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Short communication

Ag–Ni bimetallic SiBEA zeolite as an efficient catalyst of hydrodechlorination of 1,2-dichloroethane towards ethylene

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ABSTRACT

Dealuminated form of BEA zeolite with Si/Al ratio of 1500 was used for the synthesis of $Ag_{2.0}SiBEA$, $Ni_{2.0}SiBEA$ and $Ag_{2.0}Ni_{2.0}SiBEA$ by two-step postsynthesis method. The calcination of zeolite samples led to the formation of well dispersed isolated mononuclear Ag(I) and $Ag_n^{\delta+}$ clusters and a pseudo-tetrahedral Ni(II), incorporated in BEA framework as evidenced by DR UV–vis investigations. The treatment of samples in flowing 10% H_2/Ar stream gave small (average 3.1 nm) and well dispersed metal nanoparticles. Reduced catalysts were investigated in 1,2-dichloroethane hydrodechlorination at atmospheric pressure, at low reaction temperature (523 K) with ~100% of selectivity to ethylene, desired product of the reaction.

1. Introduction

The stability, activity and high selectivity towards desired product are the key factors for the design and preparation of catalysts for hydrodechlorination (HDC) and the essential issue for the industrial application of this technology [1,2]. Therefore, the finding of effective methods of synthesis of HDC catalysts is still under investigation. Hydrodechlorination is known as structural sensitive reaction, but among the researchers' opinions are divided on the effect of metal(s) dispersion and metal particle size on this process. Some of the scientists claim that higher metal particle size and smaller dispersion play the crucial role in activity and stability of HDC catalysts [3,4]. On the other hand, some of the literature data clearly show the beneficial role of excellent dispersed very small metal particles in hydrodechlorination process [5]. Our recent studies on nickel containing beta zeolite in conversion of 1,2-dichloroethane brightly demonstrated the high stability, and high selectivity of very small (~1,5 nm) nickel particles size [5]. In spite of earlier reports [6,7] the small metal particles did not deactivate during reaction and they are resistant to sintering [5]. As we have earlier shown [8] the application of dealuminated SiBEA zeolite with vacant T-atom sites played an important role on the formation stable, active and selective catalysts. Very interesting results were obtained also for bimetallic Cu–Ni systems prepared by two-step postsynthesis method [9] that consist, in the first step, dealumination of BEA zeolite by treatment with nitric acid and then, in the second step, incorporation of metal into the framework of BEA zeolite by their reaction with silanol groups of vacant T-atom sites of resulted SiBEA zeolite. The reduction of well dispersed metal species with H_2 led to the formation of small metal nanoparticles in extra-framework position. Careful investigations have shown very good activity of bimetallic Cu–Ni zeolite catalysts containing small and well dispersed Ni(0) and Cu(0) nanoparticles in hydrodechlorination of 1,2-dichloroethane and high selectivity to ethylene [9]. Inspired by our earlier work [9,10] we would like to investigate the effect of two-step postsynthesis method of preparation on catalytic properties of silver and nickel loaded BEA zeolite in the hydrodechlorination of 1,2-dichloroethane. Until now only the addition of silver to Pd in HDC of 1,2-dichloroethane was successfully investigated [11,12]. The addition of silver to palladium containing catalysts has reduced strong hydrogenating properties of palladium and led to the increasing of the selectivity to

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ethylene (desired product 1,2-DCA HDC). Therefore, we have expected to observe the same phenomenon in the case of Ag–Ni system.

2. Experimental

2.1. Catalyst preparation

A tetraethylammonium BEA (TEABEA) (Si/Al = 17) zeolite provided by RIPP (China) was calcined for 15 h at 823 K to remove template. Organic-free BEA zeolite was separated into two portions. The first, portion of 2 g of TEABEA was treated with 200 ml of 13 mol L^{-1} nitric acid solution (353 K, 4 h) to obtain dealuminated SiBEA zeolite and then washed several times with distilled water and dried at 363 K overnight. Results of chemical analysis indicate that only traces of Al remain in SiBEA after nitric acid treatment with Si/Al ratio of 1500.

