

Selective catalytic oxidation of ammonia into nitrogen over PCH modified with copper and iron species

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Available online 9 March 2006

Abstract

Porous clay heterostructures (PCH) obtained on the basis of the synthetic saponite was used as a catalytic support for the deposition of transition metal (Cu, Fe) oxides. Transition metal oxides were introduced into the parent as well as ammonia treated PCH support by the ion-exchange method. The obtained catalysts were characterized with respect to their textural parameters (BET), composition (EPMA), chemical nature of the introduced transition metal species (UV–vis–DRS) and surface acidity (NH₃-TPD, FTIR). The modified PCH materials were tested as catalysts for the selective oxidation of ammonia to nitrogen and water. The studied catalysts have shown a very high selectivity towards N₂, which did not drop below 90% in a large studied temperature range (150–550 °C). However, the Cu-containing samples were active at temperatures significantly lower than PCH modified with iron.

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Keywords: Porous clay heterostructures; PCH; Selective catalytic oxidation; Ammonia; Copper; Iron

1. Introduction

The abatement of ammonia from industrial waste streams is becoming increasingly important due to environmental concerns. The selective catalytic oxidation (SCO) of ammonia into nitrogen and water seems to be the most promising method for the cleaning of large gas flows containing oxygen and low ammonia concentrations [1,2]. This method could be applied for the treatment of waste gases emitted in processes in which ammonia is used as a reactant or ammonia is produced as a by-product. On the other hand, ammonia is an effective reducing agent used in power plants for the NO_x abatement by the selective catalytic reduction ($4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$). The commercial catalysts used for this process are based on the V₂O₅–TiO₂ oxide system [3]. To control ammonia release, the majority of the DeNO_x processes are carried out with the ratio of NH₃/NO below 1 (~0.9), which results in a decrease in efficiency of the NO_x conversion. The effectiveness of the NO_x reduction can be improved by the use of stoichiometric or even excess amount of ammonia. Afterwards, the residual ammonia could be

selectively oxidized to N₂ and H₂O in a secondary catalyst bed [4]. Various types of materials have been studied as catalysts for the ammonia SCO process. Noble metals (e.g. Pt [5,6], Pd [5,7], Ir [8,9], Ru [7], Ag [8,9]) have been found to be very active catalysts for the ammonia oxidation which operate in the low temperature region. Unfortunately, ammonia is not only oxidized to nitrogen but also to nitrogen oxides. The next group of the studied catalysts for the ammonia SCO process is based on transition metal oxides (e.g. MnO₂, Co₃O₄, Fe₂O₃, CuO, MoO₃, V₂O₅ [10–17]). In general, these catalysts show higher selectivity to nitrogen but operate at temperatures significantly higher than noble metals. Zeolites modified with transition metals have been found to be promising catalysts for the selective oxidation of ammonia. Long and Yang showed a high activity of copper and iron deposited on the ZSM-5 [18] and Y [19] zeolites. A decrease in the Si/Al ratio improves the catalytic activity of zeolites. An additional increase in the activity of the Fe-modified zeolites can be obtained by deposition of noble metals (Pt, Pd, Rh) [20]. However, an introduction of these metals into the Fe-containing zeolites resulted in a decrease in the nitrogen selectivity.

Porous clay heterostructures (PCH) are a new group of porous materials which are characterized by combined micro- and mesoporous structure, a very large surface area, porosity and high thermal stability [21]. Due to these properties, PCHs

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are very attractive materials for potential catalytic applications. The synthesis of the PCH materials consists of some steps [22]. Firstly, cationic templates and neutral amine co-templates are intercalated in the interlayer space of host clay forming micelle structures. Secondly, the silica pillars are created by in situ polymerization of silica source (e.g. TEOS) around them. Finally, the organic templates are removed from the material by a classical calcination producing a high surface area and porous material. The negative charge of the clay layers is compensated by protons formed during decomposition of the organic templates. These protons can be exchanged for other cations. Such modification of PCHs offers the possibility for an introduction of catalytically active components by a classical ion-exchange method.

2. Experimental

2.1. Catalysts preparation

Synthetic saponite (Kunimine Industries Co., Japan) characterized by the chemical formula of $(\text{Na}_{0.49}\text{Mg}_{0.14})^{+0.77}[(\text{Si}_{7.20}\text{Al}_{0.80})(\text{Mg}_{5.97}\text{Al}_{0.03})(\text{OH})_4\text{O}_{20}]^{-0.77}$ was used as a starting material for the PCH preparation. Parent clay was added to a solution of the surfactant (hexadecyltrimethylammonium chloride) and stirred at 50 °C for 24 h. Subsequently, the clay was separated from the solution and washed with demi-water till a pH of 7 was reached. In the next step, the modified clay was added to a neutral amine (dodecylamine) and a silica source (tetraethylorthosilicate, TEOS). The mixture was allowed to react for 4 h under continuous stirring. Then the modified clay was separated from the solution, dried at room temperature and finally calcined at 550 °C for 6 h to produce the PCH sample.

