



Short Communication

Catalytic conversion of trichloroethylene on nickel containing beta zeolites into value added products

A. Śrębowata^{a,*}, R. Baran^{b,c,d}, D. Lisovytskiy^a, I.I. Kamińska^a, S. Dzwigaj^{b,c,*}^a Institute of Physical Chemistry, PAS, Kasprzaka 44/52, PL-01224 Warszawa, 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^d AGH University of Science and Technology al. A. Mickiewicza 30, 30-059 Krakow, Poland

ARTICLE INFO

Article history:

Received 19 February 2014

Received in revised form 21 July 2014

Accepted 8 August 2014

Available online 23 August 2014

Keywords:

Nickel

Beta zeolites

Trichloroethylene

Hydrodechlorination

ABSTRACT

Nickel containing BEA zeolites, NiSiBEA and NiHAiBEA, with 2 wt% of Ni were prepared by a two-step postsynthesis method and conventional wet impregnation. The calcination of NiSiBEA and NiHAiBEA at 773 K for 3 h in air led to the formation of C-NiSiBEA and C-NiHAiBEA. After reduction at 873 K for 3 h in flowing 10% H₂/Ar, red-C-NiSiBEA and red-C-NiHAiBEA were obtained and investigated as the catalysts in hydrodechlorination of trichloroethylene at 503 K. Comparative study performed on red-C-NiSiBEA and red-C-NiHAiBEA showed very high stability of the catalyst prepared by a two-step postsynthesis method and strong deactivation of the catalyst prepared by conventional wet impregnation during ~17 h of reaction. Application of both catalysts resulted in high selectivity to unsaturated hydrocarbons that are the most desired products in HDC processes. TPH of the catalysts after kinetic run have shown that the main cause of deactivation of NiHAiBEA is the formation of carbonaceous species during hydrodechlorination of trichloroethylene.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Trichloroethylene (TCE) is one of the most popular chloroorganic compound widely used in the chemical industry. However, because of its carcinogenicity, TCE is a hazardous pollutant for the natural environment and human health and must be removed from waste gases and wastewater. Application of catalytic hydrodechlorination (HDC) as a method of conversion of chloroorganic compounds gives the chance for the transformation of trichloroethylene into value added products like unsaturated hydrocarbons (ethene and propene) or 1,1-dichloroethene [1,2]. They are widely used in chemical industry in polymerization, oxidation, halogenation, alkylation, fabrication of semiconductor device etc. [3–7]. Both ethene and propene are the most important starting products in petrochemical industry, but they exist in nature too. Ethene is an important plant hormone and propene is naturally produced by vegetation of plants. Therefore, they are used in the artificial process of fruit ripening [8,9].

Catalytic conversion of TCE can be effectively carried out on noble metals such as Pd and Pt and on bimetallic systems containing PdCu or PdNi [1,2,10,11]. Depending on the catalyst, ethane, ethene, propene,

chloroethene were observed as the main products. Till now, gas-phase catalytic hydrodechlorination of trichloroethylene on nickel containing catalysts has not been extensively investigated yet [12].

The aim of our study was to investigate the effect of preparation way on catalytic behavior of nickel containing beta zeolites in conversion of trichloroethylene. To the best of our knowledge this is the first report on the hydrodechlorination of TCE over nickel – BEA zeolites, prepared by conventional wet impregnation (NiHAiBEA) and two-step postsynthesis method (NiSiBEA).

2. Experimental section

2.1. Materials

Nickel containing zeolites (with 2 Ni wt%) were prepared by two-step postsynthesis method (NiSiBEA) and conventional wet impregnation (NiHAiBEA) using SiBEA and HAiBEA as a supports and aqueous solution of Ni(NO₃)₂·6H₂O as a nickel precursor. All the preparation details are described in our earlier work [13]. Both NiSiBEA and NiHAiBEA were calcined in air (100 K h⁻¹) at 773 K for 3 h under static condition and labeled as C-NiSiBEA and C-NiHAiBEA respectively. Then, a portion of C-NiSiBEA and C-NiHAiBEA were reduced at 873 K for 3 h in flowing 10% H₂/Ar to obtain red-C-NiSiBEA and red-C-NiHAiBEA, respectively, where C – stands for calcined and red – for reduced. These catalysts after kinetic run were labeled as spent-red-C-NiSiBEA and spent-red-C-NiHAiBEA, respectively.

