

Synthesis of Silica Xerogel@Mg-Al layered double hydroxide composite for CO₂ capture

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ABSTRACT

Today, the increase in the level of CO₂ gas in the atmosphere has started to cause concern. Therefore, an appropriate and rapid decrease in CO₂ gas emission levels has become a significant challenge. Capturing CO₂ on a solid surface is proposed due to its ease of application, relatively low energy requirements, and applicability in various processes. This study investigated the preparation of Xerogel@MgAl LDH (X@MAL) composite for CO₂ capture. Firstly, silica-based xerogel was synthesized by the acid and base-catalyzed two-step sol-gel method. Then, the X@MAL composite was prepared by the co-precipitation method. Based on the CO₂ capture analysis, the maximum CO₂ capture capacity of the composite at 25 °C, 75 °C, and 100 °C was 1.90 mmol.g⁻¹, 0.70 mmol.g⁻¹, and 0.40 mmol.g⁻¹, respectively. The kinetic analysis results show that the CO₂ capture of X@MAL can be well-defined by Avrami kinetic model.

Keywords: Xerogel, Layered Double Hydroxide, CO₂ Capture, Kinetics

INTRODUCTION

Emissions of carbon dioxide into the atmosphere are increasing significantly due to the energy industry, transportation sector, and human activities [1]. The excessive increase in the concentration of greenhouse gases, especially carbon dioxide, is due to the burning of fossil fuels, which causes global warming and other environmental effects [2]. It is extremely important to develop technologies that reduce greenhouse gas emissions [3]. Therefore, the most promising method to mitigate the impact of CO₂ on global climate is CO₂ capture from fossil fuels consumed by power plants. The process economics of such technologies are often not cheap enough to offset the hold costs. Thus, it is highly desirable to develop alternatives that are more energy efficient than conventional separation technologies.

Among these techniques, adsorption is one of the most promising approaches as it can reduce the costs associated with the hold step. In general, high CO₂ capture capacity, high selectivity, low material cost, and stable adsorption capacity after several cycles are the main characteristics of CO₂ adsorbents [3]. Recently, scientists have made dramatic efforts to produce suitable adsorbents capable of meeting the requirements of CO₂ emission sources. Many of the scientific community have worked on the development of various types of porous solid adsorbents based on activated carbon [4,5], mesoporous silica materials [6,7], zeolites [8], metal-organic frameworks (MOFs) [9], mesocellular foams [10], and layered double hydroxides (LDHs) [11]. LDHs are inorganic materials that are members of the family of two-dimensional clay minerals with multiple metal cations in their inner layers and anions in their interlayers. The structure of LDHs consist of brushite [Mg(OH)₂]-like positively charged metal hydroxide layers and anions and water molecules that exist as charge balancers between the layers. The potential use of LDHs in high-temperature carbon capture and storage applications is promising [12]. LDHs require less energy for regeneration in CO₂ adsorption and show better stability than some solid adsorbents [13]. They also show rapid adsorption-desorption kinetics, especially in the presence of water. This has made LDHs interesting in pre-combustion CO₂ capture applications [14,15].

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Xerogels are used as supporting materials in the preparation of various composites due to their unique properties [16,17]. By uniting LDHs with xerogel, which is found in different forms such as a monolith, powder, fiber, or film, composite materials with superior properties are created.

Xerogels are generally prepared by the sol-gel method under atmospheric pressure. Some properties such as the pore of xerogels can scale, high surface area, low intensity, thermal conductivity, dielectric constant, high optical permeability in visible light, and sound insulation of this material make it unique for several scientific and technological applications [18]. The brittleness, moisture-holding, and instability of silica xerogels in long-term applications can limit the use of these materials. These disadvantages can be eliminated with surface modification, heat treatment, or preparation of composite materials by adding various fillers [19].

To the author's knowledge, only one study has been found in the literature on the combination of xerogel with MgAl LDH. Okada et al. prepared the MgAl LDH and aluminosilicate xerogel composites for CO₂ and NH₃ gas adsorption [20]. The composition of xerogel and the synthesis procedure of the composite differs from our study. In this study, Xerogel@MgAl LDH (X@MAL) composite was synthesized for the first time for CO₂ capture application. Firstly, silica-based xerogel was synthesized by the acid and base-catalyzed two-step sol-gel method. Then, the X@MAL composite was prepared by the co-precipitation method by using the synthesized xerogel. The obtained material was characterized by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) analysis. The CO₂ capture capacity of the composite was carried out using by gravimetric method at different adsorption temperatures.

