

# Phase change of catalysts derived from a LDH-deoxycholate intercalated compound and its impacts on NO reduction from stationary source emissions

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## Abstract

Deoxycholate and keggins-type polyoxometalate (PW<sub>12</sub>O<sub>40</sub> and SiW<sub>12</sub>O<sub>40</sub>) pillared-hydroxalcite-type clay catalysts were prepared, and the effects of calcination temperature were studied on selective catalytic reduction of NO by NH<sub>3</sub> over excess oxygen in the reaction temperature range 150–450 °C. The results showed that over 99% N<sub>2</sub>/N<sub>2</sub>O selectivity was achieved at all testing temperatures for all pillared-clay catalysts. The activity of all pillared-clay catalysts increased significantly with temperature beyond 300 °C. It was found that all pillared clays had different thermal transition behaviors at various stages of calcinations temperature, which affected the SCR activity. The dehydroxylated intermediates and amorphous mixed oxide forms, whose Brønsted acid sites were still preserved after calcinations, appeared to yield high NO conversion with high N<sub>2</sub>/N<sub>2</sub>O selectivity. Generally, the PW<sub>12</sub>-clay-derived catalysts seem to have the highest activity. Five percent Fe loading by impregnation method significantly increased activity of pillared-clay catalysts while high N<sub>2</sub>/N<sub>2</sub>O selectivity was maintained. Fe-loaded catalysts also showed obviously higher N<sub>2</sub>/N<sub>2</sub>O selectivity than the commercial catalyst; 4.4% V<sub>2</sub>O<sub>5</sub>–8.2% WO<sub>3</sub>/TiO<sub>2</sub>.

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## 1. Introduction

In the commercial SCR unit for stationary sources, vanadia-based catalysts (V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst) mixed with WO<sub>3</sub> and/or MoO<sub>3</sub> as promoters are used as effective catalysts. However, their toxicity due to vanadium content and high selectivity toward toxic N<sub>2</sub>O are currently the disadvantages. Several catalysts were studied in order to overcome these disadvantages. One of the most outstanding works was accomplished by Yang's group [1–8] in which cationic clays such as bentonite intercalated with titania (TiO<sub>2</sub>-PILC) and doped with metal oxides with or without ion-exchanged elements were extensively studied as catalysts for this application. They successfully discovered that Fe-TiO<sub>2</sub>-PILC, a vanadium-free catalyst gave the best activity and selectivity among those tested and over the commercial catalysts [2,5]. Moreover, their comprehensive study showed

that pre-sulfation of the Fe-TiO<sub>2</sub>-PILC catalyst significantly enhanced NO conversion and suppressed NH<sub>3</sub> oxidation in accordance with the discovery that the activity was improved by the presence of SO<sub>2</sub> in the feed due to the increase in surface acidity [9].

Inspired by Yang's work, for this application, clays are an interesting alternative support or catalyst to us, especially hydroxalcite-type clays, which are anionic Mg-Al-based clays reported to have high capacity of SO<sub>x</sub> sorption [10,11], possibly due to basicity of the clay sheets. The SO<sub>x</sub> capturing ability was presumably expected to increase the acidic part of catalyst, and then enhance the activity. They also have attractive features such as high porosity, high thermal stability and exchangeable cations [7]. Hydroxalcite-type clay is a class of layered double hydroxide (LDH) anionic clays possessing various adjustable lateral anion spacings suitable for the negatively charged such as polyoxometalate (POM) pillars, which present a wider range of thermal stability than polynuclear transition metal halides, and hydroxyl metal cations [12–15]. Kwon et al. synthesized V<sub>10</sub>O<sub>28</sub><sup>6-</sup>-pillared hydroxalcite (*d* = 11.9 Å) by direct exchange of decavanate anion (V<sub>10</sub>O<sub>28</sub><sup>6-</sup>) with Cl<sup>-</sup> interlayer anion [16].

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Later, Drezdron [13] synthesized  $\text{Mo}_7\text{O}_{24}^{6-}$  ( $d = 12.17 \text{ \AA}$ ) and  $\text{V}_{10}\text{O}_{28}^{6-}$  ( $d = 11.8 \text{ \AA}$ )-hydrotalcite type clays starting from an organic-anion-pillared clay (terephthalate dianion-pillar) precursor, which was subsequently exchanged with appropriate POMs under mildly acidic conditions. For synthesizing POM-pillared hydrotalcite clays, Chibwe and Jones [17] was achieved by direct exposure of a calcined-hydrotalcite clay to a solution of the pillaring species, i.e.,  $\text{Mo}_7\text{O}_{24}^{6-}$  ( $d = 12.0 \text{ \AA}$ ) and  $\text{V}_{10}\text{O}_{28}^{6-}$  ( $d = 11.8 \text{ \AA}$ ).

