Mg-Al LDH is a hydrotalcite found in nature and was used as reference LDH. Nickel and cobalt are of active metals in catalytic combustion of hydrocarbons [1, 5]. So, two LDHs, i.e. Ni-Al LDH and Ni-Co LDH were synthesized and their catalytic activity was compared with Mg-Al LDH. The stability of the

catalysts was also investigated. The catalysts were characterized with XRD, FTIR and SEM.

2. Experimental

2.1. Synthesis of Ni-Al LDHs

The method used to synthesize the catalysts was the conventional co-precipitation method. At first, 100 mL of an aqueous solution containing 9.5 g of $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and 6.19 g $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was prepared (mol ratio Ni: Al was 2:1). Then, 50 mL solution containing 4 g NaOH and 1.125 g Na_2CO_3 was added dropwise to above under nitrogen gas, which resulted in white sediment formation (pH was 9-10). The resulting solution was aged for 12 h. After that, the sediment was deposited in the centrifugal system and washed several times with distilled water again. Finally, it was dried at 50 °C under vacuum for 24 h [27].

2.2. Synthesis of Mg-AL LDHs

The co-sedimentation method was used to synthesize magnesium-aluminium double-layer hydroxide. The basis of the method is to increase the drop of a solution from a solution containing metal salts to a solution at a pH-specific temperature. The molar ratio of magnesium salt to aluminium was 2 to 1. Consequently, 6.4 g $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and 4.6 g $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ dissolved in 100 ml of deionized water and the solution (I) were named. 4 g of sodium hydroxide was mixed with 1.125 g of sodium carbonate and were dissolved in 50 ml of deionized water and named the solution (II). The solution (II) was added dropwise to the solution (I) to obtain a pH of 9-10. During the adding, the solution (I) was mixed by a magnetic stirrer at room temperature. After this time, the solution was separated using a vacuum pump and dried at a temperature of 60°C [27].

2.3. Synthesis of Co-Ni LDHs

All the components used in work were obtained from Merck Company. The LDH of Co-Ni with a molar ratio of 2:1 were prepared. Under stirring, the ammonia solution (25–28%) was added to the above solution to reach the pH solution to 9-10. The resultant was aged for 12 h and separated by filtration and rinsed several times, and then dried at 60 °C for 12 h [28].

2.4. Characterization of catalyst

The catalysts were investigated by a Philips PW1800 diffractometer with a copper anode ($\lambda=0.154178$ nm) to determine their structure and crystal phase. The FTIR spectra were resulted in using a Bruker spectrometer (model TENSOR 27) with KBr compact discs at the wavenumber $3900\text{-}400\text{ cm}^{-1}$. The particle size and the morphology of the catalysts were determined by

scanning electron microscopy (SEM) using a Philips XL30 instrument [28].

2.5. Catalytic Studies

Fig. 1. shows the schematic of the setup used for the study of the toluene oxidation. The catalytic reaction of toluene carried out in a glass reactor ($l=60\text{cm}$, i.d.=0.8 cm) at 100-450 °C under atmospheric pressure. In each test, 200 mg catalyst was loaded in the reactor and fixed with quartz wool at the center of the reactor (catalyst bed length=2 cm). The gas hourly space velocity was 2500 h^{-1} . The inlet concentration of toluene to the gaseous phase was about 0.004 mol. mol^{-1} (1270 ppm).

Before the tests, the catalyst was pretreated with air at 200 °C. Also, the stability of the LDH catalysts were investigated at 250 °C for 300 min. The gases were analyzed with a Shimadzu 2010 gas chromatograph. The samples of reaction products were injected by a 1.000 μL Hamilton syringe and the conversion was calculated using equation (1).

$$X = \frac{C_{in}-C_{out}}{C_{in}} \times 100 \quad (1)$$

3. Results and discussion

3.1. XRD analysis of LDH catalyst

The XRD patterns of the samples are shown in Fig. 2. This figures show the patterns of Ni-Al and Mg-Al catalysts, represented in the 2θ range of 10-70°. The main peaks of Ni-Al sample at the XRD pattern (Fig. 2a) are at 2θ of 12, 23, 35, 42, and 63°, which exhibit the same hydroxalcite-like characteristics, which can be indexed to rhombohedral NiAl-LDH with the R_{3m} space group (JCPDS card No. 15-0087) [27, 30]. In the XRD pattern of Mg-Al sample (Fig.2b), the main peaks appeared at 2θ range of 12, 25, 33, 35, 38, 49, 62and 63.5. These peaks are assigned to miller index of (003), (006), (101), (009), (015), (012), (110) and (013), respectively (JCPDS cards No. 89-0461) [29].

These proofs confirm the formation of the layered structure [29]. The XRD pattern for Co-Ni LDH ratios is shown in Fig. 2c. The presence of broad and small peaks in the XRD spectrum of cobalt-nickel LDH shows a layered structure. The main peaks at 11.8, 24, 39.6, 44 and 70.6 (not observed in 2θ scale in Fig. 2c) are related to facets of (003), (006), (012), (015) and (110), respectively (JCPDS card No. 33-0429) [28, 31] and indicated the layered structure for the Co-Ni sample.

In LDHs that is expressed as $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]_x(\text{A}^{n-})_{x/n}\cdot m\text{H}_2\text{O}$, a fraction of divalent metal ions coordinated octahedrally by hydroxyl groups in the brucite like layers is uniformly replaced by trivalent metals with the molar ratio of $\text{M}^{3+}/(\text{M}^{3+} + \text{M}^{2+})$ (the value of x) normally between 0.2 and 0.4 [32]. It is well-established in the literature that in LDHs, cobalt is found in both cationic states of Co^{2+} and Co^{3+} [33-35]. So, it results that in both cobalt and nickel species are cationic form and cobalt has both forms of Co^{3+} and Co^{2+} in the besides of Ni^{2+} .

The average crystallite size of LDH nanoparticles was calculated using the Debye–Sherrer equation (Eq. 2) [36-38].

$$D = \frac{0.89 \lambda}{\beta \cos \theta} \quad (2)$$

Where β is the width of the peak at half maximum, λ is the radiation wavelength, and θ the Bragg angle. The average crystal size for the three LDHs was estimated to be less than 30 nm (20-29 nm).

3.2. FT-IR analysis for LDH catalysts

The FTIR spectra of the LDH samples are presented in Fig. 3. At all spectra, the band at region 400-900 cm^{-1} correspond to M-O and M-O-M' vibration [28]. The characteristic absorption related to anions in the interlayer LDH usually appeared in the range of 800-1700 cm^{-1} .

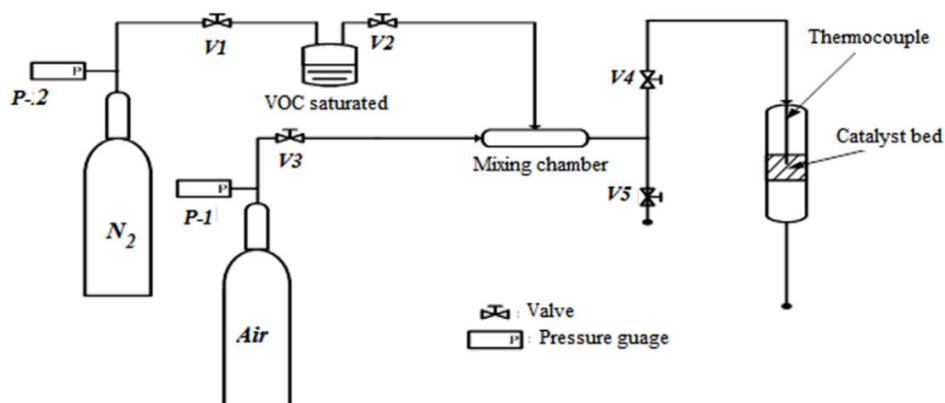


Fig. 1. The scheme of the set-up used for the catalytic oxidation of toluene in the gas phase.