EXPERIMENTAL PROCEDURES

Materials and Characterization

The materials used in the xerogel synthesis were supplied by Sigma-Aldrich. For the synthesis of X@MAL composite magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, Merck) aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, Merck), sodium hydroxide (NaOH, Merck) sodium carbonate (Na₂CO₃, Merck) were used.

The characterization analysis of the composite was carried out using a PANalytical X'Pert-Pro XRD diffractometer and Perkin-Elmer Spectrum One FT-IR spectrophotometer. The XRD measurements of xerogel and X@MAL composite were taken in the 2θ range from 5° to 100°.

Infrared spectra were collected using the KBr pellet technique in absorbance mode within the range from 4000 to 450 cm⁻¹.

The CO₂ capture analysis of the composite was studied using Perkin Elmer Pyris Diamond thermogravimetric equipment. In the capture analysis, pure CO₂ (>99.99%) gas was used.

Briefly, approximately 10 mg of sample was put in an alumina crucible, and then, it was heated to 105°C under a nitrogen atmosphere to remove its moisture. Afterward, the ambient temperature was reduced to a specific temperature at a cooling rate of 10°C.min⁻¹. For the capture analysis, the gas was changed to CO₂ at a flow rate of 100 ml per minute for 90 minutes. The weight increase of the sample was used to determine the sample's CO₂ capture capacity.

Synthesis of X@MAL Composite

To synthesize the X@MAL composite, the xerogel was first synthesized using our previous synthesis procedure available in the literature [21].

For the synthesis of the X@MAL composite, two different solutions were prepared. Initially, 0.1 g xerogel was dissolved in distilled water under ultrasonic irradiation. Then, Na₂CO₃ is added to the xerogel solution and it continued the mixing for a while. The obtained solution was named the first solution and its pH of it was adjusted to 10. In order to prepare the second solution, 0.25 g Mg(NO₃)₂·6H₂O and 0.18 g Al(NO₃)₃·9H₂O were dissolved in the distilled water under ultrasonic irradiation. The obtained second solution is slowly added to the first solution under stirring at room temperature. The resultant solution was continued to stir for 1 hour at room temperature. At the end of the time, the precipitation was collected by centrifugation, and then, it is washed with distilled water and ethanol separately. Finally, it was centrifuged again and dried under a vacuum.

RESULTS AND DISCUSSION

Characterization of Adsorbent

Fig.1 demonstrates the XRD pattern of xerogel and X@MAL composite. The XRD analysis of xerogel showed one broad diffraction peak observed between 20-30° indicating its amorphous structure [22]. In the XRD analysis of the X@MAL composite, the characteristic amorphous peak of xerogel and newly formed (003), (009), (015), and (110) diffraction peaks related to the LDH phase were seen, indicating that the layered Mg-Al LDH was formed in the xerogel structure. The characteristic (006) peak of Mg-Al LDH overlapped with the broad peak of xerogel, therefore the (006) peak of Mg-Al LDH was not observed in the patterns of X@MAL.

The FT-IR spectrum of xerogel and X@MAL composite were given in Fig. 2. In the FT-IR spectrum of xerogel, the characteristic peak at 1087 cm^{-1} corresponded to the asymmetric stretching of Si-O-Si groups [23]. The peaks at 3448 cm^{-1} and 1636 cm^{-1} were related to physically absorbed water or structural -OH groups and adsorbed water molecules, respectively [24]. The Si-OH stretching vibration was observed at 946 cm^{-1} [25]. The peaks at 797 cm^{-1} and 467 cm^{-1} were attributed Si-O-Si symmetric stretching vibrations and bending mode, respectively [26]. Compared with xerogel, the new peaks at around 1498 and 1385 cm^{-1} were observed in the composite, which can be attributed to the vibrations of carbonate species originating from the LDH structure. In addition, differences were observed in the 1000-450 cm^{-1} region due to the stretching of the Al-O and Mg-O metal-oxygen bonds [27-29].

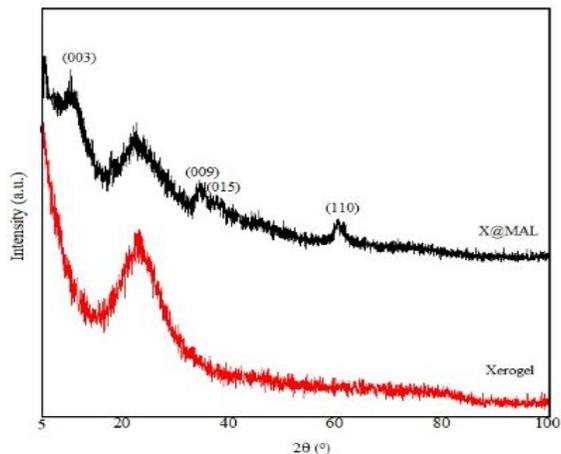


Fig.1 The XRD patterns for silica based xerogel and X@MAL

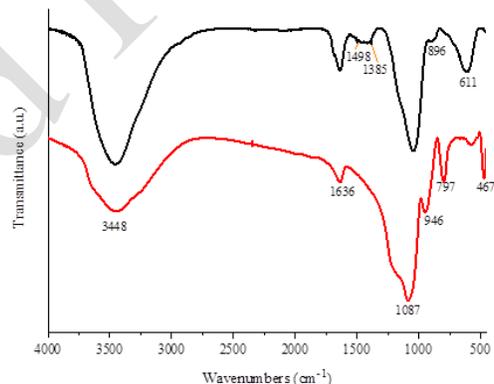


Fig.2 FTIR spectrum of xerogel (red line) and the composite (black line)

CO₂ capture measurement

The amounts of captured CO₂ at different temperatures (25°C, 75°C, and 100°C) were given in Fig. 3. The CO₂ capture capacity of the X@MAL composite decreases with increasing temperature, which is characteristic of physisorption. The CO₂ capture capacity at 75 °C and 100 °C remained constant after 35 minutes, while its capacity at 25 °C remained stable after 80 minutes. The adsorption capacities of the X@MAL composite at different temperatures followed by following trend: 1.90 mmol.g⁻¹ (25°C) > 0.70 mmol.g⁻¹ (75°C) > 0.40 mmol.g⁻¹ (100°C). At 25°C, the X@MAL exhibited approximately 5 times more capacity than the adsorption capacity at 100°C. Accordingly, it was observed that the CO₂ adsorption capacity of X@MAL decreased with the increase in temperature. This indicates that the adsorption of CO₂ into the composite is an exothermic process.

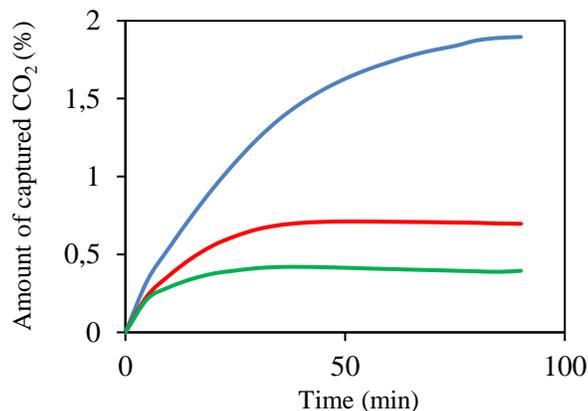


Fig.3 The CO₂ capture capacities of X@MAL composite at different temperatures (Blue line: 25°C, green line: 75°C, and red line: 100°C)

Kinetic Analysis

To determine the mechanism of CO₂ adsorption of X@MAL composite, several of the most common kinetic models from the pseudo-first-order (FO), the pseudo-second-order (SO), and the Avrami (Av) model were selected. By using the CO₂ adsorption results at different temperatures, the compatibility of these models with the experimental values will be tested.

FO model was proposed by Lagergren and assumes that the rate of adsorption is proportional to the number of free active sites on the accessible adsorbent surface [30]. This equation can be given by:

$$q_t = q_e [1 - \exp(-k_f t)] \quad (1)$$

where q_t (mg/g) and q_e (mg/g) are the amounts of adsorbed CO₂ at time t (min) and equilibrium. k_f (min⁻¹) is the FO rate constant.

SO model was proposed by Ho et al. [31]. The adsorption rate with respect to SO is directly proportional to the square of the number of free active sites on the adsorbent and the kinetic model is expressed by the equation given below.

$$q_t = \frac{q_e^2 k_s t}{1 + q_e k_s t} \quad (2)$$

where k_s (g/(mg.min)) is the SO rate constant.

