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# Short Communication

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



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#### ABSTRACT

Nickel containing BEA zeolites, NiSiBEA and NiHAlBEA, with 2 wt% of Ni were prepared by a two-step postsynthesis method and conventional wet impregnation. The calcination of NiSiBEA and NiHAlBEA at 773 K for 3 h in air led to the formation of C-NiSiBEA and C-NiHAlBEA. After reduction at 873 K for 3 h in flowing 10% H<sub>2</sub>/Ar, red-C-NiSiBEA and red-C-NiHAlBEA were obtained and investigated as the catalysts in hydrodechlorination of trichloroethylene at 503 K. Comparative study performed on red-C-NiSiBEA and red-C-NiHAlBEA 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 NiHAlBEA is the formation of carbonaceous species during hydrodechlorination of trichloroethylene.

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## 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, alcylation, 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 (NiHAlBEA) and two-step postsynthesis method (NiSiBEA).

## 2. Experimental section

#### 2.1. Materials

Nickel containing zeolites (with 2 Ni wt%) were prepared by twostep postsynthesis method (NiSiBEA) and conventional wet impregnation (NiHAlBEA) using SiBEA and HAlBEA as a supports and aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as a nickel precursor. All the preparation details are described in our earlier work [13]. Both NiSiBEA and NiHAlBEA were calcined in air (100 K h<sup>-1</sup>) at 773 K for 3 h under static condition and labeled as C-NiSiBEA and C-NiHAlBEA respectively. Then, a portion of C-NiSiBEA and C-NiHAlBEA were reduced at 873 K for 3 h in flowing 10% H<sub>2</sub>/Ar to obtain red-C-NiSiBEA and red-C-NiHAlBEA, 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-NiHAlBEA, respectively.



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### 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-NiHAIBEA 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/SiO<sub>2</sub>, and the C<sub>2</sub>HCl<sub>3</sub>/H<sub>2</sub> ratio was 1:3 (with the total flow of 42 cm<sup>3</sup> min<sup>-1</sup>). 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%  $H_2$ /He flow (25 cm<sup>3</sup> min<sup>-1</sup>) at a 10 K min<sup>-1</sup> ramp, was followed by mass spectrometry (MA200, Dycor-Ametek, Pittsburgh).

#### 3. Results and discussion

As we reported earlier [13], the two-step postsythesis 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 NiHAIBEA with the nickel incorporated into framework and extraframework 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% H<sub>2</sub>/Ar contains very small nickel nanoparticles with an average size of 1.5 nm, well dispersed in zeolite structure. In contrast, red-C-NiHAIBEA catalyst obtained from NiHAIBEA by its calcination at 773 K and then reduction at 873 K for 3 h in flowing 10% H<sub>2</sub>/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-NiHAIBEA (a) and red-C-NiSiBEA (b).



Fig. 2. XRD patterns of red-C-NiSiBEA, spent-red-C-NiSiBEA, red-C-NiHAlBEA and spentred-C-NiHAlBEA.

these materials, as reported earlier [13]. Additional investigations of the catalysts after kinetic run have shown that after hydrodechlorination of TCE the crystal structure of BEA is still preserved. Furthermore, comparison investigations of the zeolites catalysts after reduction and reaction (Fig. 2) have shown that for catalyst based on NiHAlBEA only negligible shift of the main diffraction peak is observed (from  $2\theta = 22.46$  for red-C-NiHAlBEA to  $2\theta = 22.47$  for spent-red-C-NiHAlBEA). However, for the catalyst prepared by two-step postsynthesis method significant shift of the main diffraction peak is observed (from  $2\theta = 22.54$  for red-C-NiSiBEA to  $2\theta = 22.41$  for spent-red-C-NiSiBEA). It suggests that probably upon reaction test the oxidation of nickel nanoparticles occurs on



Fig. 3. Time on stream behavior during hydrodechlorination of trichloroethene, TCE conversion at the temperature of 503 K.

red-C-NiSiBEA with formation of Ni ions that can migrate and incorporate into zeolite framework.

