Investigating the Possibility of using Acetic Acid in place of HF in Chromium-Benzenedicarboxylates (MIL-53 and MIL-101) Synthesis Applicable for CO_2 Adsorption

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Abstract

The present study concerns chromium benzenedicarboxylates MIL-53 and MIL-101 hydrothermal syntheses utilizing acetic acid, and their capabilities for CO_2 adsorption. The effect of the parameters such as reaction time, reaction temperature, water concentration, and acetic acid content on adsorption characteristics of these metal-organic frameworks (MOFs) is investigated using L8 Taguchi experimental design. In synthesized MIL-101, with adding 1 acetic acid equivalent with respect to Cr, reaction time and temperature have been reduced from 24 h and 483 K to 6 h and 463 K. Also, the CO_2 adsorption capacity has been measured by a volumetric method. The results have revealed that adding acetic acid and reducing water in the reaction mixture results in converting MIL-101 to MIL-53 which tends to an increase in CO_2 adsorption. With regard to reaction conditions, the results show that MIL-53 and MIL-101 have the maximum CO_2 adsorption capacities of 17.5 and 11.0 $mmolg^{-1}$ at 3.5 bar and 299.2 K, respectively.

Keywords: MIL-53, MIL-101, acetic acid, CO_2 adsorption.

Introduction

Fossil fuels supplies 85% of the total world energy requirement, and CO_2 emitted as a result of fossil fuel burning causes global warming effect. Therefore, there should be attempted to minimize CO_2 release to the atmosphere [**1**]. Different technologies have been employed to prevent CO_2 emissions [**2-3**]. The most effective technologies include absorption, membrane and adsorption. In amine absorption system, solvent recovery requires a great deal of energy to separate CO_2 from amine. In addition, the solvents tend to be evaporated and decomposed which causes the problems of amine loss, foaming and corrosion [**4**]. Physical adsorption processes are also attractive because they consumes less energy [**5-7**]. The main problem is finding an appropriate adsorbent having the properties such as high thermal stability, high CO_2 adsorption capacity, high CO_2 selectivity, and low cost [**8-12**]. Adsorbents such as potassium-promoted hydrotalcites, zeolite 13X, carbonaceous materials, metal oxides materials, and metal organic framework materials (MOFs) have been utilized for this purpose [**10-16**].

Metal-organic frameworks (MOFs) have received special attention to be used satisfactorily in CO_2-adsorption-based separation. Their crystalline structures are formed by assembling metal oxide clusters and organic ligands [**17-18**]. Their structures depend on the type of the organic ligand and nature of the metal oxide [**19**]. They have a porous structure with high pore volumes and large surface areas [**18-22**]. Therefore, The MOFs can be useful for gas separation and storage [**23-29**], drug delivery [**30, 31**], luminescence [**32, 33**], and catalysis [**34-38**]. Among various MOFs, MILs (Materials of Institute Lavoisier series) are synthesized by Ferey's group. Two chromium benzene dicarboxylates (Cr-BDCs), MIL-53 and MIL-101 have high surface area and pore volume. The formula of MIL-53 and MIL-101 have considered $[Cr(OH)[C_6H_4(CO_2)_2]$ and $[Cr_3(O)X(bdc)_3(H_2O)_2]\cdot nH_2O$ (bdc = benzene-1, 4-dicarboxylate, X = OH or F), respectively.

MIL-101 has a Brunauer−Emmett−Teller (BET) surface area 4230 m^2g^{-1} and pore volume 2.15 cm^3g^{-1} [**39**]. Chowdhury *et al.* have investigated CO_2 adsorption isotherms on MIL-101. The adsorption capacities of CO_2 is reported to be 8 $mmolg^{-1}$ at 5.3 bar and 283 K, and

21.3 mmolg^{-1} at 36 bar and 295 K [**25-26**]. Anbia *et al.* have reported CO_2 adsorption capacities of MIL-101 and PEHA-MIL-101, which are 0.85 and 1.3 mmolg^{-1} at 10 bar and 298 K, respectively [**27**]. Zhang *et al.* have carried out a set of experiments to obtain equilibrium and kinetic of CO_2 adsorption. They have attained that the maximum CO_2 uptake on MIL-101 is 22.9 mmolg^{-1} at 298 K and 30 bar [**28**]. Montazerolghaem *et al.* have reported CO_2 adsorption capacities of MIL-101-Cu and MIL-101-Ni equal to 11.8 and 12.4 mmolg^{-1} at 7.1 bar and 298.2 K, respectively [**40**].