After calcination, a part of the obtained PCH was treated with ammonia in order to transform protons compensating the negative charges of the clay layers into NH_4^+ cations. The modification of PCH was performed in a flow reactor. The sample was outgassed at temperature 450 °C in a flow of pure helium for 2 h. Then, the temperature of the reactor was decreased to 200 °C and a flow of helium was exchanged for a flow of a gas mixture containing 1 vol.% of NH_3 diluted in He. The reactor outlet was directly connected to a QMS detector, which continuously measured the consumption of ammonia. When ammonia appeared in the outlet gases, a flow of the NH_3 containing mixture was switch off and the sample was purged in a flow of pure helium at a temperature of 200 °C for 2 h. The PCH pre-treated with ammonia is denoted as PCH- NH_3 .

Transition metals (Cu and Fe) were introduced into the PCH support by the ion-exchange method using aqueous solutions (0.02 M) of $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ or $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The samples modified with copper and iron were dried in air at room temperature and then calcined in air at 450 °C for 3 h.

2.2. Catalysts characterization

Textural parameters of the samples were determined by N_2 sorption at -196 °C using a Quantachrome Autosorb-1-MP

automated gas adsorption system. Prior to the analysis, the samples were outgassed under vacuum at 200 °C for 16 h. The surface area was determined using the BET equation, while the micropore volumes of the samples were calculated using the t-method of DeBoer.

Transition metal loadings were determined by electron microprobe analysis performed on a JEOL JXA 733 superprobe (electron probe microanalysis, EPMA).

Diffuse reflectance Fourier transform infrared (DRIFT) spectra were recorded on a Nicolet 20SXB spectrometer for the samples (2 wt.%) diluted in KBr. Two hundred scans were taken with a resolution of 4 cm^{-1} .

The UV–vis–DRS spectra of the samples were recorded on a Nicolet Evolution 500 spectrophotometer. The measurements have been performed in the range of 200–900 nm with a resolution of 2 nm for the samples (2 wt.%) diluted in KBr.

Surface acidity of the samples was studied by temperature programmed desorption of ammonia (NH_3 -TPD). The measurements were performed in a flow microreactor system equipped with a QMS detector (VG Quartz). Prior to the ammonia sorption, a sample was outgassed in a flow of pure helium at 450 °C for 1 h. Subsequently, the microreactor was cooled down to 70 °C and the sample was saturated in a flow of a gas mixture containing 1 vol.% of NH_3 in helium for about 30 min. Then, the catalyst was purged in a helium flow until a constant baseline level was attained. Desorption was carried out with a linear heating rate (10 °C/min) in a flow of pure helium (20 ml/min) or in a flow of a gas mixture containing 5 vol.% of O_2 in He (20 ml/min). Calibration of QMS was carried out with commercial mixtures allowing recalculating the detector signal into the rate of NH_3 , N_2 , NO , N_2O and NO_2 evolution.

The chemical nature of the acid sites was studied by FTIR measurements of the samples preadsorbed with pyridine. Transmission FTIR spectra were recorded using wafers in the form of self-supporting pellets of the catalyst powder. The pellet was placed in an IR cell equipped with KBr windows properly designed to carry out spectroscopic measurements at different temperatures. The cell was connected to a vacuum line allowing all thermal treatments and adsorption–desorption experiments to be carried out in situ. Prior to pyridine adsorption, the sample was outgassed overnight at 200 °C under vacuum. Then the cell was cooled to room temperature and the catalyst was allowed to react with pyridine for 1 h. FTIR spectra were recorded on a Nicolet 20SXB spectrometer after treatment the sample at temperature 180 °C under vacuum for about 2 h. Two hundred scans were taken with a resolution of 4 cm^{-1} .

2.3. Catalytic tests

The catalytic performance of the PCH based samples in the selective oxidation of ammonia has been studied under atmospheric pressure in a fixed-bed flow reactor (i.d., 7 mm; *l*, 240 mm). The reactant concentrations were continuously measured using a quadrupole mass spectrometer (VG Quartz) connected to the reactor via a heated line. Prior to the reaction,

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