Synthesis and Characterization of Vanadia-Doped Iron-Oxide Pillared Attapulgite Clay for the Selective Catalytic Reduction of Nitrogen Oxides†

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Natural attapulgite was used as the raw material for the preparation of iron pillared clays. The iron-oxide pillared attapulgite was prepared by direct exchange of interlayer sodium cations in attapulgite for iron cations. The performance for the selective catalytic reduction of NOx at low temperature was also investigated. Vanadia (V_2O_5)-doped iron-oxide pillared attapulgite (V_2O_5/Fe-P ATP) by impregnation was characterized by X-ray diffraction, surface area and pore size distribution measurement, Fourier-transform infrared spectroscopy and scanning electron microscopy. Modified attapulgite was found to be active and selective for the reduction of Nitrogen oxides with ammonia at low temperatures. Especially at about 220 ºC, the removal ration of NOx was up to 90 %.

Key Words: Attapulgite, Fe-Pillared clays, Selective catalytic reduction, DeNOx-process.

INTRODUCTION

Nitrogen oxides have toxic effects on plants and animals, which can cause acid rain, photochemical smog and ozone depletion. Nitrogen oxides removal has become one of the most important parts in the control of atmospheric pollution. Currently, the effective method for the removal of nitrogen oxides is selective catalytic reduction by ammonia (DeNOx). The most frequently used selective catalytic reduction catalysts still have some typical problems such as the higher operating temperature; small surface area of TiO_2 and the deactivation of catalysts at high-temperature because of phase transition. Therefore, the development of new low-temperature, stable selective catalytic reduction catalysts have attracted more and more attention.

Clays are inorganic materials which are easy to get and harmless to the environment. They are now widely used for the preparation of catalysts as supports for the advantage of adjustable pore size, high thermal stability and exchangeable acidity. Many methods have been put forward to modify clays' properties for obtaining materials with special application. Through exchanging of the charge-compensating cations of the clays with large inorganic cations formed by hydrolysis of metallic salts[1], we can prepare metal oxide pillared clays with high surface area and developed porous structure. Intercalated layered clays by transition metals are studied[2-5] *e.g.*, Fe, Ti, Al, Cr, Zr. They have been observed to be the selective, stable and active catalysts for the reduction of nitrogen oxide with ammonia at low temperature[6-9].

Attapulgite (ATP) is a natural nano-structural hydrated magnesium aluminum silicate with 1-D fibrillar morphology[10] and owns reactive -OH groups on its surface. The special chain layered structure results in zeolite-like channels. Due to its special properties and large surface area, attapulgite can be used as absorbent, catalyst and catalyst support[11-14]. And iron pillared clays have been reported to be the active catalysts for the selective catalytic reduction of NO[6,7].

In this paper, we studied the preparation of V_2O_5/ Fe-P ATP. The Fe-P attapulgite was used as supports, then loaded V_2O_5 by impregnation for the selective catalytic reduction of NO in the simulated flue gas at low temperature and inspected the NO removal efficiency.

EXPERIMENTAL

Preparation of sodium form attapulgite (Na-ATP): A certain amount of attapulgite was dispersed in NaCl (0.1 M) and vigorously stirred for 6 h at room temperature. The Na-ATP was separated from the solution by filtration, then washed with deionized water until no Cl⁻ existed(tested with $AgNO_3$).

This step was repeated three times. The obtained product was dried at 80 ℃ and then grinded.

Preparation of Fe-P ATP: Fe-P ATP was prepared according to the pillaring procedure proposed by Bineesh *et al.*[15]. The prepared NaOH solution (0.4 M) was slowly added to FeCl₃ (0.2 M) under continuous stirring (the molar rate of OH/Fe was 2). The obtained mixed solution was left at room temperature for 10 h. At 40 ℃, in accordance with the ratio of Fe/ATP (n (Fe)/m (ATP)=5-15mmol/g), the pillaring solution was slowly added into the suspension of 2 wt % clay (Na-ATP) with vigorous stirring. After 24 h strring, the mixture was separated by filtration and washed with deionized water until no Cl⁻ existed(tested with AgNO₃). Finally, the modified attapulgite was dried in air and calcined at 300 ℃ for 3 h, then grinded.