Bourrelly *et al.* have reported that MIL-53 has the BET surface area of 1500m^{2}g^{-1} and pore volume 0.56 cm^{3}g^{-1}. They have investigated CO_2 adsorption isotherms on MIL-53. The adsorption capacities of CO_2 is reported to be 10 mmolg^{-1} at 25 bar and 304 K [**41**]. Düren *et al.* have investigated CO_2 adsorption isotherms on MIL-53. The adsorption capacities of CO_2 is reported to be 165cm^3 of CH_4 (STP) per cm^3 at 35 bar and 304K [**42**]. Serre *et al.* have reported CO_2 adsorption capacities of MIL-53, which has 2-3 mmolg^{-1} at 1-4 bar and 304 K [**43**].

Using an equimolar amount of hydrofluoric acid (HF), chromium and terephthalic acid was reported at pioneering work performed to synthesize MIL-101(Cr) hydrothermally [**39**]. Hong *et al.* have investigated the effect of fluorine (HF) on the formation of MIL-101 [**44**]. Millange *et al.* have reported MIL-53 hydrothermal synthesis with chromium (III) nitrate, terephthalic acid, hydrofluoric acid, and H_2O mixed in the molar ratio of 1:1.5:1:280 at 493 K for 6 days [**45**]. Zhao *et al.* have investigated the effect of nitric acid on MIL-101 synthesized hydrothermally [**46**]. HF and nitric acid are hazardous materials, which may pose danger to human health. Therefore, for the syntheses of MIL-101 and MI-53, eliminating dangerous acids have been considered. Huang *et al.* have reported conventional MIL-101 synthesis without using HF at 473 K during 8 h for adsorption of volatile organic compounds [**47**]. Khan *et al.* have reported MIL-101 and MIL-53 hydrothermal synthesis utilizing microwave and electric heating at 483 K for 3 h and 12 h, respectively. By reducing water concentration and acidity, MIL-53 was formed [**48**]. In another research Khan and coworkers have reported using NaOH instead of HF to obtain nano-sized (50 nm) MIL-101(Cr) [**49**]. Zhao *et al.* have reported MIL-101 using acetic acid to obtain nano-sized (90 nm) MIL-101(Cr), which the molar ratio of acetic acid/Cr/ terephthalic acid has been 17.5:1:1 [**50**]. Jiang *et al.* have reported MIL-101 nanoparticles synthesized hydro-thermally without using HF. They have investigated the effect of the monocarboxylic acids on MIL-101 at 453 K during 4 h for CO_2 adsorption at 273 K and 1 bar [**51**]. Rallapalli *et al.* have reported conventional MIL-101 synthesis using acetic acid and perfluorobenzoic acid. They have examined MIL-101(Cr) for H_2 adsorption [**52**]. Buragohain *et al.* have reported that functionalized Cr-MIL-101-X (X=-F,-Cl, -Br, -CH_3, -C_6H_4,-F_2,-$(CH_3)_2$) can be exhibited the CO_2 adsorption 1.7-2.9 mmolg^{-1} at 0 °C and 1 bar [**53**].

HF is commonly utilized in chromium benzenedicarboxylates' synthesis; however, it causes two major problems: (1) Because it has low vapor pressure, it increases operating pressure significantly, (2) Because it is very corrosive, it increases the equipment cost and causes corrosion problems in large scales. Using acetic acid in place of HF successfully, can alleviate these two problems considerably. Moreover, HF has shown high CO_2 adsorption capacity. Therefore, the question still remains unanswered whether acetic acid-synthesized chromium benzenedicarboxylates can create an appropriate CO_2 adsorption capacity. In the present work, the effects of the reaction conditions such as pH (by utilizing acetic acid), reaction time and temperature, and water concentration on CO_2 adsorption capacity of chromium benzenedicarboxylates are investigated.

Experimental

Materials

All the chemicals used for adsorbents synthesis in this work include terephthalic acid, (TPA, 98% purity, Merck, Germany), chromium chloride hexahydrate ($CrCl_3 \cdot 6H_2O$, Scharlau, Spain/USA), acetic acid (CH_3COOH, 99% purity, Merck, Germany), N, N-dimethylformide (DMF, 99.8% purity, Merck, Germany). The CO_2 gas used in this study was purchased from Farafan Gas Company with high purity grade, 99.995%.

