Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 137 (2008) 247–252

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Montmorillonites modified with polymer and promoted with copper as DeNO$_x$ catalysts

Monika Motak [*]

Faculty of Fuels and Energy, AGH-University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland

Abstract

Clays modified with polymer and promoted with copper cations were studied in selective catalytic reduction of NO with ammonia. The modification with polymer and promotion with copper did not influence the layered structure of pillared clays. Specific surface areas of the catalysts were between 22 and 98 m^2/g, lower or much lower than for pillared supports. The following elements of the preparation influenced positively NO conversion: acidic pretreatment (or the choice of acidic clay), modification with polymer and copper promotion. The most active catalyst was based on acidic clay modified with polymer and promoted with copper. Selectivity to N$_2$ did not deteriorate after polymer modification.

Keywords: Montmorillonite; Polymer modification; Copper; SCR

1. Introduction

Environmental pollution with nitrogen oxides forms constant challenge for researchers. The amount of NO$_x$ emitted in the last 10 years decreased but they still form a major danger to the environment. Currently the only method of NO$_x$ removal on industrial scale is selective catalytic reduction with ammonia carried out on vanadia catalyst supported on titanium oxide [1]. It is an active and selective catalyst with high resistance to nitrogen oxides and sulfur dioxide but not without certain shortcomings. First of all, it is expensive. Secondly, its optimum window is between 523 and 673 K while no good solution was found yet for lower and higher temperatures. Therefore, new catalysts are still searched, either using ammonia or hydrocarbons as reducing agents [2]. One of the types of the studied catalysts are modified layered clays [2–22]. It was shown in literature that some pillared clay catalysts showed activity higher than the commercial vanadia–titania systems [3,4,12–15]. Montmorillonites are especially interesting because of several modification possibilities. Both chemical i.e. activity, selectivity and acidic/basic, and textural properties may be changed through appropriate preparation procedure. Typical preparation steps used to tailor chemical and physical structure of layered clays are acidic/basic treatment, intercalation of hydroxycations called pillaring and promoting with transition metal oxides/hydroxides. It was pointed out lately [16–20,23] that there is a possibility of forming hybrid carbonaceous–clay systems, either through in situ polymerization of small organic molecules or sorption of polymer, followed by carbonization and activation. The application of such systems in SCR is rather seldom.

Chmielarz et al. [16–18] presented catalytic SCR (NH$_3$) tests for the following catalysts: acidic pretreated montmorillonite pillared with zirconium hydroxycations unpromoted or promoted with polymer, with the addition of manganese. Catalysts pretreated with acid were ca. twice more active than non-treated ones before pillaring. All used preparation steps—acidic treatment, pillaring and carbon deposition led to the increase in NO conversion.

On the other hand, Grzybek et al. [19] proposed as supports montmorillonites which were an industrial waste. The mentioned materials were used in industry as sorbents for cleaning edible oils of organic compounds. After prolonged application, they were deactivated by irreversible sorption of carbon species. After preparation procedure, consisting of carbonization and promotion of manganese and/or iron oxides/hydroxides, the obtained materials proved to be active and selective in SCR (NH$_3$) at low temperature region (below 473 K).

---

[*] Fax: +48 12 617 4547.
E-mail address: motakm@agh.edu.pl.

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.02.001

The subject of the work was to study the influence of different preparation parameters of montmorillonites (treated as supports for copper species) on $DeNO_x$ catalytic properties. The following preparative elements were compared in SCR: (i) polymer treated versus untreated; (ii) differently pillared (Zr or Al) or non-pillared; (iii) with or without acidic pretreatment, as well as acidic clays.

Copper species were chosen because this active material was found before to have a promising SCR behavior for zeolites [24–26] (e.g. Cu-ZSM5), active carbons [27] or clays [21,22,28]. Yang et al. [28] showed that TiO_2-pillared Cu promoted clay could by used for NO reduction with hydrocarbons. It was found, however, that C_2H_4 was interior to NH_3. In articles [21,22] Chmielarz et al. studied as SCR (NH_3) catalysts montmorillonites pillared with alumina, zirconia or titania doped with copper, cobalt or iron. The best catalysts were pillared with titania and promoted with copper cations (100% NO conversion at 523 K), while other studied samples either did not reach 100% conversion or reached it at much higher temperatures.

2. Experimental

2.1. Catalysts

The supports for the catalysts were prepared according to route 1 or route 2:

- route 1: starting clay (Mt or K5) → pillaring → MtAl, MtZr, K5Al;
- route 2: montmorillonite (Mt) → acidic pretreatment → MtH.