V₂O₅/ Fe-P ATP: V₂O₅/Fe-P ATP catalysts were prepared by loading V₂O₅ on Fe-P ATP. First, NH₄VO₃ was added into oxalic acid solution (5 wt %) under vigorous strring. In the next step, the mixture was heated at 60 ℃ and we could find the solution's colour changed from yellow into dark green and then turned dark blue. The solution was left for 12 h. Then the Fe-P ATP powders and phosphoric acid (as binder) were dispersed to the aged solution. After stirring well, the suspension was placed to water bath until the water was completely evaporated, dried at 80 ℃, calcined at 300 ℃ for 3 h.

Characterization of catalysts: The powder X-ray diffraction patterns were obtained on DX2700X diffractometer using CuK$_\alpha$ as radiation over the 2θ range of 10º-70º. The specific surface area, pore volume and pore diameter of catalysts determined by Beckman Coulter SA3100 specific surface area and pore size analyzer (Beckman Coulter). Prior to the analysis, the samples were outgassed *in vacuo* at 120 ℃ for 5 h. The surface areas were calculated through the Brunauer-Emmett-Teller (BET) equation. Using QUANTA200 scanning electron microscope (FEI Company) observed the layers' distribution of catalysts. The surface acidity of the samples were studied by adsorption of pyridine, followed by NEXUS-670 FT-IR spectroscopy (NICOLET). The measurements were performed in the range of 4000-400 cm⁻¹.

Activity tests: The selective catalytic reduction of NO with ammonia by the studied catalysts was carried out in a fixed-bed flow reactor system under atmospheric pressure. The catalysts were crushed into 20-40 mesh and then set in the reactor. The NO selective catalytic reduction activity of samples were performed at low-temperature. The experimental conditions were as follow: 0.2 g catalyst, 1000 ppm NO, 1000 ppm NH₃, 5 vol % O₂, N₂ as the balancing gas, the gas hourly space velocity (GHSV) was 38000 h⁻¹, the temperature changed from 100 to 240 ℃. The gases were adjusted by mass flow controllers and mixed, pre-heated before entering the reactor. The NO removal was calculated by the change of the concentration of NO at the entrance and exit. The efficiency of NO removal was evaluated as follows:

$$\eta_{No} = \frac{C_0 - C}{C_0} \times 100\%$$

where, η_{No} is the efficiency of NO removal, C_0 is the initial concentration of NO before reaction and C is the concentration of NO after reaction.

RESULTS AND DISCUSSION

XRD analysis: X-ray diffractograms recorded for the Na-ATP as well as Fe-P ATP, V₂O₅/Fe-P ATP are shown in Fig. 1. The textural properties of the catalysts are summarized in Table-1. The surface area (SBET) value of samples changed little, therefore, the interlayer spacing didn't increase obviously. This might be related to the structure of attapulgite, it was not a simple layered structure but a chain layered structure. So pillared attapulgite was different from pillared montmorillonite.
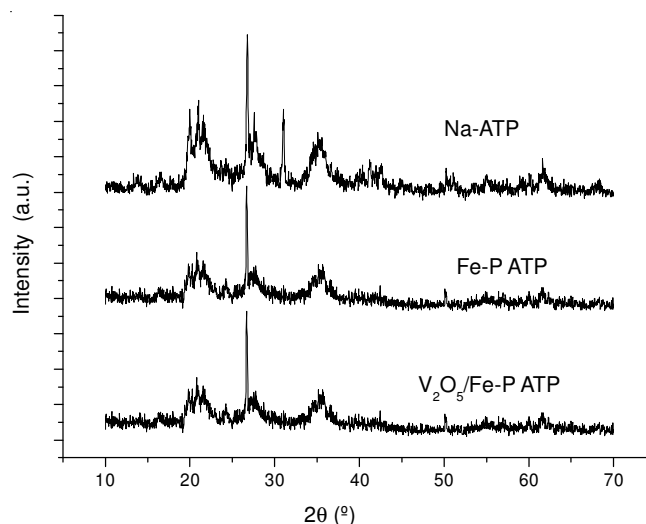