Fig. 3 and Table 1 show the results of hydrodechlorination of trichloroethylene on parent BEA zeolites and nickel-containing BEA zeolites with different Si/Al ratio. Red-C-SiBEA shows only a negligible activity which is in agreement with our earlier study observed during conversion of 1,2-dichloroethane [13]. Addition of 2 wt.% of nickel to dealuminated BEA (SiBEA) leads to formation of the active catalyst in hydrodechlorination of tichloroethylene. Time on stream behavior shows the most spectacular changes of the total conversion of TCE during the first two hours of reaction with red-C-NiSiBEA. After this time, the activity is stabilized on the value characteristic for steady state conditions (Fig. 3). For red-C-NiSiBEA the summary selectivity toward unsaturated hydrocarbons (ethylene and propylene – the most important starting products in the petrochemical industry, manufacturing of plastics) is close to 55% and additionally 1,1-dichloroethylene (the compound used for production of certain plastics, and also in semiconductor device fabrication) as the main product is formed (Table 1). Red-C-HAIBEA with Si/Al ratio of 17 shows small, but about 5 times higher conversion than this obtained on red-C-SiBEA. Both, red-C-HAlBEA and red-C-NiHAlBEA were deactivated as a function of time much stronger than red-C-NiSiBEA. The difference in catalytic behavior of two parent red-C-SiBEA and red-C-HAlBEA zeolites and nickel containing red-C-NiSiBEA and red-C-NiHAlBEA zeolites could be related to the presence of acidic sites and the ration between the amounts of Brønsted and Lewis acidic sites, as it was reported earlier [12,13]. It seems that the presence of big amounts of strong Brønsted acidic sites is responsible for the activity of red-C-HAlBEA catalyst with more than 90% of selectivity toward ethylene (desired product of HDC of TCE). The presence of small nickel nanoparticles in red-C-NiHAlBEA leads to the formation of olefins (ethylene and propylene) as the main products (Table 1) and additionally 1,1-dichloroethylene as the effect of the presence of Lewis acidic sites. Our results are in agreement with the earlier studies of hydrodechlorination of trichloroethane [12,14,15], where Lewis acidic sites were suggested to be involved in the reaction leading to 1,1dichloroethylene as the major reaction product. For nickel containing zeolites, the selectivity towards 1,1-dichloroethylene increased proportionally to amounts of Lewis acidic sites. Maximally 45% of selectivity was obtained for red-C-NiSiBEA with the most amounts of Lewis acidic centers (Table 1).

From the practical point of view, very important is the separation of the value added products of hydrodechlorination of TCE. From traditional methods of hydrocarbons separation particularly noteworthy is low-temperature distillation. In the case of ethylene /propylene separation this method is integrated with cascaded ethylene/propylene refrigeration system or even cryogenic distillation [16]. Economically, attractive method of separation is the chemical affinity based technology like  $\pi$ -complexation of the silver and copper ions [17]. Additionally, for separation of olefins from 1,1-dichloroethylene we can use rectification column, and absorbers for trapping of HCl. All of the above solutions can be used for separation of HDC TCE products.

It should be noted here that there are only few reports showing the catalytic conversion of trichloroethylene in the gas phase at a rather low reaction temperature – 503 K. Generally, hydrodechlorination of TCE were carried out at the temperature range of 373–573 K [18], but the desirable results were observed at higher temperatures [18,19]. For example, Meshesha et al. [11] showed results of hydrodechlorination of TCE at 573 K. During 270 min of reaction over Pd/NiMgAl mixed oxide, strong deactivation was observed, and the selectivity to ethylene for NiMgAl was maximally 55%. Reactions with Cu-hydrotalcite-derived catalysts [20] and Pt/CeO<sub>2</sub> [2] have shown very high activity of the catalysts at 573 K. At the temperature of 473 K the conversion for 0.2% Pt/CeO<sub>2</sub> was about 5% and ethylene and ethane were obtained as the main products [2]. In view of the literature data our results obtained for hydrodechlorination of trichloroethylene in a relatively low reaction temperature are satisfactory. It is worth noting here that rather rarely