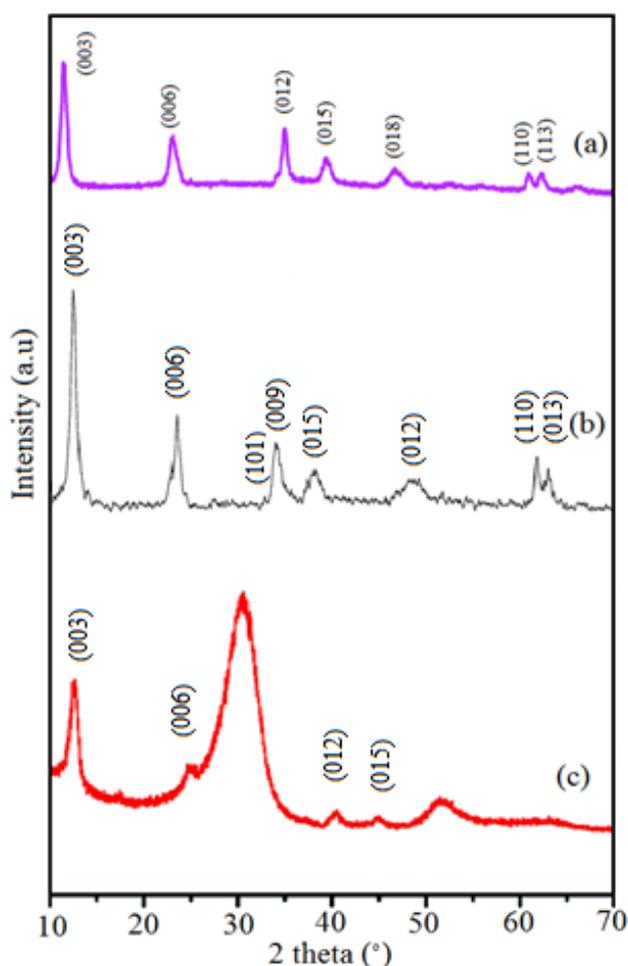


Fig. 2. XRD patterns of Ni-Al LDH(a), Mg-Al LDH(b), and Co-Ni LDH(c).

The absorption bands related to carbonate anion for asymmetric and symmetric stretching vibration appeared at about 1450 and 880 cm^{-1} , respectively. A broad absorption band was observed around 3480 cm^{-1} with a shoulder band around 3000 cm^{-1} , which was related to OH stretching vibration. The absorption band around 1620 cm^{-1} is related to the OH bending vibration [28, 39].

3.3. Investigation of particle size of catalyst (Mg-Al, Ni-Al, Co-Ni) using SEM

Figs. 4 show the morphology and particle size of the LDH samples. It is observed that the morphology of Co-Ni LDH is like to adhered flakes as it is observed in Fig. 4a. The size of them are different but the thickness seems to be the same. The particle size of the Co-Ni LDH obtained by Image J software is in range of 9-184 nm and the average size is 61 nm. In the SEM image of Mg-Al LDH (Fig. 4b), the distribution of particle size was determined 64-102 nm and the average size was 89 nm.

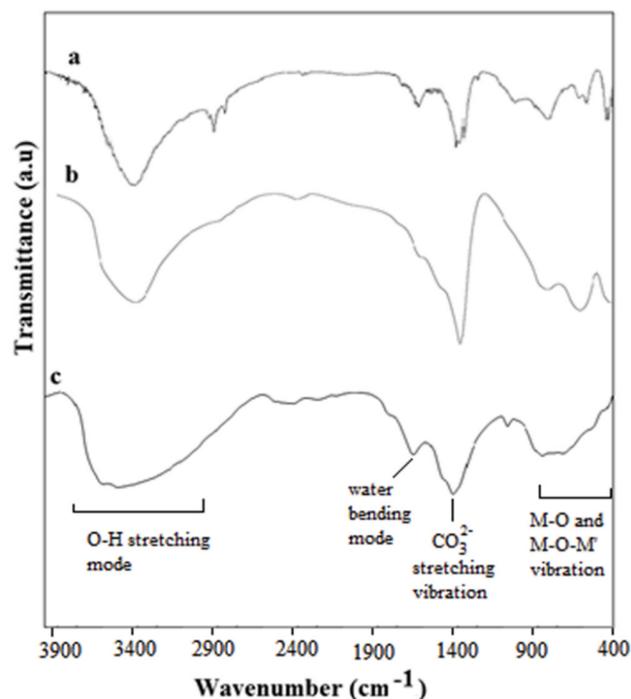


Fig. 3. FTIR spectra of Ni-Al LDH (a), Mg-Al LDH (b), and Co-Ni LDH (c).

The morphology is like to the agglomerated particles. Fig.4c shows the SEM image of Ni-Al LDH. The morphology is like smooth surface in that some cracks are observed and the range of the particle size was 107-222 nm.

3.4. Comparing LDH catalyst activity of toluene oxidation

The light-off curve is the conversion-temperature plot of a catalytic reaction. It provides to get some kinetic information such as the apparent reaction order or mass transfer limitation from the shape of the curve. The light-off curves for the toluene oxidation over the LDH catalysts are shown in Fig. 5. The studied temperature range is between 100 $^{\circ}\text{C}$ and 450 $^{\circ}\text{C}$. The shape of the curves is approximately the same, meaning that the kinetic order of the reaction over the catalysts is the same. To compare the activity of the catalysts, T_{80} (temperature for 80% conversion of toluene) was used and the results are presented in Table 1.

Based on T_{80} to judge about the activity of the nanocatalysts, the Co-Ni LDH exhibits the most activity, because the eighty percent of toluene conversion over it occur at 225 $^{\circ}\text{C}$, whereas T_{80} on the Ni-Al and Mg-Al LDHs are 277 and 350 $^{\circ}\text{C}$, respectively. Therefore, the order of the catalyst activities is as follow:

Co-Ni LDH > Ni-Al LDH > Mg-Al LDH

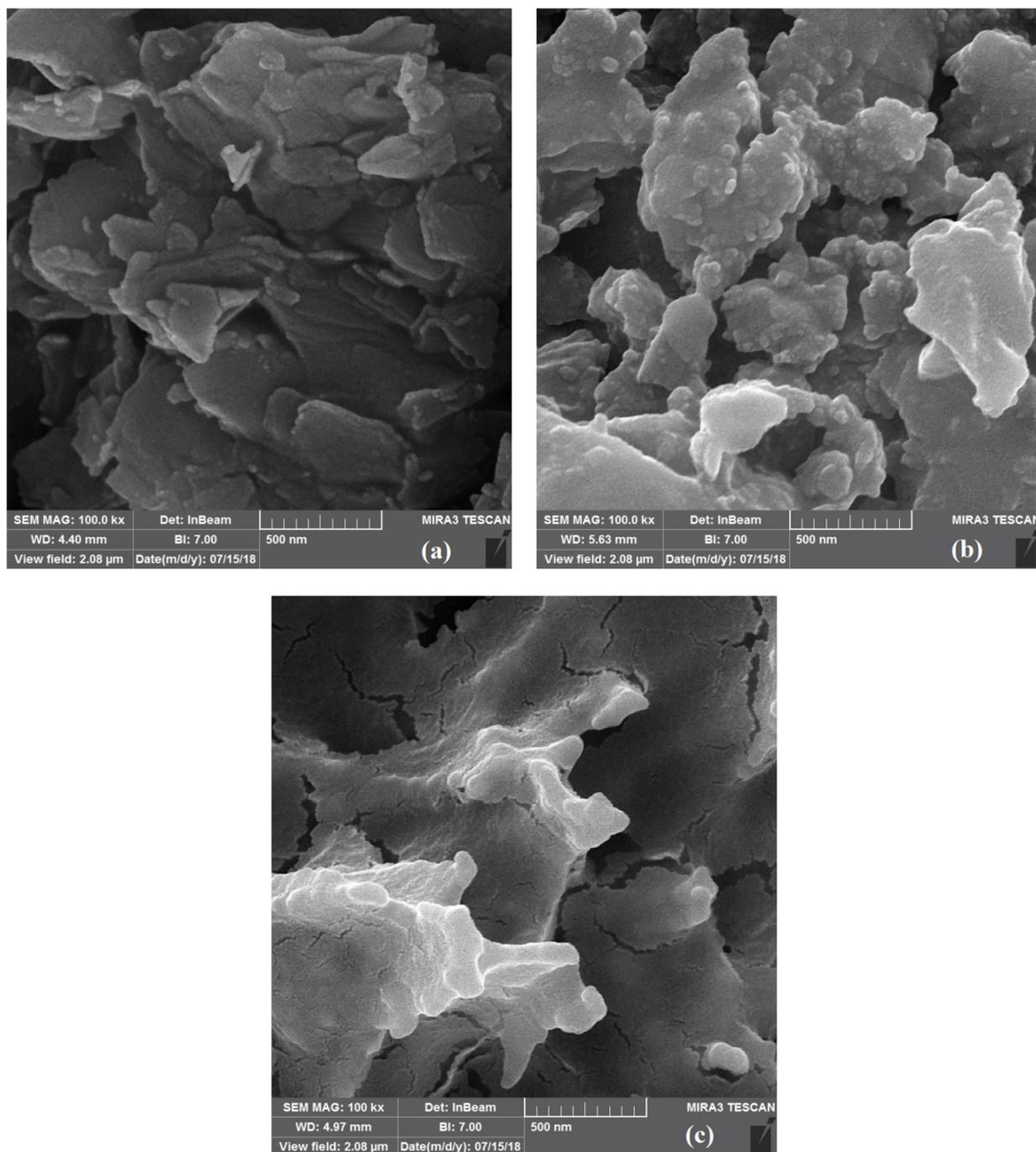


Fig. 4. SEM images of Co-Ni LDH (a), Mg-AL LDH (b), and Ni-AL LDH (c).

Table 1. T_{80} for 80% toluene conversion on different catalysts.

Entry	Nanocatalyst	T_{80} (°C)
1	Co-Ni LDH	225
2	Ni-Al LDH	277
3	Mg-Al LDH	350

By considering the Fig.5, it is clear that the slope of the light-off curve for Co-Ni LDH is sharper than others in the kinetic region of the curve, indicating that the conversion rate of toluene on this catalyst is much more than others and the low activation energy is needed. The nature of cation in LDH and ratio of cations might also be an important factor affecting the catalytic activity.

There are commonly three kinetic models: Langmuir-Hinshelwood (L-H), Eley-Rideal (E-R), and Mars-van

Krevelen (MVK), which are suitable for explaining the mechanism of the VOC catalytic oxidation. But the most common mechanism especially on the mixed oxides is MVK mechanism [40, 41, 42]. The MVK mechanism is mainly based on the redox reaction: firstly, VOC species are oxidized by surface oxygen species, and subsequently, oxygen vacancies are produced and the metal sites are reduced. Secondly, the oxygen in the air will re-oxidize the reduced metal centers, thereby eliminating the oxygen vacancies. The presence of metals with different oxidation state as confirmed by XRD strengthens the combustion of toluene by MVK mechanism. On the other hand, the LDHs were probably turned to mixed metal oxide at the process temperatures. So, this mechanism is strengthened. But in the case of the mechanism of VOC oxidation over LDH more studies and characterization are needed.

3.5. Stability of catalyst lifetime at different times on LDH catalysts

Fig. 6 shows the stability of LDH catalyst for a run time of 300 min. All catalysts are stable at early times, but, afterwards the conversion decreased. Because at early times, the catalyst surface is free of any kind of contaminants, so the more contact surface of catalysts is available for the oxidation process, but as time goes by, contaminants on the catalyst block the pores so the contaminant molecules cannot absorb on the catalyst surface. As a result, the catalyst is inactivated by spending the time, and the rate of toluene combustion decreases. Among the catalysts, Ni-Al LDH exhibited the most stability.

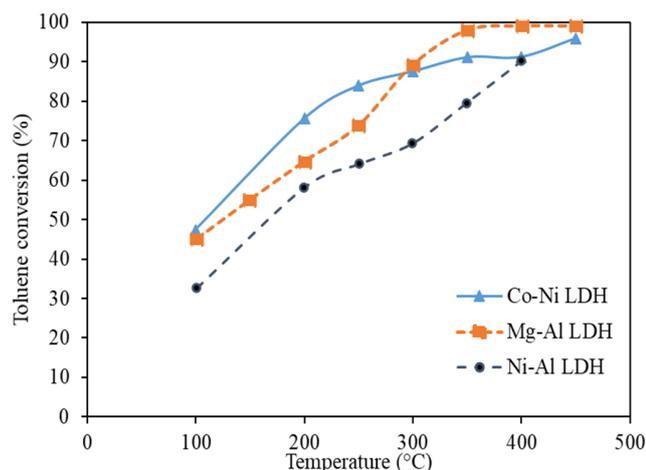


Fig. 5. The light-off curves for combustion of toluene over LDHs at different temperatures. Experimental condition: Pressure= 1 atm, catalyst loading: 200 mg and initial toluene concentration: 1270 ppm.

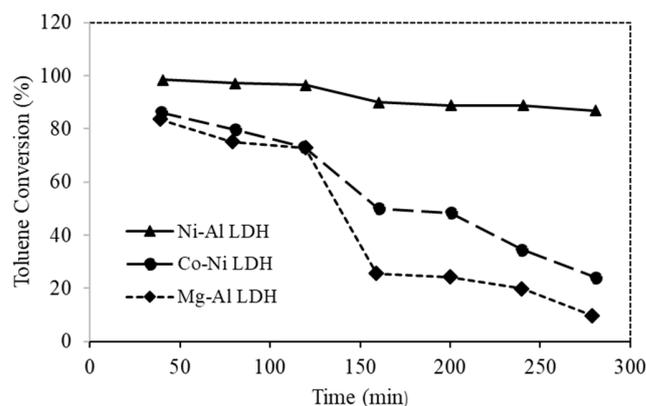


Fig. 6. The stability of the LDH catalysts at different times in a fixed bed reactor. Experimental condition: Pressure= 1 atm, temperature=250 °C, catalyst loading: 200 mg and initial toluene concentration: 1270 ppm.

4. Conclusions

Three layered-double hydroxide-based nanocatalysts with different metals were successfully synthesized and evaluated as a catalyst in the combustion of toluene from polluted air. The structure of catalysts was approved by XRD and FTIR, and the presence of different oxidation state for cobalt confirmed. This finding strengthens the proposed mechanism for toluene combustion i.e. Mars Van Krevelen mechanism. MVK is according to the redox reactions and presence of the different oxidation state for the cations in the LDH is necessary. SEM technique confirmed the nanoscale of the catalyst particle. The study indicated that layered double hydroxides could a promising catalyst for air pollution control. Among the investigated catalysts for catalytic oxidation of toluene, Co-Ni LDH showed more activity and the Ni-Al LDH exhibited the most stability. Since for a catalyst, the stability is more important than activity, the Ni-Al is selected as the best catalyst in the studied series.

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