Fig. 1.   X-ray diffractograms of Na-ATP as well as Fe-P ATP and V₂O₅/ Fe-P ATP

TABLE-1 TEXTURAL PROPERTIES OF THE CATALYSTS			
Sample	Surface area (m²/g)	Pore volume (cm³/g)	Pore diameter (nm)
Na- ATP	170.00	0.217	4.39
Fe-P ATP	179.00	0.232	4.27
V₂O₅/ Fe-P ATP	151.67	0.172	4.65

The typical diffraction peaks of pillared attapulgite centered at 2θ about 21º, 22.5º, 32º, it's due to two-dimensional diffraction by the random stacking of clay layers. Comparing with the Na-ATP, the strength of the Fe-P ATP decreased, the diffraction peak was broader, it meaned the layers were more disordered than Na-ATP. The interlayer ions and molecules' charge, size, hydrolysis behaviour and the interaction with the silicate layer, were the main factors of the layer spacing changes. There were many reports studied the influence of Fe(III) to pillared clay's (montmorillonite) interlayer spacing. Borgnino *et al.*[16] had found that the radius of Fe³⁺ and the bond length of Fe-O in [Fe(OH₂)₆]³⁺ were smaller than that of the sodium form clays, thus explained the reasons for the reduction of the interlayer spacing in theory. Chen *et al.*[17] also found that the d001 was reduced with the amount of Fe(III) increasing, they thought that there existed a strong attraction between iron and silicate in clay layers. From Fig. 1, the sodium content of Fe-P ATP was lower than Na-ATP that provided more evidences for the intercalation. Chen *et al.*[18] believed that iron crystalline phase diffraction existed in the pillared clays. However Bineesh

et al.[15] found that Fe_2O_3 phase would be present only when the pillared clay was heated at 700 ºC. In Fig. 1, the X-ray diffractogram of V_2O_5/ Fe-P ATP was similar to Fe-P ATP and didn't exhibit the peaks of crystalline vanadium oxide. Bineesh et al.[19] reported that the vanadium phase couldn't be observed in the X-ray diffractogram when the amount of impregnated vanadium was lower than 14 wt %. Chae et al.[20] also found the vanadium phase could be observed when the amount of impregnated vanadium was more than 15 wt %.

FT-IR analysis: The IR spectra of Na-ATP and Fe-P ATP were showed in Fig. 2. The water molecule stretching vibration intensity of the 1638 cm^{-1} decreased and moved to the 1636-1629 cm^{-1} after pillaring. In pillaring process, the intensity of the -OH vibrational band was reduced as a result of the inter-calated aqueous cation being substituted. The decrease of adsorbed water in pillared clay was due to the non-expansion of pillared clay. Therefore, the intensity near 1638 cm^{-1} vibrational band was decreased after pillaring.
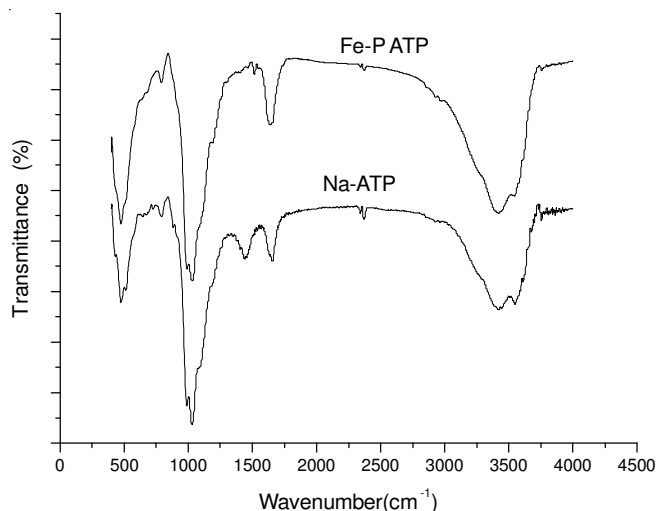