Synthesis of chromium benzenedicarboxylates (Cr-BDCs)

Chromium benzenedicarboxylates (Cr-BDCs) are synthesized using hydrothermal method. The synthesis is carried out with the reactant molar composition of $CrCl_3 \cdot 6H_2O$/TPA/ (250,400) H_2O. The solution mixture is poured into a Teflon lined autoclave, and it is placed in a preheated electric oven for a given time at 463 and 483 K under autogenous pressure. In order to study the effect of pH on synthesis performance, acetic acid is utilize to adjust initial pH. The reaction solution is held still during the reaction. The reaction conditions are summarized in **Table 1**. This table shows 11 cases, which the first eight cases, from A to H, are obtained based on Taguchi experimental design method with different level factors (method of upgrading). Factors are included molar composition, heating time, temperature and acetic acid equivalent (pH). Molar composition, heating time, and temperature have two levels except acetic acid equivalent that has four levels. Molar composition has two levels $CrCl_3 \cdot 6H_2O$/TPA/250H_2O and $CrCl_3 \cdot 6H_2O$/TPA/400H_2O, heating time has two levels 6 h and 12 h, temperature has two levels 463 K and 483 K, and acetic acid equivalent with respect to Cr has four levels 1, 3, 5, 8. The four factors are investigated on yield and CO_2 adsorption capacity. I and J are synthesized for comparison with the first eight cases, while K is carried out for the investigation of increased pH and the promotion of dissolved terephthalic acid in water at environment temperature.

After reaching the reaction time, the autoclave is cooled to room temperature and solid products are recovered by centrifugation, washing with water and drying. To eliminate unreacted crystalline TPA, the as-synthesized MOF samples are treated with N, N-dimethylformide under ultrasound for 1 h at 343 K [**54**]. The purified Cr-BDCs are dried at 423 K for 5 h.

Table 1. Reaction conditions for the synthesis of MOFs.

Sample	Molar composition	time h	Tem K	Acetic acid[a]	pH[b]
A	$CrCl_3{\cdot}6H_2O$/TPA/400 H_2O	6	463	1	2.23
B	$CrCl_3{\cdot}6H_2O$/TPA/250 H_2O	12	483	1	1.81
C	$CrCl_3{\cdot}6H_2O$/TPA/400 H_2O	6	483	3	1.87
D	$CrCl_3{\cdot}6H_2O$/TPA/250 H_2O	12	463	3	1.67
E	$CrCl_3{\cdot}6H_2O$/TPA/400 H_2O	12	463	5	1.63
F	$CrCl_3{\cdot}6H_2O$/TPA/250 H_2O	6	483	5	1.36
G	$CrCl_3{\cdot}6H_2O$/TPA/400 H_2O	12	483	8	1.15
H	$CrCl_3{\cdot}6H_2O$/TPA/250 H_2O	6	463	8	0.95
I	$CrCl_3{\cdot}6H_2O$/TPA/250 H_2O	6	483	0	2.65
J	$CrCl_3{\cdot}6H_2O$/TPA/400 H_2O	24	483	0	3.07
K	$CrCl_3{\cdot}6H_2O$/TPA/250 H_2O [c]	6	483	-	3.57

[a]Acetic acid equivalents with respect to Cr and TPA
[b] after mixing for 2 min
[c]$NaHCO_3$ is added to obtain the given pH $_{initial}$

Characterizations

X-ray diffraction (XRD) was carried out in a D8ADVANCE XRD instrument (Bruker Corporation) diffractometer using Cu Kα radiation (λ = 1.54 Å) in the 2-theta range of 1-30.

CO_2 sorption isotherm measurement

To investigate the CO_2 adsorption capacities of Cr-BDCs samples, an experimental setup based on volumetric method was used [**40**]. The CO_2 isotherms were measured at 299.2 K and pressures ranging from 0 to 3.5 bar. 40 mg sample was first outgassed at 423.2 K overnight, and then was loaded into the adsorption chamber. After that, the adsorption chamber was filled with CO_2 pure gas up to an appropriate pressure, and it was allowed to reach equilibrium with giving adequate time. The equilibrium amount of the adsorbed CO_2 was calculated by using the difference of initial and final pressures in adsorption cell using material balance. The accuracies in measurements of pressure and temperature were evaluated as much as 1000 Pa and 0.1 K, respectively.

Results and discussion

Effect of acetic acid content on the Cr-BDCs

The effect of acid and water contents in the synthesis reaction mixture is important because even only a small change in acid concentration while maintaining all other parameters the same can tend to shift the product from MIL-101 to MIL-53 or vice versa [**48**]. Thus, further investigation on this effect is introduced in this study.

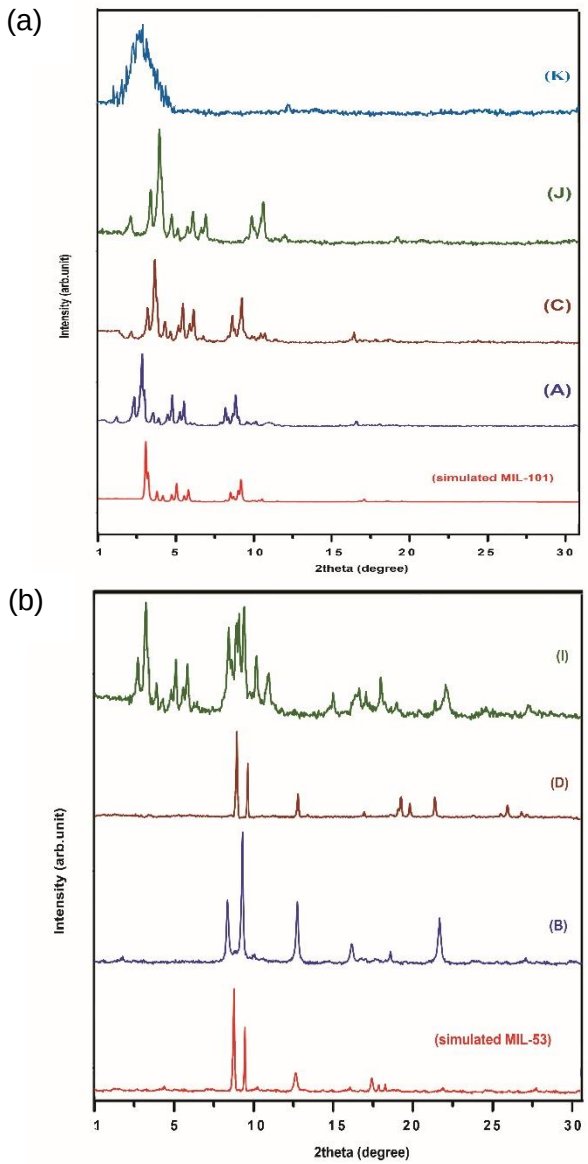

Fig. 1. (a) XRD the patterns of the reactant composition of $CrCl_3.6H_2O$/TPA/400H_2O, (b) XRD the patterns of the reactant composition of $CrCl_3.6H_2O$/TPA/250H_2O.

Fig. 1 shows the XRD patterns of Cr-BDCs obtained for different acid and water contents in the reaction mixture. By comparing these plots with the standard XRD patterns [**39, 55**] released in literature it can be concluded that MIL-53 is produced when the water content is low while high water content results in MIL-101.

The effects of water concentration and acidity are investigated by Khan *et al.* [**56**]. They have reported MIL-101 synthesized when the water content is high, the acidity is low and MIL-53 obtained when the water content is low, the acidity is high, respectively. They have shown that phase transformation between MIL-101 and MIL-53 can be happened. The phase-selectivity was explained with thermodynamic stability. They have verified their results with the XRD patterns [**48**]. This work is confirmed by their research and revealed the XRD patterns. The XRD patterns of A, C, J

and I cases (**Fig. 1(a)**) are in good agreement with those released in literature demonstrating the formation of the MIL-101 structure [**39**]. Moreover, comparison A and J show that MIL-101 is formed by adding 1 acetic acid equivalent at 463 K and 6 h, which has shown a decrease in reaction time and temperature. Also, the XRD patterns of B and D cases (**Fig. 1(b)**) confirms the formation of the MIL-53 structure [**45**]. MIL-53 structure is evidenced by the presence of the peak at 2-theta close to 12.2° and MIL-101 structure is revealed by the presence of the peaks separately at 2-theta close to 3.2°, 5.10°, and 9.02° [**57, 58**]. These patterns are matched to their standard patterns.