Ogawa and Asai [18] synthesized a LDH-deoxycholate intercalated compound having the gallery height ( $d$ -spacing) of  $32.9 \text{ \AA}$ . Its height is sufficiently large for exchange with polyoxometalate anions such as a Keggin heteropolyanion typically represented by the formula  $\text{XM}_{12}\text{O}_{40}^{x-8}$ , which themselves have advantages as a catalyst in several reactions including SCR of NO [19]. Dimotakis and Pinnavaia [20] have accomplished the preparation of Keggin-type POM-pillared hydrotalcite, i.e.,  $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$  ( $d = 14.8 \text{ \AA}$ ) from terephthalate interlayer precursors. From Wang et al. [21], the POM ions with Keggin-type structure-,  $\text{PV}_3\text{W}_9\text{O}_{40}$ , pillared hydrotalcites ( $d \sim 13.0 \text{ \AA}$ ) were successfully prepared in an aqueous one-step reaction. Several starting materials and treatment conditions were also studied in the previous works. Therefore, the LDH-deoxycholate intercalated compound hereby called “DA-Clay” was employed in this study as a precursor and support to prepare keggin-type ( $\text{PW}_{12}\text{O}_{40}$  and  $\text{SiW}_{12}\text{O}_{40}$ ) pillared-hydrotalcite-type clay catalysts for SCR of NO by ammonia. However, it was reported that hydrotalcite clays have different thermal transition behaviors in the different calcination stages [22,23]. Due to a wide range of reaction temperatures, the catalysts derived from the DA clay thus can be altered upon reaction temperature. For a catalytic application, a catalyst must be stable during the course of reaction. The knowledge on its stability toward the reaction is therefore inevitably essential.

In this contribution, the DA-clay and its two derived Keggin-intercalated clays were synthesized and used as catalysts for SCR of NO by ammonia. The impact of phase change of catalysts was investigated on activity toward the SCR reaction. The structure models of the intercalated clays at different temperatures were also presented in this work. Moreover, the effect of Fe loading on the activity was also examined. Their activity and selectivity were compared with those obtained from the commercial catalysts.

## 2. Experimental

### 2.1. Synthesis of pillared-clay catalysts

Hdrotalcite-type clays intercalated with an organic compound and two Keggin-type polyoxometalates were prepared by hydrothermal [18] and anion exchanging method [20,21] consecutively. The prepared pillared clays were calcined for 12 h, then ground and sieved to 80–120 mesh (0.125–0.178 mm) before being used as catalysts for selective catalytic reduction of nitric oxide by ammonia.

#### 2.1.1. Deoxycholate-pillared hydrotalcite-type clay (DA-clay)

DA-clay was similarly synthesized by the method established by Ogawa and Asai [18]. 1.28 g of  $\text{Mg}(\text{OH})_2$ , 0.44 g of  $\text{Al}(\text{OH})_3$ , 10.76 g of deoxycholic acid and 0.1 g of NaOH were mixed in 100 ml of deionized water at room temperature with vigorous stirring (pH 8–10). Then, the suspension was transferred into an autoclave and heated at  $150 \text{ }^\circ\text{C}$  for 48 h. The solid precipitate was collected by filtration and washed with deionized water subsequently. The product was dried at  $110 \text{ }^\circ\text{C}$  overnight, and calcined for 12 h before being used as catalysts for SCR of NO by  $\text{NH}_3$  and also as the precursor to prepare  $\text{PW}_{12}\text{O}_{40}$ -pillared hydrotalcite-type clay ( $\text{PW}_{12}$ -clay) and  $\text{SiW}_{12}\text{O}_{40}$ -pillared hydrotalcite-type clay ( $\text{SiW}_{12}$ -clay), using the method established by Wang et al. [21].

#### 2.1.2. Polyoxotungstophosphate-pillared hydrotalcite-type clay ( $\text{PW}_{12}$ -clay)

A suspension of 1.0 g of dried DA-clay in 50 ml of deionized water was added to a solution containing 1.74 g of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and 0.1 g NaOH in 500 ml of deionized water (pH 8) at the temperature of  $70 \text{ }^\circ\text{C}$ . The reaction mixture was stirred for 12 h, and then the precipitate was recovered by filtration and washed with deionized water. The product was then dried at  $110 \text{ }^\circ\text{C}$  overnight, and calcined for 12 h before being used as catalysts for SCR of NO by  $\text{NH}_3$ .

#### 2.1.3. Polyoxotungstosilicate-pillared hydrotalcite-type clay ( $\text{SiW}_{12}$ -clay)

A suspension of 1.0 g of dried DA-clay in 50 ml of deionized water was added to a solution containing 1.31 g  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  and 0.15 g NaOH in 500 ml of deionized water (pH 8) at the temperature of  $70 \text{ }^\circ\text{C}$ . The reaction mixture was stirred for 12 h and then the precipitate was recovered by filtration and washed with deionized water. The catalyst was dried at  $110 \text{ }^\circ\text{C}$  overnight, and calcined for 12 h before being used as catalysts for SCR of NO by  $\text{NH}_3$ .

#### 2.1.4. Fe-loaded pillared-clay catalysts

To study the promoting effects of iron to pillared clays, iron was loaded on the pillared-clay catalysts by an impregnation method. Appropriate amount of ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) solution was impregnated into the calcined pillared clays to obtain 5%wt of Fe. After that, the solid were dried at  $110 \text{ }^\circ\text{C}$  for overnight, and calcined for 12 h before being used as catalysts for SCR of NO by  $\text{NH}_3$ .

### 2.2. Catalyst characterization

The changes in characteristics of pillared clay such as phase transition, morphology, and surface area upon temperature were studied by several techniques, i.e., TGA, XRD, SEM and BET. The prepared catalysts were characterized by a DuPont TGA 2950 Thermogravimetric analyzer. The specimen was heated up from  $30$  to  $700 \text{ }^\circ\text{C}$  with a rate of  $10 \text{ }^\circ\text{C}/\text{min}$ , followed by cooling down to  $30 \text{ }^\circ\text{C}$  with a rate of  $10 \text{ }^\circ\text{C}/\text{min}$ . XRD was

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