The Avrami method is a first-order fractional kinetics for particle nucleation and has recently been used to describe CO₂ capture on solid adsorbents [32,33]. This model was described using the following equation:

$$q_t = q_e [1 - \exp \exp(-(k_a t)^{n_a})] \quad (3)$$

Where k_a and n_a are the rate constant and kinetic order of Av, respectively.

The error was determined using the following equation to determine the accuracy of the kinetic model:

$$Error(\%) = \sqrt{\frac{\sum_{i=1}^p \left[\frac{q_e(\text{exp}) - q_e(\text{model})}{q_e(\text{exp})} \right]^2}{p - 1}} \times 100\% \quad (4)$$

where $q_e(\text{exp})$ and $q_e(\text{model})$ are the value of adsorption capacity experimentally and obtained from the fitted model, respectively and p is the number of total experimental data.

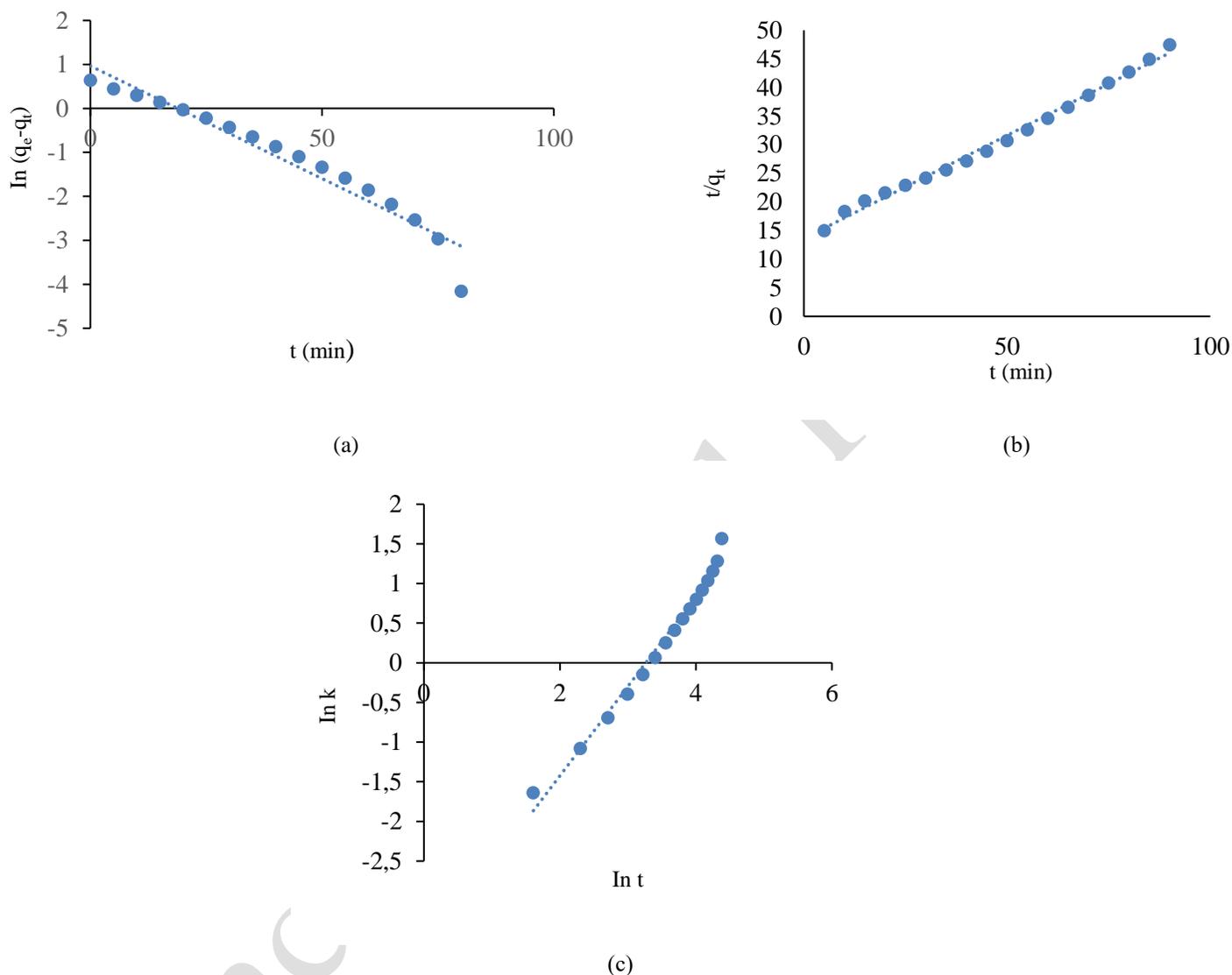


Fig.4 The kinetic model curves of CO₂ capture on X@MAL at 25°C (a) FO, (b) SO and (c) Av