Fig. 2. FT-IR spectra of Na-ATP and Fe-P ATP

The surface acidity of modified ATP was determined by FT-IR. The adsorption of ammonia resulted in the emergence of a broadband at about 1400 cm^{-1}. The asymmetric bending of ammonium ions was a result of proton transfer from the surface hydroxyl groups to ammonia molecules[21-23]. Through pillaring, the intensity of the broadband at 1400 cm^{-1} and water bending vibration were increased after ammonia adsorption[23].

SEM analysis. The SEM images of Na-ATP and Fe-P ATP are shown in Figs. 3 and 4, respectively. It was clear that the ATP had fibrous structure[24]. We could find the surface changed a lot owing to pillaring. Fig. 3 showed that the structure of Na-ATP before pillaring was compact and there was no layered structure. After pillaring, loose structure, obvious layered structure could be seen in Fig. 4 and existed some cavities.

Catalytic activity. Fig. 5 shows the selective catalytic reduction results of NO by attapulgite and V_2O_5/Fe-P ATP at various temperature. ATP itself also had the performance of NO removal, whereas the NO removal efficiency was not high, less than 20 %. After iron oxide pillaring and V_2O_5 loading, the activity increased remarkably. The NO conversion into N_2 increased passing through a maximum and then decreased at

higher temperatures. Besides, it was observed that highest conversion of NO into N_2 was up to 92.80 % at around 220 ºC. With further increased in temperature, the conversion of NO into N_2 decreased. It could be the presence of oxygen in reactants, resulting in a side reaction of ammonia oxidation. Chmielarz et al.[7,25] found that at low temperatures, comparing with other metal oxides, iron oxide modified clays were more actived for NO removal.
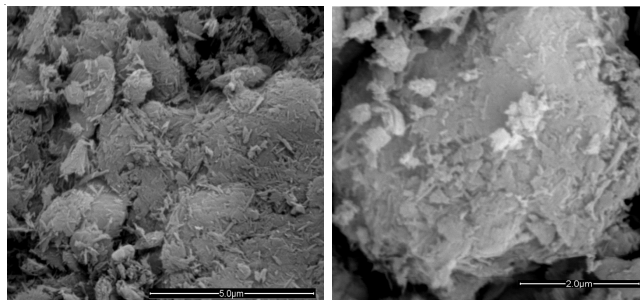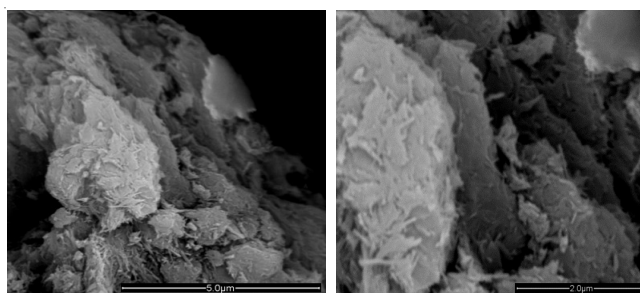