In this study it is attempted to adjust pH by utilizing $NaHCO_3$ which can increase pH up to 6.5. However, neither MIL-53 nor MIL-101 is not attained when $NaHCO_3$ is added to the solution mixture but is demonstrated an unknown peak. Moreover, Cr-BDCs cannot be formed when pH is reduced to 0.95 and the product is not obtained to solid formed.

Khan and Jhung have investigated the effect of reaction time that kinetically MIL-101 is synthesized when reaction time is short while, thermodynamically MIL-53 is obtained when reaction time is long. They have reported with the reactant composition of $CrCl_3.6H_2O/TPA/400H_2O$ that MIL-101 can be obtained after 1 day and MIL-53 after 2 or 5 days at 483 K and the yields are resulted in approximately 30% and 37%, respectively [**48**]. In the present work with adding 1 equivalent acetic acid, MIL-101 can be obtained at 463 K for 6 h (sample A) and MIL-53(sample B) can be synthesized at 483 K for 12 h. The yields are resulted in 34.5% and 30.1%, respectively. Moreover, MIL-53 can be obtained at 483 K for 6 h in the reactant composition $CrCl_3.6H_2O/TPA/250H_2O$ with adding 5 equivalent acetic acid, which has exhibited the yield 37.5%.

Fig. 2 clearly demonstrates that MIL-101 yield increases with increasing pH while, the yield of MIL-53 decreases with increasing pH. In addition, comparison B and I show that the reaction efficiency is significantly increased by adding 1 acetic acid equivalent and MIL-101 is converted to MIL-53. The phase transformation between MIL-101 and MIL-53 can be explained by decreasing pH.

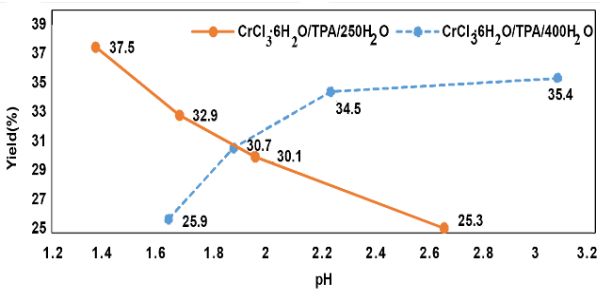

Fig. 2. Yields of Cr-BDCs depending on the pH of the reaction mixture.

For the synthesis of MIL-101, chromium trimmers or/and benzenedicarboxylate require [**39**]. Increasing the pH from 2 or 4, concentration of chromium trimmers increases because the Cr(III) is formed. Moreover, with increasing pH, the deprotonation of TPA will be accelerated. TPA can be converted into benzenedicarboxylate. Also, MIL-53 requires benzenedicarboxylate. By decreasing the pH, the efficiency of MIL-53 increases. On the contrary, the trimer is not necessary for the MIL-53 structure [**55**].

CO_2 adsorption

The CO_2 sorption isotherms of Cr-BDCs are determined at 299.2 K and pressures ranging from 0 to 3.5 bar. **Fig. 3** and **Fig. 4** show the adsorption isotherms. These Figures show that the CO_2 adsorption capacity of Cr-BDCs always increases with increasing pressure. The results indicate a typical physisorption behavior and potential for use in pressure swing adsorption (PSA) [**59**]. In **Fig. 3**, the reactant molar compositions of $CrCl_3{\cdot}6H_2O/TPA/400H_2O$ demonstrate linear adsorption curve. The CO_2 sorption isotherms of A, C, E, G and J cases show that the increase in pH does not have much effect on adsorption.

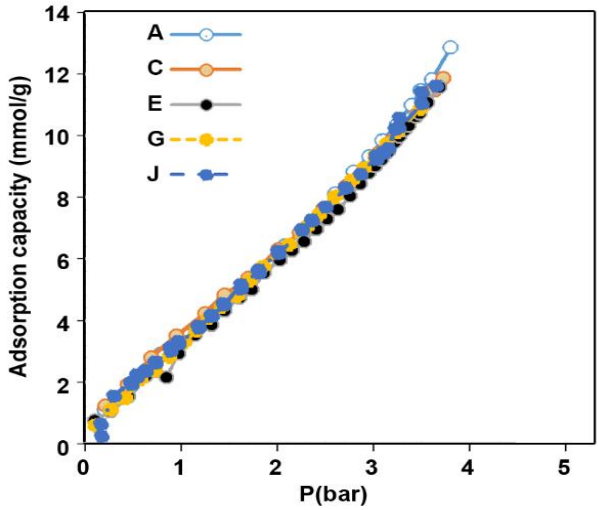

Fig. 3. The CO_2 adsorption isotherms for the reactant compositions ($CrCl_3{\cdot}6H_2O/TPA/400H_2O$) at 299.2 K.