All kinetic models were fitted to explain the capture of CO₂ on X@MAL at 25°C (Fig.4). The calculated kinetic parameters of the fitted models are demonstrated in Table 1. It is seen that the SO provides the best fit among the three kinetic models as per the correlation coefficient (R²) values for X@MAL. However, it was found that the Av kinetic model presented a lower error value than the error values calculated from the FO and SO. In addition, when the fitted data shown in Fig.5 are examined, it is seen that the fitted data from the Av model are very close to the experimental data. Thus, the Av model is applied to predict the CO₂ capture process of X@MAL. The kinetic order of Av (n_a) is found as 1.128 indicating the multiple kinetic order of the CO₂ capture.

Table 1 The kinetic parameters for CO₂ capture on X@MAL composite at 25°C

Kinetic Model	Parameter	Value
F _O	q _{e, exp} (mmol.g ⁻¹)	1.890
	k _f	0.051
	R ²	0.941
	Error (%)	9.712
S _O	q _e (mmol.g ⁻¹)	2.624
	k _s	0.010
	R ²	0.994
	Error (%)	11.363
A _v	q _e (mmol.g ⁻¹)	1.934
	k _a	0.038
	n _a	1.128
	R ²	0.983
	Error (%)	0.600

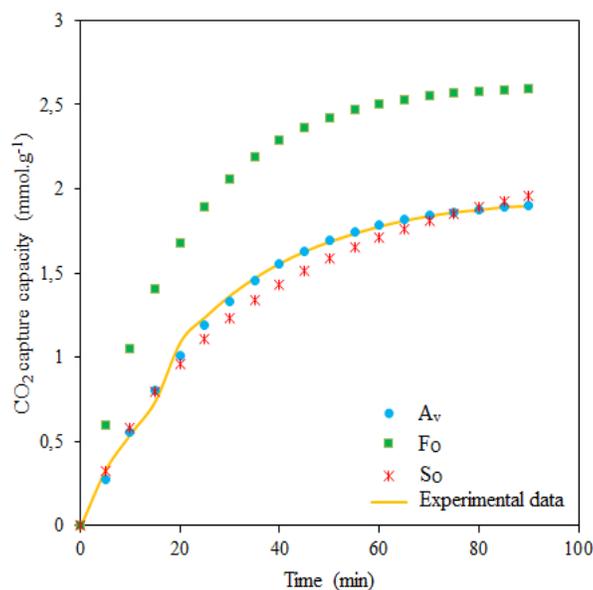


Fig.5 Corresponding fit of X@MAL applying three kinetic models

Comparison with other adsorbents

A comparison of the CO₂ uptake capacity of silica xerogel and MgAl LDH-based adsorbents found in the literature are listed in Table 2. Compared with the silica xerogel-based adsorbents, X@MAL showed either close or better adsorption capacity. The CO₂ adsorption performance of X@MAL is superior to MgAl LDH-based adsorbents. Overall, it is seen that the X@MAL composite has a good enough capacity to compete with the adsorbents in the literature.

Table 2. Comparison of the CO₂ adsorption capacity of various composites.

Adsorbent	Capacity (mmol.g ⁻¹)	References
<i>Silica xerogel-based</i>		
MMS-6	1.90	[3]
PEI functionalized xerogel	1.94	[34]
Polyurethane/ silica xerogels	1.10	[35]
<i>MgAl LDH-based</i>		
MgAl LDH	0.9	[36]
POM/MgAl LDH	0.74	[37]
GO/MgAl LDH	0.54	[38]
X@MAL	1.90	In this study

CONCLUSION

In this study, the X@MAL composite was prepared by the co-precipitation method. The XRD and FTIR characterization results showed that the composite was synthesized successfully. The CO₂ capture experiments at different temperatures indicated that the maximum capture capacity of the composite was 1.90 mmol.g⁻¹ at 25°C. Adsorption kinetics demonstrated that the Av model had a better fitting effect and was more suitable for describing the CO₂ capture process.

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Uncorrected Proof