* Corresponding author.

** Correspondence to: A. Śrębowata, Institute of Physical Chemistry, PAS, Kasprzaka 44/52, PL-01224 Warszawa, Poland. Tel.: +48 1 22 343 3215.

E-mail addresses: asrębowata@ichf.edu.pl (A. Śrębowata), stanislaw.dzwigaj@upmc.fr (S. Dzwigaj).

2.2. Techniques

Nickel containing beta zeolites were investigated by chemical analysis, powder X-ray diffractograms (XRD), diffuse reflectance UV–vis (DR UV–vis), X-ray Photoelectron Spectroscopy (XPS), temperature-programmed reduction (TPR), oxygen and CO chemisorption.

Hydrodechlorination of TCE (analytical reagent from POCh, Gliwice, Poland, purity >99.5%) lasted in glass - flow system equipped with fritted disk to place a catalyst charge, described with details earlier [13]. Portion of red-C-NiSiBEA or red-C-NiHAlBEA were cooled to 503 K, and then contacted with the reaction mixture. The mass of the catalysts was 100 mg. A typical run was carried out ~17 h. Hydrogen and argon were purified by MnO/SiO₂, and the C₂HCl₃/H₂ ratio was 1:3 (with the total flow of 42 cm³ min⁻¹). All reactions were followed by gas chromatography (HP 5890 Series II with FID, a 5% Fluorcol/Carbopack B column (10 ft) from Supelco). The results of GC analysis were elaborated using HP ChemStation.

HRTEM investigations were carried out using FEI TITAN Cubed electron microscope operated at an acceleration voltage of 300 keV and equipped with an energy dispersive X-ray (EDX) EDAX spectrometer. 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 and purified with plasma cleaner.

After kinetic runs, nickel catalysts were investigated by a temperature-programmed hydrogenation (TPH) to detect species that can be

removed by hydrogen from spent catalysts. Progress of TPH runs, using a 20% H₂/He flow (25 cm³ min⁻¹) at a 10 K min⁻¹ ramp, was followed by mass spectrometry (MA200, Dycor-Ametek, Pittsburgh).

3. Results and discussion

As we reported earlier [13], the two-step postsynthesis method led to formation of the NiSiBEA zeolites with the nickel mainly incorporated into framework position as isolated pseudo-tetrahedral Ni(II) species and the conventional wet impregnation led to the formation of NiHAlBEA with the nickel incorporated into framework and extra-framework positions as pseudo-tetrahedral and octahedral Ni(II) species respectively.

These different ways of zeolites preparation strongly influenced catalysts properties, especially metal particles size distribution. Red-C-NiSiBEA catalyst obtained from NiSiBEA by its calcination at 773 K and then reduction at 873 K for 3 h in flowing 10% H₂/Ar contains very small nickel nanoparticles with an average size of 1.5 nm, well dispersed in zeolite structure. In contrast, red-C-NiHAlBEA catalyst obtained from NiHAlBEA by its calcination at 773 K and then reduction at 873 K for 3 h in flowing 10% H₂/Ar contains Ni(0) with larger size of nanoparticles (average size of 5 nm) (Fig. 1).