Ag_xSiBEA (x = 2 Ag wt.%), Ni_xSiBEA (x = 2 Ni wt.%) or Ag_xNi_ySiBEA (x = 2 Ag wt.% and y = 2 Ni wt.%) were prepared by co-impregnation of 2 g of SiBEA with $Ag(NO_3)_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ and $Ag(NO_3)_2 \cdot 6H_2O$ solutions, respectively, with appropriate concentration of Ag and Ni. Firstly, all suspensions were stirred for 24 h at 298 K in excess solvent using 200 mL of the precursor solutions. Then, the suspensions were stirred in rot-evaporator under vacuum of a water pump for 2 h in air at 333 K until complete evaporation of water. The catalysts obtained in this ways are labeled $Ag_{2.0}SiBEA$, $Ni_{2.0}SiBEA$ and $Ag_{2.0}Ni_{2.0}SiBEA$. All these materials were calcined in static air at 773 K for 3 h and labeled C-$Ag_{2.0}SiBEA$, C-$Ni_{2.0}SiBEA$ and C-$Ag_{2.0}Ni_{2.0}SiBEA$, respectively. Then, a portion of these materials were reduced at 873 K for 3 h in flowing 10% H_2/Ar to obtain red-C-$Ag_{2.0}SiBEA$, red-C-$Ni_{2.0}SiBEA$ and red-C-$Ag_{2.0}Ni_{2.0}SiBEA$, where C — stands for calcined and red — for reduced. These catalysts after kinetic run were labeled with additional prefix spent-, as spent-red-C-$Ag_{2.0}SiBEA$, spent-red-C-$Ni_{2.0}SiBEA$ and spent-red-C-$Ag_{2.0}Ni_{2.0}SiBEA$.

2.2. Catalyst characterization

Chemical analysis was performed at room temperature on SPECTRO X-Lab Pro apparatus.

DR UV–vis spectra were recorded at ambient atmosphere on a Cary 5000 Varian spectrometer equipped with a double integrator with polytetrafluoroethylene as reference.

Temperature-programmed reduction (TPR) for both of the catalysts, after calcination step, was carried out using the glass-flow system. TPR runs were performed in flowing 10% H_2/Ar (25 cm^3 min^{-1}), ramping the temperature at 10 K min^{-1} and using 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).

Chemisorption measurements of H_2 and CO using a conventional static method were carried out with a Micromeritics ASAP 2020 Chem instrument. Prior to chemisorption measurement 0.1 g of C-$Ag_{2.0}Ni_{2.0}SiBEA$ was reduced in flowing 10%H_2/Ar (25 cm^3 min^{-1}), ramping the temperature from room to 873 K (at 10 K min^{-1}) and kept at 873 K for 3 h. Then the catalysts were cooled down to the room temperature and connected with ASAP 2020 instrument. Next, the samples were heated in flowing He at 383 K for 30 min with an additional evacuation for 10 min. At this temperature, the helium flow was switched for the hydrogen flow and the temperature increased (10 K min^{-1}) to 653 K and the samples were reduced for 120 min, subsequently outgassed for 30 min, and finally cooled to 343 K with 30 min evacuation. The hydrogen adsorption isotherm was established. After evacuation at 343 K, a second H_2 isotherm was performed. The gas uptake was obtained by extrapolating to zero pressure the linear portion of the isotherm above the saturation pressure. The first hydrogen isotherm provided the sum of the reversibly and irreversibly adsorbed hydrogen while the second isotherm represented only the reversibly adsorbed hydrogen. The amount of chemisorbed hydrogen was given by the difference. After the second isotherm, the same sample was heated in H_2 at 653 K and outgassed at this temperature for 30 min. Then, the H_2 flow was switched for He and the sample was cooled down to the temperature 298 K with additional 10 min evacuation. CO adsorption isotherm was measured at room temperature and was established similarly like in the case of hydrogen adsorption procedure. The metal dispersion (D, in %), and metal particle size (d, in nm) were determined from both the H_2 and CO chemisorption data, assuming that H/Ni_s ratio equals 1 [13,14] and CO/Ni equals 0.5 at room temperature [15,16].