# Table 1

Representative kinetic data of trichloroethylene conversion over red-C-NiSiBEA and red-C-NiHAlBEA catalysts: reaction rates, turnover frequencies (TOFs), overall conversions, products selectivities after 1000 min of reaction at 503 K

Catalysts	Activity/TOF (µmol/g <sub>cat</sub> )/(s <sup>-1)</sup>	Conversion (%)	Selectivity (%)			
			C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	$1,1\text{-}C_2H_2Cl_2$	Others <sup>a</sup>
red-C-SiBEA	0.020/nc	0.2	2.00	25.8	-	72.2
red-C-NiSiBEA	0.530/0.002	6.8	34.9	20.1	45.0	-
red-C-HAIBEA	0.080/nc	1.0	93.1	6.90	-	-
red-C-NiHAlBEA	0.200/0.003	2.6	51.5	25.5	23.0	-

<sup>a</sup> Mainly C<sub>2</sub> and C<sub>3</sub> hydrocarbons and chlorohydrocarbons like: C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>3</sub>Cl, and CH<sub>3</sub>Cl.

catalytic runs were carried out for more than 3-5 h [2,10,11,20]. Our experiments were carried out for ~17 h, and during this time we did not observe deactivation for red-C-NiSiBEA catalyst but deactivation for red-C-HAIBEA and red-C-NiHAIBEA was observed (Fig. 3). It can be related to the particular properties of Ni-containing zeolites that are often recommended as the catalysts for light olefin oligomerization processes [21,22]. The application of a relatively low reaction temperature (503 K) in our catalytic test decreases the ability of nickel containing zeolites to creation huge amounts of oligomers or coke and provides the formation olefins as the main products. Obviously, we cannot completely rule out the carburization process, because we suppose that this phenomenon is responsible for the deactivation of red-C-NiHAlBEA in TCE hydrodechlorination. On the other hand, during hydrodechlorination strong surface chlorination is also observed [23], which is responsible for NiCl<sub>2</sub> formation, deactivation and metal sintering [13,23]. To confirm our suppositions, temperature-programmed hydrogenation (TPH) investigations were used to detect the main reason of deactivation of catalysts. During TPH of the spent-red-C-NiSiBEA and spent-red-C-NiHAlBEA after hydrodechlorination of trichloroethylene particular attention has been focused on the changes of the m/z 15 and m/z 36 corresponding to elimination of carbonaceous species and HCl from used catalysts, respectively. Fig. 4a and b show that during conversion of trichloroethylene on the catalysts are deposited species containing both carbon and chlorine. Comparison of the results obtained for spent-red-C-NiSiBEA and spent-red-C-NiHAlBEA (Fig. 4a and b) shows that more carbonaceous and chlorine species were formed on the catalyst prepared by



Fig. 4. Temperature-programmed hydrogenation profiles of post reactions deposits: (a) methane evolution  $(m/z \ 15)$  and HCl evolution  $(m/z \ 36)$ .

conventional wet impregnation than on the catalyst prepared by twostep postsynthesis method. A very high temperature needed for purification of the catalysts indicates that the carbon deposits were strongly bound to zeolite materials.

#### 4. Conclusions

Red-C-NiSiBEA, red-C-HAIBEA and red-C-NiHAIBEA are active catalysts of hydrodechlorination of trichloroethene at a relatively low reaction temperature (503 K).

The small size of nickel nanoparticles present in red-C-NiSiBEA and red-C-NiHAlBEA is responsible for the conversion of trichloroethylene toward value added products (ethylene, propylene and 1,1dichloroethylene) with higher selectivity.

Catalytic stability of catalysts and product distribution depends on the presence of Lewis and Brønsted acidic sites and their related amount.

During catalytic processes both carburization and chlorination take place, but these phenomena have important effect only on catalytic behavior of HAIBEA-based catalysts.

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