



CO₂ Adsorption by Several Types of Pillared Montmorillonite Clays

Ke Wang¹ · Xinlong Yan² · Sridhar Komarneni³

Received: 22 March 2018 / Accepted: 25 June 2018 / Published online: 29 June 2018
© The Author(s) 2018

Abstract

CO₂ has been found to be the main anthropogenic contributor to the greenhouse gas effect, thus, the development of carbon capture and storage (CCS) technology is extremely urgent. In this work, two kinds of Al₂O₃ pillared montmorillonite, one ZrO₂-pillared montmorillonite and one TiO₂ + SiO₂ pillared montmorillonite were prepared and characterized by X-ray diffraction (XRD) for phase formation and N₂ adsorption–desorption isotherms for surface area and pore-size distribution. Equilibrium adsorption of CO₂ gas was measured at 273 K. CO₂ adsorption capacities of pillared clays increased with the increase of their pore volume. The uptakes of CO₂ by pillared clays were in the range of 0.53–1.18 mmol/g.

Keywords Montmorillonite · Pillared clays · CO₂ adsorption

Introduction

Global climate change caused by increased concentrations of greenhouse gases in the atmosphere has become a worldwide urgent environmental issue [1, 2]. It is well known that CO₂ is the major anthropogenic greenhouse gas (GHG) in the atmosphere mainly due to the extensive utilization of fossil fuels as energy source. The atmospheric concentration of CO₂ has increased to 384 ppm in 2007 from its pre-industrial level of ca. 280 ppm, and is expected to reach 550 ppm by 2050 even if CO₂ emission is stable for the next four decades [3]. Therefore, a great deal of effort has been devoted to stabilize the CO₂ concentration in the atmosphere by controlling the emission of CO₂ from various sources. Carbon capture and storage (CCS) is believed to be one of the keys to reducing greenhouse gas emissions.

Adsorption is potentially a cost-effective technique to capture CO₂ from flue gases of fixed sources or directly from

air. As a consequence of this, various kinds of materials have been investigated as possible CO₂ adsorbents, such as activated carbon, carbon molecular sieves, zeolites, mesoporous materials, metal oxides, anionic clays or hydrotalcite-like materials, metal–organic frameworks (MOFs), amine functionalized solid sorbents and alkali-metal carbonate-based sorbents [4–6].

Modified clay materials have been studied for different gas adsorptions, such as N₂, O₂, CH₄, CO, CO₂, and C₂H₂ etc. [7–9]. Venaruzzo et al. [20] reported the adsorptions of CO, CO₂ and SO₂ gases by two bentonitic clay minerals. The clay minerals were tested for gas adsorption at 25 °C and 100 Kpa. The adsorption values of the CO₂ were in the range of 0.218–0.516 mmol/g. Obviously, the CO₂ adsorption capacities of the above modified clay materials are still very low compared to other sorbents.

Pillared clays are inorganic oxide-clay nanocomposites, which are an interesting class of 2-dimensional microporous materials. Due to their high surface area and permanent porosity, they are widely used as adsorbents and catalyst supports [10, 11]. However, there is scarce information about the CO₂ gas adsorption properties of pillared clays.

In this paper, Al₂O₃, ZrO₂ and TiO₂-SiO₂ pillared clays were prepared using montmorillonite clay and characterized by XRD and N₂ physisorption technique. In addition, the CO₂ adsorption isotherms of these samples were measured and compared for determining their potential use in CO₂ separation.

✉ Xinlong Yan
yanxl@cumt.edu.cn

¹ China Petroleum Engineering and Construction Co., Ltd., Southwest Branch Company, 610041 Chengdu, China

² School of Chemical Engineering and Technology, China University of Mining and Technology, 221116 Xuzhou, China

³ Department of Ecosystem Science and Management, Materials Research Institute, 205 Materials Research Laboratory, The Pennsylvania State University, University Park, USA

Experimental

Materials

Preparation of Al₂O₃-pillared montmorillonite (MMT)

Al polymer pillaring solution was prepared as follows: The pillaring precursor solution was prepared by titrating 500 ml of 0.4 molar NaOH ($\geq 96.0\%$) into 250 ml of 0.4 molar Al(NO₃)₃·9H₂O ($\geq 99.0\%$) at 2.5 ml per min under vigorous stirring (Na:Al=2:1). After the titration and 1 h stirring, the solution was heated at 65 °C for 4 h in a sealed container and then stored at room temperature in a container before use.

Pillaring process with Al₂O₃

A 0.2 g of Na-montmorillonite, Wyoming or a sodium montmorillonite supplied by Kunimine Industrial Company, Japan (designated as Kunipia from hereafter) was added slowly to 20 ml of deionized water. After 30 min stirring 20 ml of the pillaring solution was added into the suspension. The suspension was stirred for 8 h after the precursor addition and then centrifuged to collect the solid. To make sure that the intercalation of Al pillars was complete, the above solid was again treated with 20 ml of deionized (DI) water and 20 ml of the pillaring solution by stirring for 1 day. The resultant pillared clays were washed with DI water several times and finally with ethanol. The final product was dried in air. The above preparation of Al₂O₃-pillared montmorillonite was based on a previously described procedure by Malla and Komarneni [12]. The Al₂O₃-pillared montmorillonites (MMT) are hereinafter referred to as Al-pillared kunipia and Al-pillared Na-MMT.

Preparation of ZrO₂-pillared montmorillonite

Hydroxy zirconium solution was first prepared as follows: A solution of 0.2 M ZrOCl₂ ($\geq 99.0\%$) was heated at 60 °C for 48 h to synthesize hydroxyl Zr polymers. For obtaining a ZrO₂-pillared montmorillonite, a 1% suspension of montmorillonite, Wyoming was mixed with excess amount of pillaring (> 25 times the CEC of clay) solution and reacted for 2 h at 25 °C. The above preparation of ZrO₂-pillared montmorillonite was based on a previously described procedure by Malla et al. [13].

Preparation of TiO₂-SiO₂ pillared montmorillonite

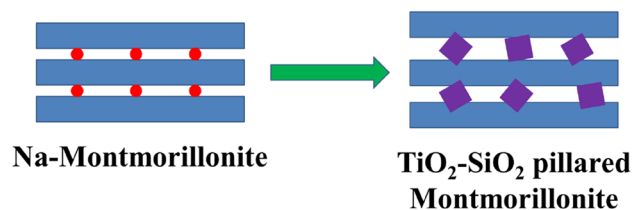
Titania Sol was first prepared as follows: Ti isopropoxide ($\geq 98.0\%$) was added to 1 M HCl solution to hydrolyze and obtain Ti polymeric sol and the resulting slurry was peptized

to a clear solution by stirring for 3 h at room temperature. The molar ratio of HCl to the alkoxide was about four. Silica Sol was then prepared as follows: Silica sol solution was prepared by mixing tetraethoxysilane, 2 M HCl and ethanol in a ratio of 41.6 g/10 ml/12 ml. Silica sol is negatively charged and therefore, it cannot be directly used as a pillaring agent but can be used in the form of mixed sols with titanium (IV) hydroxide deposited on the silica sols. Therefore, titania-silica mixed sol was prepared as follows: The silica and the titania sol solutions prepared above were mixed in a molar ratio of TiO₂/SiO₂ = 1/10 and stirred for 1 h at room temperature. For obtaining TiO₂-SiO₂ pillared montmorillonite (Scheme 1), about 1% suspension of montmorillonite, Wyoming in water was reacted with the mixed sol solution. The ratio of the mixed sol of TiO₂-SiO₂ to the cation-exchange capacities (CEC) equivalent of the clay was 30. The mixture was allowed to react for 3 h under stirring at 50 °C and then the products were separated by centrifugation, washed with water several times, and then dried at room temperature. The above preparation of TiO₂-SiO₂ pillared montmorillonite was based on a previously described procedure by Yamanaka et al. [14].

All the above pillared clays were heated/calced at 450 °C for 5 h to convert polymeric hydroxy cations to ceramic oxides. The as-prepared pillared clays and calcined pillared clays were characterized by different techniques as described below.

Characterization

X-ray diffraction patterns for the samples were recorded on a Panalytical Xpert PRO X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$, 45 kV, 40 mA). Nitrogen adsorption and desorption isotherms were measured on an Autosorb-1 sorption analyzer by Quantachrome instrument at liquid nitrogen temperature. The samples were degassed at 150 °C for 6 h prior to analysis. The total pore volume (V_t) was determined as the volume of liquid nitrogen adsorbed at a relative pressure of 0.99. The pore size distribution was calculated from the desorption isotherm using the BJH method.



Scheme 1 Schematic illustrating the preparation of TiO₂-SiO₂ pillared montmorillonite

CO₂ adsorption

The CO₂ adsorption isotherms at 273 K were measured by using a Quantachrome Autosorb-1 sorption analyzer with pure CO₂ (99.999%). Prior to each adsorption experiment, the sample was degassed for 2 h at 373 K under vacuum.

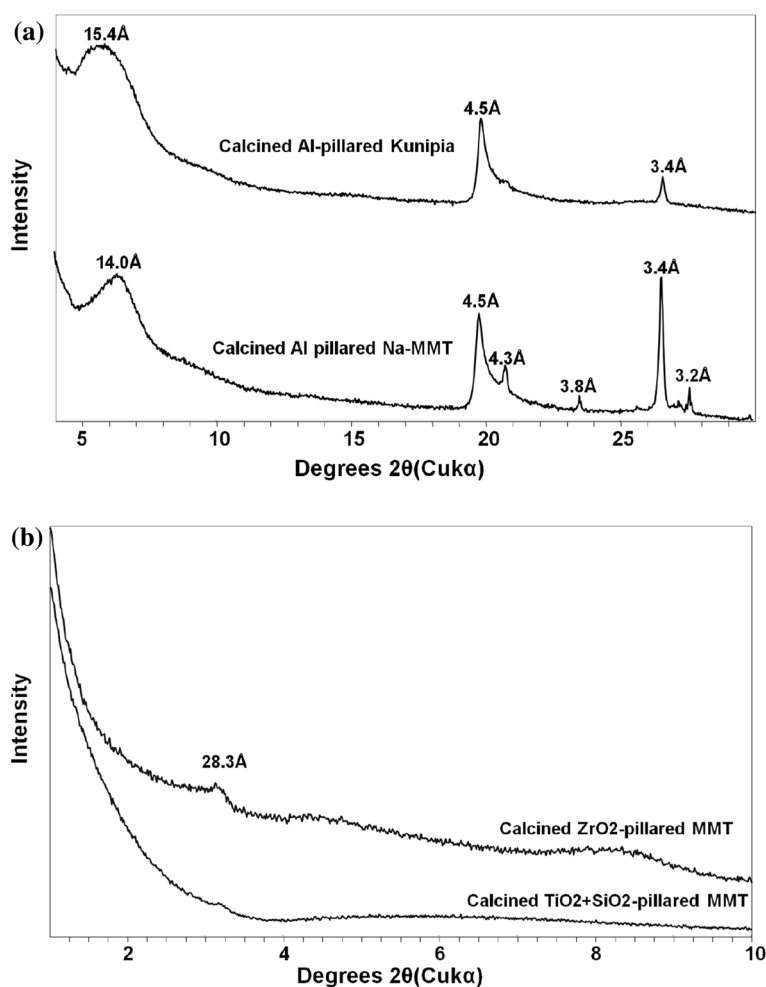
Results and discussion

Figure 1a, b show the XRD patterns of Al-pillared kunipia, Al-pillared Na-MMT, ZrO₂-pillared MMT and TiO₂+SiO₂ pillared MMT. It can be seen that both Al-pillared Kunipia and Al-pillared MMT show the characteristic peaks of the montmorillonite crystalline layered structure in the position (2 theta) of ~7.5°, as well as peaks at 20° and 26.5°, corresponding to the quartz commonly found in clays. The ordered pillaring of layered materials will result in the shifting of the (001) to lower 2θ region [15]. The *d*₀₀₁ value of Al-pillared Kunipia is 1.54 nm, which is slightly larger than that of Al-pillared MMT (1.40 nm). These *d*₀₀₁ values of calcined pillared clays decreased compared to the

as-prepared Al pillared clays, which showed *d*₀₀₁ values of around 1.8 nm. For ZrO₂ and TiO₂+SiO₂ pillared MMT samples, the (001) peaks obtained are almost absent in the lower 2θ region, which is because of the lack of a sufficiently ordered and oriented silicate layer structure. The poor long range ordering may be due to the disordered distribution of different sizes of pillaring oxides in the clay layers.

Figure 2 shows the N₂ adsorption–desorption isotherms of the four different kinds of pillared clays, and Table 1 summarizes the textural properties of the samples prepared in this work. The isotherms of all the four different pillared clay samples are of type IV and show steep hysteresis of type H₄ at high relative pressures corresponding to the mesoporous nature of the pillared clay materials (Fig. 2a). It can be seen that TiO₂+SiO₂ Pillared clay showed the largest surface area of 437 m²/g and total pore volume of 0.28 cm³/g, whereas Al-pillared Na-MMT showed the lowest surface area and pore volume of 169 and 0.19 cm³/g, respectively (Table 1). All the four pillared clay samples showed a very close pore size distribution with a peak centered at 3.9 nm (Fig. 2b). Note that, TiO₂ pillared clay were reported by many researchers

Fig. 1 XRD patterns of pillared clays calcined at 450 °C for 5 h (a) Al-pillared kunipia, and Al-pillared Na-MMT and (b) ZrO₂-pillared MMT and TiO₂+SiO₂ pillared MMT



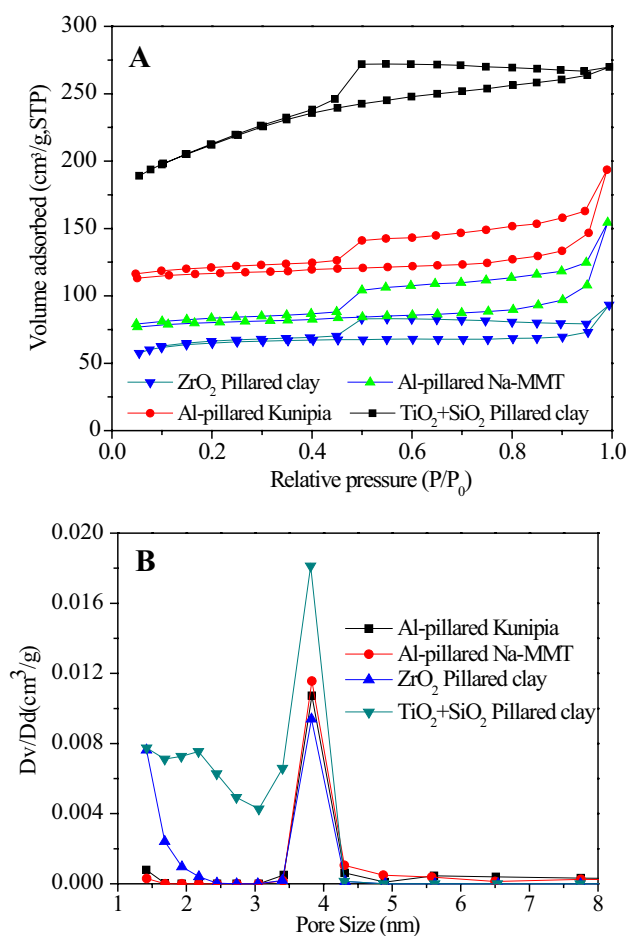


Fig. 2 Nitrogen adsorption–desorption isotherms (a) and pore size distributions (b) of pillared clays. The isotherms for samples ZrO_2 pillared clay, Al-pillared Na-MMT, Al-pillared Kunipia and $TiO_2 + SiO_2$ pillared clay are shifted by 0, 30, 60 and 90 cm^3/g , STP

Table 1 Textural properties and CO_2 uptake of pillared clays

Samples	BET surface area m^2/g	Pore Volume cm^3/g	CO_2 adsorption capacity $mmol/g$ (1 atm)
Al-pillared Kunipia	181	0.21	0.80
Al-pillared Na-MMT	169	0.19	0.65
ZrO_2 Pillared clay	249	0.15	0.53
$TiO_2 + SiO_2$ Pillared clay	437	0.28	1.18

[16–19], the specific surface areas of the samples were around 250 m^2/g . However, with the adding of SiO_2 , the surface area of $TiO_2 + SiO_2$ pillared clay increased to more than 400 m^2/g , because the composite pillar particles were probably tightly packed in the interlayers forming small pores between the particles and silicate layers. The presence of positively charged TiO_2 particles coated on the negatively charged SiO_2 particles enabled the pillaring

with SiO_2 producing more micropores and hence the surface area increased significantly [12, 14].

The adsorption–desorption isotherms of CO_2 gas measured at 273 K on various pillared clay adsorbents are depicted in Fig. 3. All the isotherms show a modest increase in the amount of CO_2 adsorbed with an increase of pressure and the gas adsorption data are fully reversible. All the samples exhibited a slight hysteresis, which indicated their good affinity for CO_2 . Furthermore, it is noticed that there are no plateaus in adsorption isotherms in the pressure range investigated. The equilibrium adsorption capacities of these adsorbents at 1 atm are compiled in Table 1. It can be seen that the $TiO_2 + SiO_2$ Pillared clay sample showed the highest adsorption capacity (1.18 $mmol/g$ at 273 K and 1 atm) among these pillared clay samples correlating with its surface area, which is the highest among the four pillared clays studied here. All the pillared clays showed much higher sorption capacities than unmodified bentonite (montmorillonite) which only showed a CO_2 adsorption capacity of 0.218 $mmol/g$ (25 °C and 1 atm) [20]. The CO_2 adsorption capacity increased with the increase of pore volume (Table 1) of these four different pillared clays and correlated well with the surface areas of these samples except with that of the ZrO_2 pillared clay. This appears to suggest that ZrO_2 has less affinity for CO_2 than Al_2O_3 in the interlayers of clay. As has been found previously with many adsorbents, physical adsorption of CO_2 generally correlates with surface areas of the adsorbents [4], which is what was found in this study with various pillared clays. Further tailoring of the pillared clays could lead to increased CO_2 adsorption.

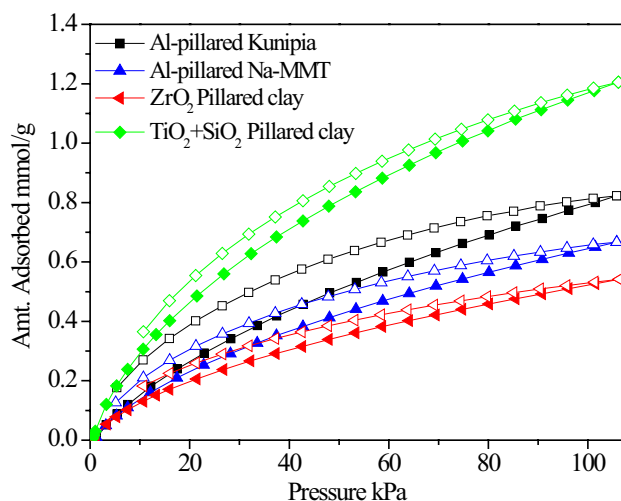


Fig. 3 Adsorption–desorption isotherms of CO_2 on various pillared clay adsorbents. (Filled and open symbols represent adsorption and desorption, respectively)

Conclusions

Montmorillonite clay minerals pillared with metal oxides were found to be effective in improving clay's adsorption for CO₂. The CO₂ adsorption capacities of four different pillared clays were found to increase with the increase of their pore volume and correlated with surface areas in general. Among the four pillared clays studied here, the N₂ BET surface areas of the TiO₂ + SiO₂ pillared montmorillonite greatly increased to more than 400 m²/g as compared to about 27 m²/g for the Na-montmorillonite and therefore, the TiO₂ + SiO₂ pillared montmorillonite exhibited the best CO₂ adsorption capacity of 1.18 mmol/g at 273 K and 1 atm.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