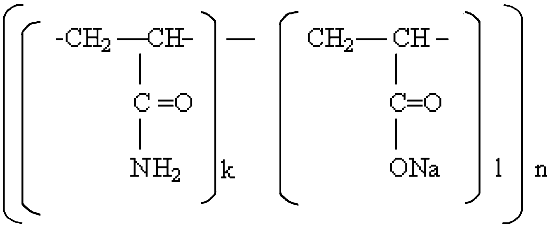
The starting clays were montmorillonite (designation Mt) sedimented from bentonite from Milowice, and commercially available acidic montmorillonite K5 (producer Sigma–Aldrich GmbH). The % composition of the starting motmorillonites Mt and K5 was (respectively): SiO_2(56.3; 65.0); Al_2O_3 (23.2; 19.0); Fe_2O_3 (3.0; 4.8); CaO (0.1; 0.2); MgO (0.8; 2.4); Na_2O (0.3; 1.6); K_2O (2.6; 1.5) [29,30]. The materials contain relatively high amounts of Fe_2O_3, which is known to be catalytically active at SCR. This may explain why all supports, as shown further in the text, exhibit ca. 3–35% conversions, depending on temperature.

Pillaring was carried out with: (i) Al-polycations (designation "Al") with chlorhydrol according to the procedure described by Vaughan [31] or (ii) zirconium polycations (designation "Zr") prepared from $ZrOCl_2$ as proposed by Yamanaka and Brindley [32].

Acidic pretreatment of Mt was carried out with 20% HCl solution at boiling temperature for 1 h. Activation time was chosen based on previous experiments [33].

The next step of preparation was (i) either impregnation with aqueous solution of copper nitrate(V) or (ii) a treatment with polymer, followed by impregnation with aqueous solution of $Cu(NO_3)_2$.

The polymer treatment was carried out similarly as described in detail in [33]: an aqueous suspension of the support and 3% aqueous solution of polymer were contacted for 48 h at room temperature under constant stirring. After sorption water was removed by evaporation and montmorillonite was carbonized at 773 K for 30 min. The polymer used was polyacryloamide (commercial name Gigtar, produced by Zakłady Azotowe, Tarnów, Poland):



$$\left[\left[\begin{array}{c}-CH_2-CH-\\ |\\ C=O\\ |\\ NH_2\end{array}\right]_k-\left[\begin{array}{c}CH_2-CH-\\ |\\ C=O\\ |\\ ONa\end{array}\right]_l\right]_n$$

Copper species – in each case 5 wt.% – were introduced by incipient wetness technique.

Before reaction all samples were calcined in situ.

3. Characterization

The characterization of the samples included: (i) elemental analysis C (content) using Elemental Analyser Vario-EL (Elementar-Analyser Systeme GmbH, Hanau); (ii) structure by X-ray diffraction XRD using Philips PV 3020 X' Pert and Cu Kα radiation (line = 0.15418 nm). Clay samples were prepared by settling a suspension of montmorillonite onto a glass slide, similarly as described in [23]. All clay mounts were dried. No calcinations was carried out; (iii) S_{BET} by nitrogen sorption at 77 K using a volumetric method (Micromeritics ASAP 2000). Prior to sorption the samples were outgassed at 453 K for several hours; and (iv) surface composition by X-ray photoelectron spectroscopy XPS using Hemispherical Energy Analyzer PHOIBOS 150 MCD (SPECS GmbH). The main Si 2p peak at 103.1 eV was used as an internal standard to calibrate binding energies. The areas of main peaks Cu $2p_{3/2}$, Al 2p, Si 2p and O 1s and sensitivity factors of Scofield were used to determine surface composition.

Catalytic properties in NO reduction with ammonia (NO conversion and N_2O formation) were studied under the following conditions: mass of catalyst 200 mg; reaction mixture: 800 ppm NO, 800 ppm NH_3, 3% O_2, He; flow: 100 ml/min. The experiment was carried out as follows: first catalysts were calcined on-line at 773 K in helium (100 ml/min) for 30 min. Then temperature was decreased under helium to 423 K and gas flow was switched to the reaction mixture. After 60 min on-line, temperature was raised by 50 K and next experimental point was measured, followed again by the same procedure. Experimental points were taken at 423, 473, 523, 573 and 623 K. NO and N_2O concentrations were measured at the outlet of the reactor by NDIR (Hartmann and Braun) every 10 min for each experimental temperature.

4. Results and discussion

From elemental analysis it may be observed that although the procedure of polymer modification is identical in all cases, the C content distinctly differs both for supports and copper-promoted catalysts and forms the following sequence: