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Effect of Co content on the catalytic activity of CoSiBEA zeolites in N_2O decomposition and SCR of NO with ammonia

Paweł Boroń[a,b,c], Lucjan Chmielarz[a,*], Sandra Casale[b,c], Christophe Calers[b,c], Jean-Marc Krafft[b,c], Stanislaw Dzwigaj[b,c,**]

[a] Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland
[b] Sorbonne Universités, UPMC Univ Paris 06, UMR 7197, Laboratoire de Réactivité de Surface, F-75005 Paris, France
[c] CNRS, UMR 7197, Laboratoire de Réactivité de Surface, F-75005 Paris, France

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ABSTRACT

A series of Co_xSiBEA zeolite catalysts has been prepared by postsynthesis procedure with various Co content (from 1 to 9 wt% Co). The catalytic properties of these materials in SCR of NO with ammonia and N_2O decomposition were studied. XRD, FTIR, DR UV–vis, TPR and XPS results show that two-step postsynthesis method allows to control the introduction of cobalt into zeolite and to obtain catalyst with specific Co sites. Introduction of cobalt into SiBEA zeolite leads to an increase in unit cell parameters of the BEA matrix and consumption of silanol groups present in vacant T-atom sites of dealuminated BEA as shown by XRD and FTIR spectroscopy. Cobalt is stabilized in Co_xSiBEA in the form of two kinds of Co(II) species. They are characterized by an unusually high reduction temperature, which indicates that the cobalt is in strong interaction with the SiBEA support. It is shown by DR UV–vis and XPS that for low content (<2 wt% Co) cobalt is successfully incorporated into the framework of zeolite as pseudo-tetrahedral Co(II). For higher cobalt content, framework pseudo-tetrahedral and extra-framework octahedral Co(II) are detected by DR UV–vis and XPS. The catalytic activity of Co_xSiBEA zeolites depends on the amount and nature of Co species. The framework pseudo-tetrahedral Co(II) are responsible for catalytic activity of $Co_{1.0}SiBEA$ catalyst. The higher amount of Lewis acidic sites present in $Co_{4.0}SiBEA$ and $Co_{9.0}SiBEA$ than in $Co_{1.0}SiBEA$ seems to be responsible for the higher activity of former than latter in N_2O decomposition and SCR of NO with ammonia.

1. Introduction

Nitrogen oxides, NO, NO_2 and N_2O, generated by fuel combustion processes are a major source of air pollution. Due to a harmful impact of NO and N_2O on the environment, researchers have investigated several ways to reduce the emission of these compounds into atmosphere. Both the direct decomposition of N_2O into N_2 and O_2 and the selective catalytic reduction (SCR-NO) in the presence of hydrocarbons, NH_3 or urea have been extensively studied on transition metal ion (TMI)-exchanged zeolites [1–7]. In particular, Co-containing zeolites have been found to be active in these reactions [8–15]. As reported earlier, Co-containing zeolites can catalyze the selective reduction of NO [14,16,17]. Since then, several authors have investigated the nature of cobalt species in ion exchanged Co-zeolites [14,16,17]. However, despite numerous papers on Co-zeolites, the mechanisms of these catalytic systems are still unclear. One of the main obstacles to unravel the reaction mechanism is that several types of Co sites are present in Co-zeolites: isolated framework and extra-framework Co species, Co oligomers and Co oxides. Furthermore, framework and extra-framework Al species as well as cation impurities are also involved. Moreover, as it was reported the catalytic activity of Co-zeolite is not linearly proportional to Co content [14,16,17] indicating that the location and coordination of cobalt at different cationic sites might play an important role in the catalytic activity.

The presented studies include the synthesis of Co-containing BEA zeolites by two-step postsynthesis procedure. As shown earlier [18–20], this method allowed for low metal content (0.7 wt% Co) to incorporate cobalt as isolated framework pseudo-tetrahedral Co(II) without an appearance of Co oligomer or cobalt oxide. For

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[*] Corresponding author: at Faculty of Chemistry, Jagiellonian University, Krakow, Poland. Tel.: +48 12 6632006.
[**] Corresponding author at: Sorbonne Universités, UPMC Univ Paris 06, UMR 7197, Laboratoire de Réactivité de Surface, F-75005 Paris, France. Tel.: +33 1 44272113.
E-mail addresses: chmielar@chemia.uj.edu.pl (L. Chmielarz), stanislaw.dzwigaj@upmc.fr (S. Dzwigaj).

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higher metal content (3.6 wt% Co), framework pseudo-tetrahedral and extra-framework octahedral Co(II) was identified. At Co content above 3.6 wt%, some cobalt oxides are also formed.

The main objective of this work is to compare physicochemical and catalytic properties of these Co-containing zeolites using XRD, DR UV–vis, TPR, XPS, TEM, FTIR with CO and NH_3-TPD methods to draw the conclusions about the state and nature of Co species as well as acidity of Co_xSiBEA zeolite and their role in SCR of NO with ammonia and N_2O decomposition.

2. Experimental

2.1. Catalysts preparation

Co_xSiBEA zeolites (x = 1.0, 4.0, 9.0 wt% Co) were prepared by the two-steps postsynthesis method reported earlier [21]. In the first step, 2 g of AlBEA zeolite, obtained by calcination of tetraethylammonium BEA (TEABEA) zeolite (Si/Al = 12.5) at 823 K for 15 h, was treated with a 13 mol L^{-1} HNO_3 solution under stirring (4 h, 353 K) to remove aluminium. In the second step, the resulting solid SiBEA (Si/Al = 1000) obtained after filtration were stirred for 24 h at room temperature in aqueous solutions (pH 2.8) containing from 1.7×10^{-3} to 1.3×10^{-2} mol L^{-1} of $Co(NO_3)_2{\cdot}6H_2O$. The suspensions were further stirred in air at 353 K for 2 h until evaporation of water. The all obtained samples were calcined at 773 K for 2 h. The solids with 1.0, 4.0 and 9.0 wt% of Co were labelled as $Co_{1.0}$SiBEA, $Co_{4.0}$SiBEA and $Co_{9.0}$SiBEA, respectively.

2.2. Catalysts characterization

The structure of the studied zeolite samples was determined by powder X-ray diffraction. Diffraction patterns were obtained by a PW 3710 Philips X'pert (Philips X'pert APD) diffractometer using Ni-filtered Cu Kα radiation (λ = 1.54056 Å). The measurements were performed in the range of 2θ from 5° to 45° with a 0.02° step.

The structure of the obtained zeolite samples on microscopic level was studied by FTIR spectroscopy. FTIR spectra were recorded by DRIFT measurements performed with a Nicolet 6700 Thermo Scientific spectrometer. The sample was grounded with KBr (1 wt% of the sample in KBr). 200 scans were collected in the range of 600–4000 cm^{-1} with a resolution of 4 cm^{-1}.

The DR UV–vis spectra were recorded using an Evolution 600 (Thermo) spectrophotometer. The measurements were performed in the range of 200–800 nm with a resolution of 2 nm. DR UV–vis spectroscopy was applied to determine chemical nature of cobalt species in the zeolite structure.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a hemispherical analyzer (PHOIBOS 100, SPECS Gmbh) using Mg Kα (1253.6 eV) radiation. The power of the X-ray source was 300 W. The area of the sample analyzed was about 3 mm^2. The powder samples were pressed on an indium foil and mounted on a special holder. Binding energy (BE) was measured by reference to the O 1s peak at 532.5 eV, corresponding to the binding energy of oxygen bonded to silicon. Before analysis, samples were outgassed at room temperature to a pressure of 10^{-7} Pa. All spectra were fitted with a Voigt function (a 70/30 composition of Gaussian and Lorentzian functions) in order to determine the number of components under each XPS peak.

Temperature-programmed reduction (TPR) for all Co-containing BEA zeolites were carried out using the glass flow system. Hydrogen temperature-programmed reduction (TPR) was carried out in a flow of 5 vol% of H_2 in Ar (25 mL min^{-1}). The sample was placed in a quartz microreactor and the quantitative consumption of H_2 from 300 to 1120 K (7.5 K min^{-1}) was monitored by a Gow-Mac thermal conductivity detector (TCD). Injections of known amounts of hydrogen into the hydrogen-argon flow were provided for calibration (before and after each TPR run).

TEM studies for the catalysts after reduction step and after catalytic reaction were carried out using JEOL JEM-100CXII electron microscope operated at an acceleration voltage of 100 keV. The samples were prepared by dispersing in pure alcohol using ultrasonic cleaner and putting a drop of this suspension on carbon films on copper grids.

The acidity of all the obtained samples was studied by FTIR using CO as a probe molecule. Before CO adsorption experiment, the wafers of samples were activated by calcination at 723 K for 2 h in a flow of 2.5 vol% of O_2 diluted in Ar and then outgassed at 573 K (10^{-3} Pa) for 1 h. Following thermal treatment, the samples were cooled down to 100 K. CO was introduced in increasing amounts up to an equilibrium pressure of 133 Pa. Infrared spectra were recorded using a Bruker Vertex 70 spectrometer (resolution of 2 cm^{-1}, 128 scans). The spectra were obtained after subtraction of the spectrum recorded after calcination and prior to CO adsorption.

The acidity (concentration and strength of acidic sites) of the zeolite samples was also determined by temperature-programmed desorption of ammonia (NH_3-TPD). NH_3-TPD measurements were carried out in the temperature range of 343–923 K in a fix bed continuous flow microreactor. Reaction temperature was measured by a K-type thermocouple located in a quartz capillary immersed in the catalyst bed. Molecules desorbing from the zeolite samples were monitored on line by a quadrupole mass spectrometer (VG Quartz) connected directly to the reactor outlet via a heated line. Before NH_3-TPD experiments, the zeolite sample (100 mg) was outgassed in a flow of pure helium (20 mL min^{-1}) at 773 K for 1 h. Subsequently, the sample was cooled down to 373 K and saturated for about 30 min in a flow of 1 vol% of NH_3 diluted in He (20 mL min^{-1}). Then the catalyst was purged in a flow of pure helium until a constant baseline level was attained. Desorption was carried out with the linear heating rate (10 K min^{-1}) in a flow of pure helium (20 mL min^{-1}). Calibration of quadrupole mass spectrometer with commercial mixtures allowed to recalculate the detector signal into a desorption rate.

2.3. Catalytic tests

$Co_{1.0}$SiBEA, $Co_{4.0}$SiBEA and $Co_{9.0}$SiBEA were studied as catalysts for N_2O decomposition and SCR of NO with ammonia.

2.3.1. Catalytic decomposition of N_2O

Catalytic tests were performed in a plug flow microreactor system. The catalyst sample (100 mg) was loaded at the central position of the reactor onto a quartz wool plug. A flow of the reaction mixture was kept at 50 mL min^{-1} using mass flow controllers (Brooks 5850E), with a weight hourly space velocity (WHSV) of about 30,000 mL h^{-1} g^{-1}. The reaction products were monitored by a SRI 8610 C gas chromatograph (equipped with two packed columns—Hayesep-D and Molsieve-5A as well as TCD detector). Prior to the catalytic run the sample was outgassed at 723 K in a flow of pure helium. The dosing reaction mixture containing: $[N_2O]$ = 0.5 vol%, $[O_2]$ = 4.5 vol% and [He] = 95 vol% was started immediately after outgassing process. Reaction temperature was increased from 423 to 873 K in steps of 50 K. The first gas chromatography (GC) analysis at each selected temperature was performed after 15 min since the reactor temperature was stabilized.

2.3.2. SCR of NO with ammonia

Catalytic experiments were performed in a fixed-bed flow microreactor system. The reactant concentrations were continuously measured using a quadrupole mass spectrometer (VG Quartz) connected directly to the reactor outlet. Prior to the reaction,