

Effect of Co content on the catalytic activity of CoSiBEA zeolites in the N₂O decomposition

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Introduction

Control of N₂O emissions has become one of the major challenges in environmental protection. N₂O is a potential contributor to the greenhouse gases with its global warming potential as high as 310 [1]. Direct catalytic decomposition of N₂O is a relatively simple method to convert nitrous oxide into harmless products of N₂ and O₂.

Transition-metal ion-exchanged zeolites (TMI-Z), especially Fe-, Co- and Cu-exchanged zeolites, exhibit unique and fascinating properties, were widely used for the catalytic decomposition of N₂O [2,3,4]. The nature of the TMI species was intensively studied [2,3,4], wherein the isolated cations or oxocations of transition-metal ions (TMI) with low nuclearity were thought to be the most catalytically active species [2,3,4]. The number of studies related to N₂O decomposition in the presence of Co-containing BEA zeolites was up till now very limited [5], so a detailed investigations of this reaction on this kind of zeolite material seem to be interesting.

In this work, CoSiBEA zeolites have been prepared by two step postsynthesis method and their catalytic properties investigated in decomposition of N₂O.

Materials and Methods

A series of the CoSiBEA zeolite catalysts has been prepared by postsynthesis method, resulting in incorporation of various Co content (1 - 9 wt %) in zeolite structure.

The structure of CoSiBEA zeolite was determined by XRD and FTIR. Diffuse reflectance UV-vis and XPS spectroscopies were applied to determine the chemical nature of the Co species in the zeolite structure. The state of cobalt in catalysts after calcination, reduction and catalytic test was characterized by TPR and XPS. The presence of Brønsted and Lewis acidic centers were evidenced by FTIR in CoSiBEA zeolites preadsorbed with CO. Acidity (concentration and strength of acidic sites) of obtained materials was investigated by temperature programmed desorption of ammonia (NH₃-TPD). The measurements were carried out in a flow microreactor system equipped with QMS detector. Catalytic tests were performed in a plug flow microreactor system for the catalyst sample of 100 mg. A flow of the reaction mixture was kept at 50 mL min⁻¹, with a weight hourly space velocity (WHSV) of about 30000 mL h⁻¹ g⁻¹. The reaction products were monitored by a SRI 8610C gas chromatograph. The dosing reaction mixture containing: [N₂O] = 0.5 vol. %, [O₂] = 4.5 vol. % and [He] = 95 vol. % was started immediately after outgassing process.

Results and Discussion

XRD, DR UV-vis, TPR and XPS results show that the two step postsynthesis method allows to control the introduction of cobalt into zeolite and to obtain catalysts with

specific Co sites. Introduction of cobalt into SiBEA zeolite leads to an increase of unit cell parameters of the BEA matrix and consumption of silanol groups in vacant T-sites of dealuminated BEA. Cobalt is stabilized in the form of two kinds of Co(II) sites. They are characterized by an unusually high reduction temperature (1130 K), which indicates that the cobalt species are in strong interaction with the SiBEA support. It is shown by DR UV-vis and XPS that for low Co content (< 2 Co wt %) cobalt can be successfully incorporated into the framework positions of zeolite as tetrahedral Co(II) species. For higher cobalt content, some amounts of extra-framework octahedral Co species are detected by DR UV-vis and XPS. Figure 1 shows the results of DeN₂O process over the studied catalysts. The catalytic activity of Co_xSiBEA zeolites (with x = 1.0, 4.0, and 9.0 Co wt %) strongly depends on the amount and nature of the Co species. The framework Co(II) sites have influenced the catalytic properties of the catalysts. The higher strength and concentration of acidic centres in Co_{4.0}SiBEA and Co_{9.0}SiBEA comparing to Co_{1.0}SiBEA seems to be responsible for their higher activity in the N₂O decomposition.

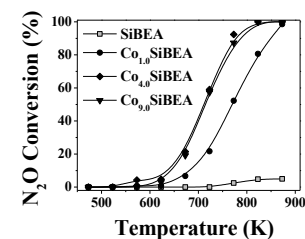


Figure 1. N₂O conversion in N₂O decomposition on SiBEA, Co_{1.0}SiBEA, Co_{4.0}SiBEA and Co_{9.0}SiBEA.

Significance

CoSiBEA zeolites have been found to be active catalysts for the N₂O decomposition process. Their catalytic activity strongly depends on the Co speciation and amount of cobalt introduced into zeolite structure as well as their acidity.

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