N₂ and CO₂ Adsorption by TMA- and HDP-Montmorillonites

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N₂ and CO₂ gases adsorption by tetramethylammonium(TMA)-montmorillonites and hexadecylpyridinium(HDP)-montmorillonites was carried out using volumetric equipment at 25 °C and 0.1 MPa. The addition of organic compounds to montmorillonites was 1 and 4 times the cation exchange capacity (CEC) of the montmorillonites and the contact times between the TMA (or HDP) and the montmorillonites were 4 and 24 h. The adsorptions of CO₂ by TMA-montmorillonites (0.383-0.477 mmol/g) were higher than those by HDP-montmorillonites (0.027-0.060 mmol/g). N₂ gas retentions by organo-montmorillonites were small: in the range of 0.038-0.065 mmol/g TMA-montmorillonites and around 0.010 mmol/g HDP-montmorillonites. The interlamellar spacing of the organo-montmorillonites, the structure of the intercalated organic molecule, and the type of montmorillonites influenced the gas adsorption values.

Keywords: gas adsorption, CO₂, N₂, TMA, HDP, organo-montmorillonite

1. Introduction

Gas adsorption by carbon and zeolites has been reported for gas separation in different papers. The montmorillonite clays are recognized as good adsorbents due to their ability to exchange interlayer cations for charged organic or metal cations in solution. The montmorillonite can be converted into organo-montmorillonite and it could be effective for adsorption organic compounds. Yang and Baksh and Yang and Cheng started studies of gas adsorption by pillared clays. Recently, the studies about gas retention by inorganic modified clays (pillared clays, modified aluminum pillared clays, acid clays, amorphized kaolinitic) have indicated that these materials have potential for gas separation; nevertheless, up to now there is only scarce information about retention of gases by organo-clays. The montmorillonites are clay minerals 2:1 layer phyllosilicates: two Si tetrahedral sheets are separated by one Al octahedral sheet (T-O-T). The isomorphic substitutions in the sheets, mainly in octahedral ones for montmorillonites, originate deficits of positive electric charges. These charges are balanced by exchangeable cations in interlayer positions. The organo-montmorillonites can be obtained by intercalating organic species within the interlayer sites of the montmorillonites. Cheto- and Wyoming-montmorillonites are the main types of montmorillonite; the Cheto-type has higher Mg content than the Wyoming-type in octahedral sheet.

The aim of this paper is to analyze the adsorption of N₂ and CO₂ gases at 25 °C and 0.1 MPa by TMA- and HDP-montmorillonite clays. The organo-montmorillonites were obtained by tetramethylammonium (TMA) or hexadecylypyridinum (HDP) cation intercalation into two different type-montmorillonites. One n-alkylammonium and one n-alkylpyridinium were chosen as organic cations, as example of different molecule structure, because different results can be obtained on gas retention by organo-smectites.

2. Materials and Methods

The montmorillonites used in this study were SAz-1, Ca montmorillonite (Cheto type), Apache County, Arizona, U.S.A. and Swa-1, Na montmorillonite (Wyoming type), Wyoming, U.S.A. The samples were named M1 and M2, respectively.

Tetramethylammonium (TMA) and hexadecylypyridinum (HDP) cations were used to prepare organo-montmorillonites as it has been informed in a previous paper. Aqueous solution of TMA chloride or HDP chloride salts were added to montmorillonite suspensions and allowed to stand for 4 and 24 hours. The solids were washed to re-
move the excess of salts and stored at room temperature. The amounts of organic cations added to the montmorillonites were 1 and 4 times the Cation Exchange Capacity (CEC) of the montmorillonites. The organo-montmorillonites were named M1 or M2, followed in brackets by two numbers: the first was the amount of organic cation in CEC time added, 1 or 4; and the second ones was the contact time, 1 or 24 hours. The CEC of the M1 and the M2 montmorillonites were 110 and 97 meq/100 g, respectively; the half-unit cell compositions calculated in a previous paper are shown in Table 1. The higher CEC of M1 is due to higher isomorphous substitution in the structure in which the Al was replaced by Mg in the octahedral sheet.

X-ray diffraction (XRD) patterns were obtained by scanning at 1 °/min between 3-70 ° using a Philips 3020 Goniometer with PW 3710 Controller using Cu Kα radiation (λ = 1.5405 Å) at 40 kV and 20 mA and Ni filter.

Equilibrium adsorption was measured using standard volumetric apparatus. Samples were degassed at 100 °C for 12 hours prior to measurement. N2 and CO2 were the gases tested for their adsorption behavior. Adsorption was measured at 25 °C and 0.1 MPa.