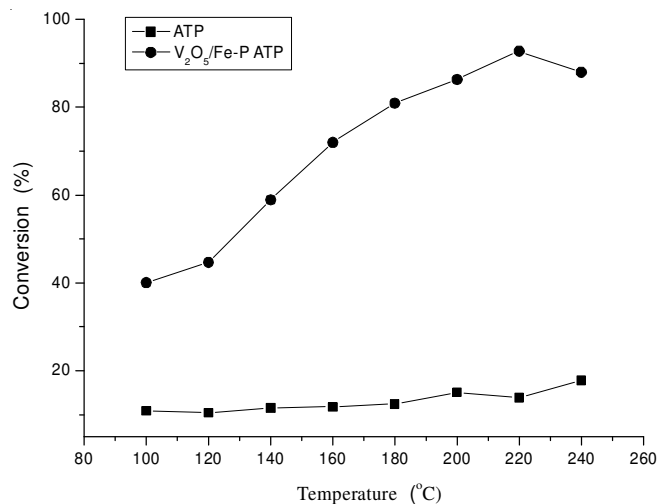Fig. 3. SEM images of Na-ATP

Fig. 4. SEM images of Fe-P ATP

Fig. 5. NO removal efficiency at different temperatures for ATP and V_2O_5/Fe-P ATP

Fig. 6 shows the catalytic activity of V_2O_5/Fe-P ATP catalysts prepared at different ratio of Fe/clay. The ratio of Fe/clay (n(Fe)/m (ATP)) was mainly from 5-15 mmol/g. It was observed that the V_2O_5/Fe-P ATP(n (Fe)/m (ATP) = 15 mmol/g) sample had the highest NO removal efficiency of 92.8 % at around 220 ºC. With the ratio of Fe/ATP increasing, the NO removal activity improved significantly. It might be the low ratio of Fe/clay led to a poor performance in cross-linking, Fe_2O_3 oxide columns between layers and active sites were aslo less.

Nevertheless it didn't mean the higher of ratio brought the higher of NO removal efficiency. Sheng *et al.*[26] found that when the pillared metal oxide exceeded a certain amount, NO removal efficiency decreased. It was due to the excessive oxide columns blocked the interlayer, which eventually led to form no holes or little holes pillared clay. Therefore, selecting the appropriate metal oxide pillared is crucial. As the main conclusion, it should be remarked that the conversion of NO into N_2 and the low-temperature activity over the studied catalysts increased with the increase of Fe/clay.
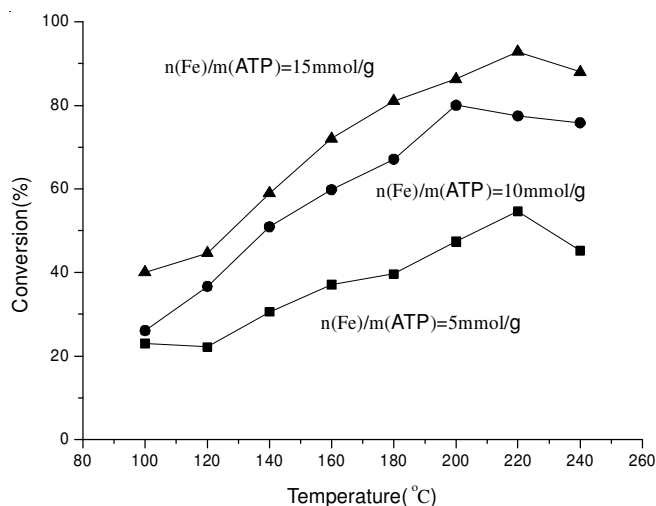

Fig. 6. Effect of Fe/ATP on NO removing efficiency

Conclusion

A series of V_2O_5/Fe-P ATP catalysts were synthesized, characterized and studied for selective catalytic reduction of NO. The modification of the Na-ATP with Fe_2O_3 resulted in an increase of surface area, which enhanced the dispersion of V_2O_5. The test results showed that V_2O_5/Fe-P ATP played an important role at low temperature for removal of NO. The increase of the ratio of n(Fe)/m (ATP) could cause the improvement of the conversion from NO into N_2 and the activity at low temperature. At 220 °C, the NO removal efficiency was up to 92.8 %.

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