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Zeolite Y modified with palladium as effective catalyst for selective catalytic oxidation of ammonia to nitrogen

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ABSTRACT

Zeolites HY modified with palladium (0.05–2.5 wt.%) were found to be active and selective catalysts in the process of the selective oxidation of ammonia to nitrogen (NH_3-SCO). Parent zeolite and its modifications with palladium were investigated with regard to their structural, textural, and redox properties. The IR spectroscopy, X-ray diffraction, and BET methods were employed for these purposes. Correlation between loading and aggregation of Pd-species deposited on zeolites and their activity and selectivity in the NH_3-SCO process was found. Studies of adsorption forms of ammonia and product of its conversion done by IR spectroscopy as well as catalytic tests performed with various space velocities gave insight into the reaction mechanism. Zeolite Y modified with palladium is an interesting catalyst of selective ammonia oxidation for potential application in diesel car exhaust gas purification system.

1. Introduction

An efficient technology for NO_x (=NO + NO_2) abatement from power plant flue gases and mobile sources is its selective catalytic reduction (NH_3-SCR, $DeNO_x$) with ammonia ($4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$). Although the stoichiometry of the reaction involves a 1 to 1 consumption ratio of NH_3 to NO, majority of the $DeNO_x$ installations operate under the conditions of $NH_3/NO < 1$ (≈0.9–0.95) to control ammonia slip [1].

A strategy for improving the abatement of NO_x emission together with keeping the goal of low NH_3 slip could be a connection in series, downstream of the $DeNO_x$ converter, additional reactor for the NH_3-SCO process, in which ammonia unreacted in the $DeNO_x$ process will be converted into nitrogen and water vapor:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \tag{1}$$

An alternative could be adding of the additional catalytic bed into the $DeNO_x$ converter, downstream to NH_3-SCR catalyst, responsible for the selective ammonia oxidation to nitrogen. This technology seems to be very promising because it does not need supplying of any additional reactant for the NH_3-SCO process (oxygen, which plays a role of oxidizing agent, is a typical component of flue gases). The problem is only the development of suitable catalyst, which will be able to selectively convert ammonia to nitrogen at relatively low temperatures ($T < 400$ °C) in order to avoid additional heating of flue gases. Moreover, the catalyst should be stable under reaction conditions and resistant for poisoning by all components present in flue gases. Various types of materials have been studied as potential catalysts for the selective ammonia oxidation to N_2. Among them the most important are as follows: (a) noble metals [e.g. 2–4], (b) transition metal oxides [e.g. 5,6], and (c) ion-exchanged zeolites [e.g. 7,8]. An early review by Il'chenko [9] on NH_3 oxidation compared catalytic performance of various zeolite-based catalysts for the low-temperature process. It was shown that zeolite Y modified with different transition metals by ion-exchange method was active in the NH_3-SCO process. The following order of decreasing activity of transition metal modified zeolites was reported: CuY > CrY > AgY > CoY > FeY > NiY ≈ MnY. In all cases the selectivity to N_2 was relatively high (>95%) with an exception of AgY and CrY. Li and Armor [10] studied ZSM-5 doped with Pd, Rh, and Pt as catalysts for the NH_3-SCO process. Among them, relatively high activity and selectivity to N_2 in the low-temperature range (⩽300 °C) were found for the Pd-containing catalysts. Similar results, proving high activity of the Pd-ZSM-5 catalyst under different conditions, were also reported by Long and Yang [11]. For both Y and ZSM-5-based catalysts, it was shown that loading, aggregation, and location of noble metal species strongly influence their catalytic performance [e.g., 12,13]. In spite

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of numerous studies focused on this problem, it has not been fully explained in the case of the NH_3-SCO process, and therefore, further studies are necessary. Also studies of the mechanism of ammonia oxidation over zeolites modified with noble metals have not given full explanation; however, various possible mechanisms were proposed in the scientific literature. One of them, which is often called the imide mechanism, was proposed by Zawadzki [14]. In the first step, ammonia is oxidized with the formation of imide (NH); then, imide species react with molecular oxygen (O) to form the nitrosyl (HNO) intermediate, which in the next step reacts with imide resulting in the formation of N_2 and H_2O. N_2O is formed by reaction of two nitrosyl species, while reaction between NH and O_2 leads to the formation of NO. According to this mechanism, dissociation of O_2 and formation of active atomic oxygen species (O) is the key reaction step determining reaction rate.

Another mechanism of selective ammonia oxidation, called the hydrazine mechanism [15,16], involves, in the first step, oxidation of ammonia to amide (NH_2) species by atomic oxygen (O) and subsequently the formation of hydrazine-type intermediate (N_2H_4). In the next step, N_2H_4 is oxidized by O_2 to N_2 and N_2O. It should be noted that also in case of this mechanism, active oxygen species play an important role in ammonia conversion.

The i-SCR (internal selective catalytic reduction) [17–19] is another mechanism of ammonia oxidation. This mechanism consists of two main steps. In the first step, part of ammonia molecules is oxidized to NO:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \tag{2}$$

where N_2 and N_2O are formed in the subsequent reactions between NO and ammonia (reactions 3a and 3b, respectively), which was not consumed in the process (reaction 2):

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{3a}$$

$$4NO + 4NH_3 + 3O_2 \rightarrow 4N_2O + 6H_2O \tag{3b}$$

Thus, in this case, the effective catalyst should be active in two processes, ammonia oxidation to NO (reaction 2) and reduction of NO by NH_3 with the formation of N_2 (reaction 3a).

In this paper, a series of the Pd-catalysts was prepared by wetness impregnation of palladium species from $PdCl_2$ solution on zeolite Y. The resulting materials were examined by XRD, FTIR spectroscopy, and nitrogen adsorption techniques. The sorption of NH_3 allowed to follow in quantitative manner the changes in concentration of Brønsted and Lewis acid centers, resulted from Pd deposition on zeolite. Furthermore, the experiments of ammonia and carbon monoxide sorption led to quantitative interpretation of Pd-forms. The effects of both the Pd content and the active component distribution on the catalytic performances of the studied materials were discussed. Additionally, the preliminary studies of the reaction mechanism by analysis of adsorbed species formed on the catalyst surface under reaction conditions by FTIR spectroscopy and catalytic tests performed with various space velocities were done.

2. Experimental

2.1. Catalyst preparation

The synthesis of catalysts containing palladium was conducted based on previously developed methods [20–22], using aqueous solution of $PdCl_2$ (2.23×10^{-3} M). The pH of solutions was kept in the range of 3–4 by the addition of suitable amounts of HCl solution (0.1 M). The molar ratio of $PdCl_2$:HCl was 1:5.

The synthesis of catalysts was conducted as follows: to specified volume of $PdCl_2$ solution – an appropriate amount of steamed zeolite Y (Zeolyst, CBV500, NH_4-form, Si/Al = 2.6) was added, and the obtained suspension was stirred at room temperature using magnetic stirrer until the complete adsorption of Pd^{2+} ions. Completeness of adsorption was colorimetric monitored by the reaction with thiourea. Then, the solid was filtered and washed with distilled water until Cl^- ions were absent in a filtrate. Finally, the samples were dried at room temperature.

Solutions of precursor were prepared in situ. Time necessary to complete adsorption of Pd^{2+} ions was 24 h. Detailed conditions of the impregnation procedure of NH_4Y zeolite are given in Table 1.

2.2. Characterization methods

It should be mentioned that all characterization methods discussed below were applied to the non-reduced samples (without any treatment under air or hydrogen conditions). The only exception was the CO sorption experiment, in which the hydrogen treated samples were used.

2.2.1. Chemical analysis of metal content, low-temperature N_2 sorption, and X-ray diffraction studies

Pd content was determined by ICP AES analysis (Table 1) using a high-performance sequential plasma spectrometer (Model ARL 3410 ICP). Palladium was marked at wavelengths of 360.955 and 340.458 nm. In the first step, the solid samples were digested (in a mixture of HF, HCl and HNO_3) in a microwave oven for special temperature program. Then, aliquots of solution were diluted to a volume of 100 ml using deionized water. The Pd content in the resulting samples varied from 0.05 to 2.5 wt.%. The sample codes include information about the Pd loading.

The BET surface area and pore volume of the samples were determined by N_2 sorption at −196 °C using a 3Flex (Micromeritics) automated gas adsorption system. Prior to the analysis, the samples were degassed under vacuum at 250 °C for 24 h. The specific surface area (S_{BET}) was determined using Brunauer–Emmett–Teller (BET) model according to Rouquerol recommendations [23]. The micropore volume and specific surface area of micropores were calculated using the Harkins–Jura model (*t*-plot analysis).

The X-ray diffraction (XRD) patterns of the samples were recorded with a D2 Phaser diffractometer (Bruker) using Cu Kα radiation ($\lambda = 1.54060$ Å, 30 kV, 10 mA).

2.2.2. IR spectroscopy studies with probe molecules

Prior to FTIR studies, all the samples were pressed into the form of self-supporting wafers (ca. 5 mg/cm^2) and in situ thermally treated in an IR cell at 550 °C under vacuum for 1 h. For carbon monoxide (Linde Gas Poland, 3.7) sorption experiment, after pretreatment, the samples were cooled down to 200 °C and then contacted with hydrogen (80 Tr in gas phase). Reduction was performed at 200 °C for 2 h. After this time, the samples were evacuated at 500 °C for 1 h and cooled down to room temperature.

Table 1
Conditions of Pd ion-exchange for studied zeolites HY and results of chemical analysis.

Zeolite	Chemical analysis of Pd content (μmol g^{-1})	Volume of $PdCl_2$ solution (cm^3)	Support mass (g)	Time of exchange (h)
HY	–	–	–	–
0.05 wt.% Pd/HY	5	2.10	1.00	24
0.1 wt.% Pd/HY	10	4.20	1.00	24
0.25 wt.% Pd/HY	24	10.75	1.00	24
0.5 wt.% Pd/HY	47	21.10	1.00	24
1 wt.% Pd/HY	94	42.23	1.00	24
1.5 wt.% Pd/HY	141	63.10	1.00	24
2.5 wt.% Pd/HY	235	105.00	1.00	24