3. Results and Discussion

The distance between the top of the Si tetrahedral silica sheet (T) and the top of the Si tetrahedral sheet in the next layer (Fig. 1) is the d(001) spacing or basal spacing of the montmorillonite. The initial d(001) spacings of M1 and M2 montmorillonites were 13.00 Å and 14.90 Å, Ca2+ and Na+ being the principal cations in interlayer position, respectively, Table 1, Fig. 2a and 2b shows the XRD of the M1 and M2 montmorillonites before and after TMA treatments. The intercalation of TMA cations in montmorillonites changed the d(001) spacings to the range of 13.71 to 14.87 Å. According to Lagaly et al. the alkylammonium cation, such as TMA, is arranged in monolayer form. Lee et al. found the d(001) spacing value of 13.80 Å in montmorillonite treated with similar amount of added TMA (3-5 times CEC). In general, an increase of the basal spacing was observed in montmorillonites treated with higher additions of such organic substance. The final XRD of the TMA-montmorillonites was modified after different additions of TMA (1-4 times of CEC) and contact time (4-24 h), where the TMA-M1 and TMA-M2 patterns showed peaks corresponding to TMA species (Figs. 2a and 2b).

The intercalation of montmorillonites with HDP cations resulted in an increase in basal spacing from 13.00-14.90 Å of the original montmorillonites, M1 and M2, respectively, to the range of 18.15-26.75 Å, as it was showed in Figs. 3a and 3b. HDP produces larger basal spacing due to its arrangement in the interlayer. Lagaly et al. mentioned that n-alkylpyridinium cations (as HDP) occur as a bilayer. High contact time and several additions of HDP originated an important modification in XRD patterns (Figs. 3a and 3b), where new peaks as HDP species appeared.

The higher d(001) spacing of organo-M1 samples than that of organo-M2 samples could be attributed to the more retention organic substance in interlayer position due to the greater CEC of the M1 in relation to that of the M2 original montmorillonites, Table 1.

Figure 1. Montmorillonite structure. T: tetrahedral sheet; O: octahedral sheet.

Figure 2. X-ray diffraction: a) TMA-M1 serie; b) TMA-M2 serie. T: tetramethylammonium specie; S: smectite; Q: quartz.
Table 2 shows the adsorption of gases by original montmorillonites and after TMA or HDP cation intercalations. The N₂ retentions by organo-montmorillonites were lower than the CO₂ ones. The reason could be attributed to the fact that compared to N₂, the CO₂ possesses a larger quadruple moment (-1.5 x 10⁻²⁶ and -4.3 x 10⁻²⁶ Erg¹/₂.cm⁵/₂, respectively). Previous studies conducted that the amount of gas retention varies either as function of physicochemical properties of the adsorbates, as it was observed by Yang and Baksh²⁰ or as function of physicochemical characteristics of the adsorbents (clays, modified clays, zeolites)²⁰⁻²⁸.

Different types of binding interaction may occur between the gas molecule and the interlayer of the organo-montmorillonite, depending on the structural composition of montmorillonite. The montmorillonites treated with TMA retained larger amounts of gases than the original montmorillonite; however, after treatment with HDP the adsorption values were smaller. This could be due to the smaller size of TMA that do not form a continuous organic phase on the clay surface and in the interlayer, leaving a free siloxane mineral surface²³.

The retention values of CO₂ by TMA-M2 samples (0.423-0.477 mmol/g) were higher than those by TMA-M1 samples (0.383-0.445 mmol/g). The N₂ gas retentions by TMA-M2 samples (0.055-0.065 mmol/g) were also higher than those by TMA-M1 samples (0.038-0.055 mmol/g). This behavior could be explained by the fact that the montmorillonite with higher CEC (M1), Table 3, retained more TMA in interlayer position, leaving less free space available for gas adsorption. Lee et al.²¹ mentioned that the closer packing of TMA ions in the high-charge smectite (similar to our M1) resulted apparently in a decrease in the free surface area of the clay mineral.

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the large HDP molecule in interlayer position originated less free space available for sorption capacity.

The CO$_2$ gas retentions by the TMA-montmorillonites (0.383-0.477 mmol/g) were higher than those by Al-, Zr-, Cr- and Ti-pillared clays (0.210, 0.185, 0.100 and 0.141 mmol/g); the modified Al-PILCs (0.300 mmol/g)\textsuperscript{14}; the amorphous kaolinite derivatives (0.226-0.294 mmol/g)\textsuperscript{15,16} and the acidified smectites (0.357 mmol/g)\textsuperscript{17}; however, they were smaller than those by acid modified kaolinite (0.602 mmol/g)\textsuperscript{18} under the same experimental adsorption conditions as it was reported in previous papers. However, it is important to take into account that the modified clays were prepared under different experimental conditions.

The relative high gas retention by TMA-montmorillonites may be explained by the combined effect of the interaction between gas and TMA and the adsorption on the montmorillonite surface.

4. Conclusions

The N$_2$ and CO$_2$ gas adsorptions by two Cheto and Wyoming types montmorillonites increased after treatment with tetramethylammonium (TMA). Nevertheless, an important reduction in adsorption values after intercalation of hexadecylpyridinium (HDP) cation was observed.

The retention of N$_2$ gas by TMA-montmorillonites was small (0.038-0.065 mmol/g) whereas the values corresponding to CO$_2$ retention were high (0.383-0.477 mmol/g).

The interlayer spacing of the organo-montmorillonite, the structure of organic substance intercalated into the montmorillonite and the type of montmorillonite strongly influenced the N$_2$ and CO$_2$ gas retention values.

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