Fig. 4 shows that the molar compositions of $CrCl_3{\cdot}6H_2O/TPA/250H_2O$ exhibit linear adsorption capacity. Moreover, the adsorption capacities for B and D are more than F, I and K.

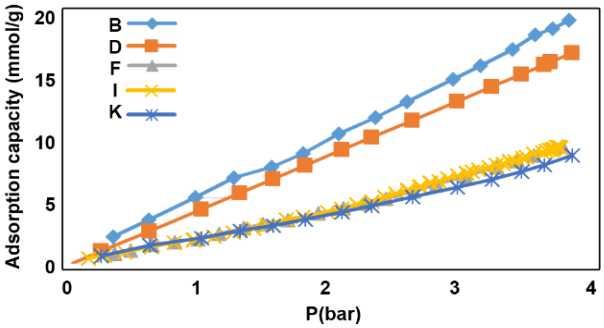

Fig. 4. The CO_2 adsorption isotherms for the reactant compositions ($CrCl_3{\cdot}6H_2O/TPA/250H_2O$) at 299.2 K.

Fig. 4 shows the same trends as **Fig. 3** does. However, B and D have a higher adsorption capacity than the others. As illustrated XRD patterns in **Fig. 1**, the case of B and D are demonstrated MIL-53 production. On the contrary, the others are indicated that MIL-101 is formed. Also, the MIL-53 and MIL-101 are not created in the case of K because pH has increased with increasing $NaHCO_3$. However, K is illustrated CO_2 adsorption. **Table 2** shows the CO_2 adsorption capacity at 299.2 K and 3.5 bar.

Table 2. CO_2 adsorption capacity at 299.2 K and 3.5 bar and yield and for Cr-BDCs.

Sample	CO_2 adsorption capacity (mmolg^{-1})	Yield (%)
A	11.0	34.5
B	17.5	30.1
C	10.5	30.7
D	15.1	32.9
E	10.4	25.9
F	8.3	37.5
G	10.6	24.7
H	-	0
I	8.4	25.3
J	11.0	35.5
K	7.2	25.7

By comparing B and D with other samples in **Table 2**, it can be found out that B and D have exhibited a higher adsorption capacity than the others. As mentioned before, low pH is caused to form the MIL-53. So that the CO_2 adsorption is significantly increased by adding 1 acetic acid equivalent for the reactant composition $CrCl_3{\cdot}6H_2O$/TPA/250H_2O. This reactant composition has CO_2 adsorption with 1 acetic acid equivalent and without acetic acid 17.5 and 8.4 mmolg^{-1}, respectively. Zhou *et al.* have investigated CO_2 adsorption on MIL-53 and GrO(graphene oxide doping)@MIL-53(Cr) composites. The adsorption capacities of CO_2 are reported to be 4.814, 5.279, and 10.81 mmolg^{-1} for MIL-53, 1GrO(doping (1%)) @MIL-53, and 10GrO(doping (10%))@MIL-53 adsorbents, respectively at 298 K and pressure≤5 bar [**57**]. Synthesized MIL-53 (sample B) in the study has exhibited the adsorption capacity 17.5 mmolg^{-1} at 299.2 K and 3.5 bar. Therefore, acetic acid improves the CO_2 adsorption capacities for MIL-53.

MIL-53 is very interesting because of the breathing effect [**60, 61**]. Their ''breathing'' crystal structures alter with the change of pressure, so that the pore structure of MIL-53 can spread and open upon increased pressure and can close upon a reduction in gas pressure [**62**]. Serre *et al.* have investigated the effect of large breathing in the MIL-53 structure that is due to the existence of OH groups [**43**]. The CO_2 adsorption mechanism can be enhanced by a hydrogen-bond interaction between CO_2 molecules and μ_2-OH groups [**62-63**]. Vimont *et al.* have indicated the formation of electron donor–acceptor complex between CO_2 molecules and hydroxyl groups by spectroscopic [**64**]. Therefore, the higher CO_2 adsorption capacity of B and D may be explained by the stronger interaction between a quadrupole moment CO_2 and the polar acetic anions in the structure. The CO_2 adsorption capacities of J and I are 11 and 8.4 mmolg^{-1} at 299.2 K and 3.5 bar, respectively, in reasonable agreement with the results of Khan *et al.* They have reported surface area of the reactant composition $CrCl_3{\cdot}6H_2O$/TPA/400H_2O and the reactant composition $CrCl_3{\cdot}6H_2O$/TPA/250H_2O, which have 3160 and 2735 m^2g^{-1}, respectively [**49**]. Therefore, the higher CO_2 adsorption capacity of J may be explained by the higher its surface area. The reactant composition ($CrCl_3{\cdot}6H_2O$/TPA/250H_2O/ $NaHCO_3$) has the lowest CO_2 adsorption capacity because MIL-101 or MIL-53 cannot be formed. Its CO_2 adsorption capacity may be described by the interaction between CO_2 and the polar bicarbonate anions in the unknown formed structure.

By comparing the reactant compositions $CrCl_3{\cdot}6H_2O$/TPA/400H_2O with the reactant compositions $CrCl_3{\cdot}6H_2O$/TPA/250H_2O, it can be found that acetic acid content has influenced on the CO_2 adsorption capacity. Moreover, the reactant compositions $CrCl_3{\cdot}6H_2O$/TPA/400H_2O have exhibited the adsorption capacity approximately between 10.5 and 11.0 mmolg^{-1} at 299.2 K and 3.5 bar. Montazerolghaem *et al.* have carried out a set of experiments to obtain equilibrium of CO_2 adsorption. The adsorption capacities of CO_2 are reported to be 9.7, 10.6, 11.8 and 12.4 mmolg^{-1} for the parent MIL-101, activated MIL-101, MIL-101-Cu and MIL-101-Ni adsorbents, respectively at 7.1 bar and 298.2 K [**40**].

As demonstrated in results, the amount of acetic acid can rarely affect the CO_2 adsorption. On the contrary, the amount of acetic acid affects the CO_2 adsorption for the reactant compositions $CrCl_3{\cdot}6H_2O$/TPA/250H_2O. As illustrated XRD patterns in **Fig. 1**, in the reactant compositions $CrCl_3{\cdot}6H_2O$/TPA/250H_2O, MIL-101 is converted to MIL-53 when changes the acetic acid content.

Conclusion

The effect of synthesis conditions on the phase (MIL-53 or MIL-101), yield and the CO_2 adsorption capacity of chromium benzenedicarboxylates has been studied. Increasing acetic acid content in reaction mixture in both reactant compositions of $CrCl_3{\cdot}6H_2O$/TPA/400H_2O and $CrCl_3{\cdot}6H_2O$/TPA/250H_2O showed different effect. Increasing acetic acid content in $CrCl_3{\cdot}6H_2O$/TPA/250H_2O improved yield; however, the yield was reduced for $CrCl_3{\cdot}6H_2O$/TPA/400H_2O. The reaction time and temperature significantly decreased for $CrCl_3{\cdot}6H_2O$/TPA/400H_2O by adding 1 acetic acid equivalent. Moreover, a further increase in acetic acid content leads to changing CO_2 adsorption capacity for both reactant compositions. With regard to various water concentrations and acetic acid contents, $CrCl_3{\cdot}6H_2O$/TPA/400H_2O has the maximum CO_2 adsorption capacity 11.0 mmolg^{-1} while, $CrCl_3{\cdot}6H_2O$/TPA/250H_2O has the maximum CO_2 adsorption capacity 17.5 mmolg^{-1} at 299.2 K and 3.5 bar. The CO_2 adsorption capacity significantly increased for $CrCl_3{\cdot}6H_2O$/TPA/250H_2O by adding 1 acetic acid

equivalent. 1 acetic acid equivalent improved CO_2 adsorption capacity 17.5 mmolg^{-1} while, CO_2 adsorption capacity was 8.4 mmolg^{-1}without acetic acid.

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Author's contributions

Conceived the plan: Fariba Soltanolkottabi, Mohammad Reza Talaie, Seyedfoad Aghamiri, Shahram Tangestaninejad; Performed the expeirments: Fariba Soltanolkottabi, Mohammad Reza Talaie; Data analysis: Fariba Soltanolkottabi, Mohammad Reza Talaie; Wrote the paper: Fariba Soltanolkottabi, Mohammad Reza Talaie..

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