1. Chu S (2009) Carbon Capture and Sequestration. *Science* 325:1599
2. Haszeldine RS (2009) Carbon capture and storage: how green can black be? *Science* 325:1647–1652
3. Raupach MR, Marland G, Ciais P, Le Quéré C, Canadell JG, Klepper G, Field CB (2007) Global and regional drivers of accelerating CO₂ emissions. *Proc. Natl. Acad. Sci. USA* 104(24):10288–10293
4. Alessandro DMD, Smit B, Long JR (2010) Carbon dioxide capture: prospects for new materials. *Angew Chem Int Ed* 49(35):6058–6082
5. Wang Q, Luo J, Zhong Z, Borgna A (2011) CO₂ capture by solid adsorbents and their applications: current status and new trends. *Energy Environ Sci* 4(1):42–55
6. Drage TC, Snape CE, Stevens LA, Wood J, Wang J, Cooper AI, Dawson R, Guo X, Satterley C, Irons R (2012) Materials challenges for the development of solid sorbents for post-combustion carbon capture. *J Mater Chem* 22(7):2815–2823
7. Yang RT, Baksh MSA (1991) Pillared clays as a new class of sorbents for gas separation. *AIChE J* 37(5):679–686
8. Volzone C, Ortega J (2000) O₂, CH₄ and CO₂ gas retentions by acid smectites before and after thermal treatment. *J Mater Sci* 35(21):5291–5294
9. Melnitchenko A, Thompson JG, Volzone C, Ortega J (2000) Selective gas adsorption by metal exchanged amorphous kaolinite derivatives. *Appl Clay Sci* 17(1–2):35–53
10. Louloudi A, Papayannakos N (2000) Hydrogenation of benzene on Ni/Al-pillared montmorillonite catalysts. *Appl Catal A Gen* 204:167–176
11. Su H, Zeng S, Dong H, Du Y, Zhang Y, Hu R (2009) Pillared montmorillonite supported cobalt catalysts for the Fischer–Tropsch reaction. *Appl Clay Sci* 46(3):325–329
12. Malla PB, Komarneni S (1990) Synthesis of highly microporous and hydrophilic alumina-pillared montmorillonite: water sorption properties. *Clays Clay Miner* 38(4):363–374
13. Malla PB, Yamanaka S, Komarneni S (1989) Unusual water vapor adsorption behavior of montmorillonite pillared with ceramic oxides. *Solid State Ion* 32/33(1):354–362
14. Yamanaka S, Nishihara T, Hattori M (1988) Adsorption and acidic properties of clays pillared with oxide sols. In: *Proceedings of Materials Research Society*, vol 111, pp 283–288
15. Sterte J (1986) Synthesis and properties of titanium oxide cross-linked montmorillonite. *Clays Clay Miner* 34:658–664
16. Yamanaka S, Makita K (1995) Optical and electrochemical properties of titania pillared clays. *J Porous Mater* 1:29–41
17. Kaneko T, Fujii M, Kodama T, Kitayama Y (2001) Synthesis of titania pillared mica in aqueous solution of acetic acid. *J Porous Mater* 8(2):99–109
18. Ooka C, Yoshida H, Horio M, Suzuki K, Hattori T (2003) Adsorptive and photocatalytic performance of TiO₂ pillared montmorillonite in degradation of endocrine disruptors having different hydrophobicity. *Appl Catal B Environ* 41(3):313–321
19. Jagtap N, Ramaswamy V (2006) Oxidation of aniline over titania pillared montmorillonite clays. *Appl Clay Sci* 33(2):89–98
20. Venaruzzo JL, Volzone C, Rueda ML, Ortega J (2002) Modified bentonitic clay minerals as adsorbents of CO, CO₂ and SO₂ gases. *Microporous Mesoporous Mater* 56(1):73–80

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.