

SiO₂-Fe₂O₃-pillared Clay Nanohybrid with an Enhanced Gas Removal Property

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New layered inorganic-inorganic nanohybrids with highly porous structures were prepared by pillaring SiO₂-Fe₂O₃ nanoparticles into montmorillonite via exfoliation and reassembly. Gas removal activity of SiO₂-Fe₂O₃-pillared clay is much higher than that of active carbon, suggesting that pillaring strategy could be an effective method for removal of various gases.

Recently, heterostructured nanohybrids with enhanced physicochemical properties, such as inorganic-inorganic, organic-inorganic, and bio-inorganic nanohybrids have attracted considerable research interests.¹⁻³ Such enhanced properties originate from the dimensional confinements due to the nanosized building blocks.⁴ On the other hand, much research effort has been focused on the removal of toxic gases because of the increased interests in clean environment.⁵ Generally, gas removal activity is deeply affected by the porous nature of a framework. Nanoporous structures with high specific surface areas could provide easy accessibility of gas molecules into active sites for adsorption. Layered clays can be one of the best candidates for gas removal due to their high chemical stabilities and nontoxic properties. Furthermore, porous properties of clay materials such as specific surface areas and pore volumes can be tailored by using pillaring reactions.⁶ In the present study, we have been quite successful in developing highly porous nanohybrids composed of mixed SiO₂-Fe₂O₃ nanosol particles and clay nanosheets. Our key strategy is to fabricate open frameworks with thermally stable properties that would facilitate both high porosity and gas removal by reassembling exfoliated clay nanosheets with SiO₂-Fe₂O₃ nanoparticles.

To obtain fully exfoliated clay nanosheets, a 1.0 wt % aqueous suspension of montmorillonite was preswollen for 24 h. Silica nanosol solution was prepared by mixing tetraethyl orthosilicate (TEOS), 2 M HCl, and ethanol. On the other hand, iron hydroxide suspension was obtained by the titration of aqueous FeCl₃ solution with NaOH for 1 h, where the molar ratio of Fe to NaOH was fixed to 3. And then, the obtained iron hydroxide suspension was added dropwise to silica nanosol solution, in which the molar ratio between Si and Fe (Si:Fe = 30:*m*) was varied in the range of 30:1-30:4. The resulting translucent slurry was aged to prepare clear SiO₂-Fe₂O₃ mixed sol solution by tuning stirring time (*n*) from 3 to 12 h at room temperature. This SiO₂-Fe₂O₃ mixed sol solution was reacted with 1 wt % preswollen montmorillonite at 80 °C for 2 h to exchange Na⁺ ions with the positively charged SiO₂-Fe₂O₃ nanoparticles. The dried product was heat-treated at 400 °C for 2 h to complete pillaring reaction. Hereafter SiO₂-Fe₂O₃-pillared montmorillonite will be abbreviated as SFM-*m*-*n*: *m* is the molar ratio of Fe to 30 mol of Si, and *n* is aging time for the mixed solution of iron hydroxide suspension and SiO₂ nanosol solution.

By the deposition of iron oxide on the surface of silica, we modified the surface charge of silica nanosol particles from negative to positive, which resulted in SiO₂-Fe₂O₃ mixed nanosol

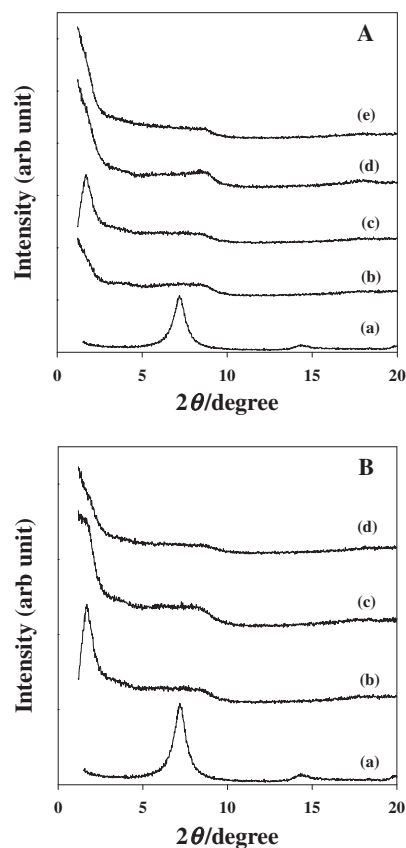


Figure 1. Powder XRD patterns for the samples: (A) (a) the pristine montmorillonite, (b) SFM-1-3h, (c) SFM-2-3h, (d) SFM-3-2h, and (e) SFM-4-3h; (B) (a) the pristine montmorillonite, (b) SFM-2-3h, (c) SFM-2-6h, and (d) SFM-2-12h.

particles. Figure 1A shows X-ray diffraction (XRD) patterns for SiO₂-Fe₂O₃-pillared montmorillonite nanohybrids, along with that of the pristine montmorillonite. To examine the effect of iron content in mixed sol particles for pillaring reaction, the molar ratios between Si and Fe (Si/Fe) were varied from 30/1 to 30/4, while the aging time was fixed to 3 h. The pristine Na⁺-montmorillonite exhibits basal spacing of 1.26 nm, which is the sum of the van der Waals diameter of hydrated Na⁺ ion (ca. 0.30 nm) and the layer thickness of montmorillonite (ca. 0.96 nm). After pillaring reaction, SFM-2-3h clearly shows very large interlayer spacing up to about 5.1 nm. Such a large gallery expansion of about 3.8 nm suggests that the present SiO₂-Fe₂O₃-pillared montmorillonite is a “supra-gallery” pillared clay,⁶ in which SiO₂-Fe₂O₃ nanoparticles are intercalated and multistacked in the interlayer spaces of clays. The multistacked nanoparticles could result in the high porosity,