TEM studies for the catalysts after reduction step were carried out using a JEOL JEM-100CXII electron microscope operated at an acceleration voltage of 100 keV. The samples were prepared by dispersing them in pure alcohol using an ultrasonic cleaner and putting a drop of this suspension on carbon films on copper grids. Independent STEM and HRTEM experiments were carried out on the electron microscope Titan G2 60–300 kV FEI Company, equipped with: field emission gun (FEG), monochromator, three condenser lenses system, the objective lens system, image correction (Cs-corrector), HAADF detector and EDS spectrometer (Energy Dispersive X-ray Spectroscopy) EDAX Company with detector Si(Li). Microscopic studies of the catalysts were carried out at an accelerating voltage of the electron beam equal to 300 kV. The mapping was carried out in the STEM mode by collecting point by point of EDS spectrum of each of the corresponding pixels in the map. The collected maps were presented in the form of a matrix of pixels with the color mapped significant element and the intensity corresponding to the percentage of the element.

X-ray diffractograms (XRD) for red-C-$Ag_{2.0}SiBEA$, red-C-$Ag_{2.0}Ni_{2.0}$ SiBEA, spent-red-C-Ag_xSiBEA, and spent-red-C-Ag_xNi_ySiBEA were recorded on a Rigaku-Denki (Japan) diffractometer with nickel filtered and CuKα radiation. Data acquisitions for sample after reduction step and after kinetic run were recorded in the 2θ range of 5–90° with step of 0.02°.

2.3. Catalyst activity measurements

The reactions of hydrodechlorination of 1,2-dichloroethane (1,2-DCE, HPLC grade, 99.8% pure from Sigma-Aldrich, Germany) were carried out at atmospheric pressure, in a glass flow reactor equipped with fritted disk to place a catalyst charge. Prior to reaction, 0.2 g of the catalyst, after calcination step at 773 K, was reduced in flowing 10% H_2/Ar (25 cm^3 min^{-1}), ramping the temperature from room temperature to 873 K (10 K min^{-1}) and kept at 873 K for 3 h. After this time, the catalysts were cooled to 523 K, then contacted with the flowing reaction mixture (H_2 + Ar + 1,2-DCA) of 2.86×10^{-5} mol s^{-1} (42 cm^3 min^{-1}). The contact time was of 0.7 s and the space velocity (SV) of 0.0035 (m^3 kg^{-1} s^{-1}). 1,2-DCE was provided from a saturator kept at 273 K to give the partial pressure of 1,2-dichloroethane of 2.9 kPa. The partial pressure ratio pH_2/p1,2-DCE was 1:1. The flows of H_2 and Ar, were fixed by using Bronkhorst Hi-Tec mass flow controllers. The reaction was followed by gas chromatography, using a HP5890 series II gas chromatograph with FID, a 5% Fluorcol/Carbopack B column (10 ft) from Supelco. The results of GC analysis were elaborated using HP Chemstation. The total FID signal from the first two analyses was similar to that observed in subsequent GC analyses.

3. Results and discussion

3.1. Diffuse reflectance UV–vis investigation

In the DR UV–vis spectrum of C-$Ni_{2.0}SiBEA$ (Fig. 1) the bands at 460 and 555 nm are related to Ni(II) in tetrahedral or strongly distorted tetrahedral coordination and correspond to oxygen-tetrahedral Ni(II) charge transfer transitions [17,18]. DR-UV–vis spectrum of C-$Ag_{2.0}SiBEA$ (Fig. 1) contains characteristic band at 214 nm, strongly related to the charge transfer transition between $4d^{10}$ and $4d^95s^1$ level of highly dispersed mononuclear Ag(I), in line with earlier reports for Ag-MFI, Ag^+/ZSM-5 and AgBEA zeolites, or Ag/Al_2O_3 [18–22]. Additionally, the