Both NiSiBEA and NiHAlBEA zeolites are characterized by similar BEA zeolite structure as shown by similar XRD patterns (results not shown) and their further calcination and reduction did not affect crystallinity of

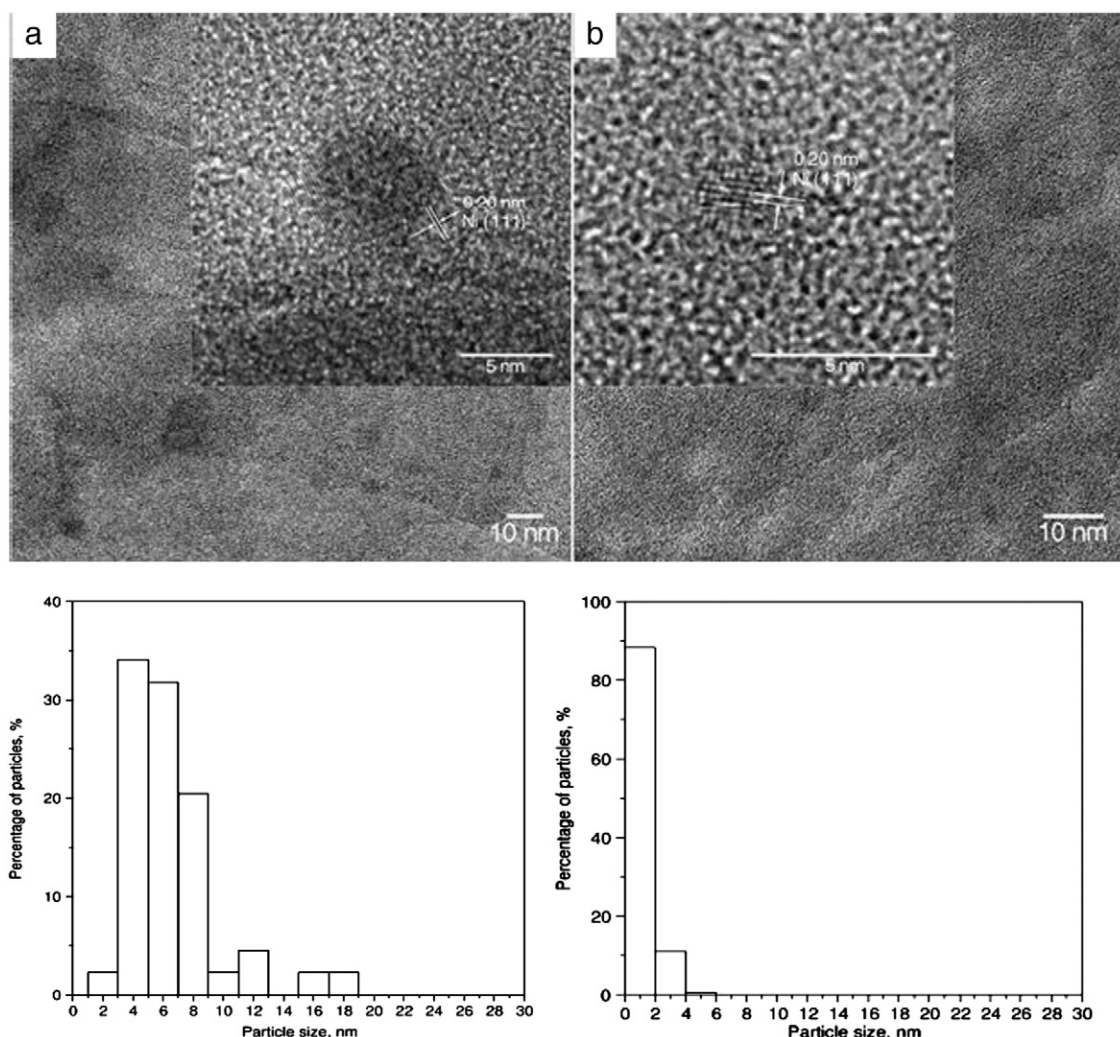


Fig. 1. HRTEM results and nickel particle size distribution for red-C-NiHAlBEA (a) and red-C-NiSiBEA (b).

Download English Version:

<https://daneshyari.com/en/article/50654>

Download Persian Version:

<https://daneshyari.com/article/50654>

[Daneshyari.com](https://daneshyari.com)