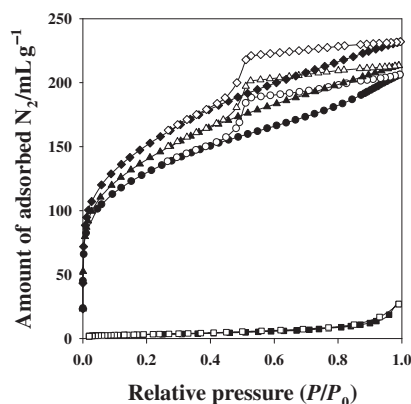


Figure 2. N_2 adsorption–desorption isotherms for pristine montmorillonite (■), SFM-2-3h (●), SFM-2-6h (▲), and SFM-2-12h (◆).

leading to the effective application in the adsorption of gas molecules. When the Fe content in mixed sol solution is too low (SFM-1-3h) or too high (SFM-3-3h and SFM-4-3h), no distinct 00l reflection is detected because of the irregular restacking of clay nanosheets with $SiO_2-Fe_2O_3$ nanoparticles. From above findings, it is found that the optimal ratio of Si/Fe is 30/2. Figure 1B shows the influence of aging time for pillaring reaction. When the aging time is 3 h, SFM-2-3h indicates the basal spacing of 5.1 nm as described before. As the aging time is longer, the interlayer spacing of SFM-2-6h is larger up to about 5.5 nm due to the increased sizes of intercalated nanoparticles. After 12 h of aging, there was no 00l reflection, suggesting that the particle size of the intercalated mixed nanosol is much bigger than 4.5 nm.

Nitrogen adsorption–desorption isotherms for samples were measured to probe the porous properties of pillared clays (Figure 2). The isotherm for pristine montmorillonite can be assigned to type III according to the BDDT (Brunauer, Deming, Deming, and Teller) classification,⁷ indicating that the pristine material has a nonporous nature. However, after pillaring of montmorillonite with $SiO_2-Fe_2O_3$ nanoparticles, the isotherms for $SiO_2-Fe_2O_3$ -pillared montmorillonite derivatives can be characterized as the mixed type between I and IV. The large hysteresis for $SiO_2-Fe_2O_3$ pillared montmorillonite corresponds to the type B in Boer's five types representing the presence of open slit-shaped pores.⁷ This result clearly shows that $SiO_2-Fe_2O_3$ nanoparticles are intercalated into the gallery spaces of clays. As the aging time is longer, the BET specific surface area becomes larger from 450 (SFM-2-3h) to 530 $m^2 g^{-1}$ (SFM-2-12h), furthermore, the total pore volume becomes also larger from 0.31 (SFM-2-3h) to 0.35 $m^2 g^{-1}$ (SFM-2-12h). As a consequence, the $SiO_2-Fe_2O_3$ -pillared montmorillonite nanohybrids could allow gas molecules to easily access the entire surface of nanohybrids as a result of their enhanced porosity developed by pillaring reaction, which could eventually result in the enhanced gas removal activity.

To explore the gas removal properties of these porous materials, we have investigated the adsorption of ammonia and hydrogen sulfide over nanohybrid material (Figure 3). Because the SFM-2-12h shows the highest porosity among samples according to the N_2 adsorption–desorption, we used it for gas adsorption. For comparison, an activated carbon was also used for gas adsorption experiments. SFM-2-12h adsorbed nearly all the ammonia molecules after 30 min, whereas only about 30% of ammonia was adsorbed by activated carbon at the same condition. In case of the adsorption of hydrogen sulfide, 83% of H_2S was removed by SiO_2-

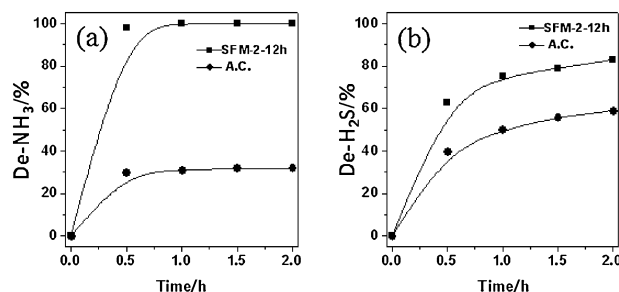


Figure 3. (a) Ammonia and (b) hydrogen sulfide removal performance over samples.

Fe_2O_3 -pillared montmorillonite after 2 h; however, only 59% of H_2S was adsorbed by the active carbon after 2 h. It is worthwhile to note here that all the ammonia gas molecules were completely removed by $SiO_2-Fe_2O_3$ -pillared montmorillonite after 2 h. It is highly plausible that the acid–base reaction between $SiO_2-Fe_2O_3$ -pillared montmorillonite and ammonia leads to the high removal activity. Because ammonia is a basic molecule and $SiO_2-Fe_2O_3$ nanoparticles in pillared clays can be regarded as an acid, acid–base reaction might be favored, leading to the high adsorption of ammonia onto the pores of $SiO_2-Fe_2O_3$ -pillared montmorillonite.⁸ Transition-metal-oxide-pillared clays could offer a number of acidic sites in the interlayer spaces,⁹ resulting in high interaction of basic molecules and pillared clays. However, in the case of acidic molecules such as H_2S , it takes much time to remove H_2S by $SiO_2-Fe_2O_3$ -pillared montmorillonite because both pillared nanohybrid and hydrogen sulfide are acidic. From the above findings, it is, therefore, concluded that the present synthetic method is very efficient in fabricating the porous structures for the removal of gas with an odor.

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