

Application of Ni loaded FAU zeolites in catalytic conversion of 1,2-dichloroethane towards value-added products

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Abstract

The catalytic performance of nickel loaded zeolite materials was found to be dependent on their acidic feature that influenced metal speciation and its dispersion. The selectivity to ethane and ethane of the Ni loaded catalysts increased when reducing both the number of acid sites and average nickel particle size in zeolite catalysts.

Keywords: nickel, zeolites, 1,2-dichloroethane hydrodechlorination, IR spectroscopy

1. Introduction

One of the crucial environmental problems is contamination of air, soil and ground water by chlorine-containing volatile organic compounds (Cl-VOC's) (Huang B. *et al.*). The 1,2-dichloroethane (1,2-DCA) is a representative industrial chlorinated volatile organic compound widely used in the chemical industry as a solvent or an intermediate in the organic synthesis process. Despite its popularity, 1,2-DCA making great hazardous to the environment and human health (Tiana M *et al.*, Śrębowata A *et al.*). Among different method of its utilization, only 1,2-DCA hydrodechlorination leads to the formation of useful and/or environmentally friendly products: ethylene, ethane, and vinyl chloride monomer (a monomer in the polymerization process), respectively. Therefore, the aim of this study was to investigate the influence of textural parameters, nickel particles size, and acidic characteristic of zeolite materials on catalytic properties of Ni loaded FAU and MFI zeolites in hydrodechlorination of 1,2-dichloroethane.

2. Experimental

Four zeolite materials were synthesized as follow: The zeolites Y were provided by Zeolyst Co.: ultrastable Y-type (NH₄-form, CBV 500) and super dealuminated ultrastable Y (H-form, CBV 760), hereafter denoted as USY and SDUSY. Dealuminated form of zeolite USY (USY_DeAl) was obtained by mild leaching with 0.2M HCl solution at 333 K for 2 h, filtration, and washing with distilled water. Next, the resulted material was dried at room temperature. The nickel-containing zeolites, with different metal loading, were prepared by twofold ion-exchange procedure with 0.2M Ni(NO₃)₂

solution at 338 K. Then, the zeolites were filtrated, washed, and dried at room temperature. Afterwards, nickel catalysts, were calcined in nitrogen at 773 K for 1 h then reduced with hydrogen (10% H₂/Ar at atmospheric pressure) for 3 h at 923 K. All of the zeolite materials were thoroughly characterized by ICP, XRD, low-temperature N₂ sorption studies, H₂-TPR, IR spectroscopy, X-ray photoelectron studies, SEM and EPR. The hydrodechlorination reaction (HDC) of 1,2-dichloroethane(1,2-DCA, pure 99,8% from Sigma-Aldrich, Germany) was carried out with nickel-containing zeolite catalysts. Prior to reaction, 0.2 g of catalyst was reduced in flowing 10% H₂/Ar (25 mL min⁻¹), ramping the temperature from 298 to 873 K (at 10 K min⁻¹) and kept at 873 K for 3 h. Subsequently, every catalyst was cooled down into 523 K and contacted with the reaction mixture (H₂+ Ar + 1,2-DCA). Total gas flow was 42 mL min⁻¹. 1,2-DCA was provided from a saturator kept at 273 K. The partial pressure ratio p(H₂)/p(1,2-DCA) was 1:1. The flows of H₂ and Ar were fixed by using Bronkhorst Hi-Tec mass flow controllers. The contact time was 0.7 s and the space velocity was 0.0035 (m³kg⁻¹s⁻¹). The exhaust gas stream was analyzed with gas chromatography, using an HP 5890 series II Hewlett Packard (USA), gas chromatograph with FID detector, a 5% Fluorcol/Carbopac B Supelco (USA)column (10 ft). The results of GC analysis were elaborated using HPChemstation.

3. Result and Discussion

Both acidic forms of the zeolites and Ni loaded zeolites were thoroughly characterized with respect to their structural (XRD), textural (low-temperature nitrogen sorption, STEM) and acidic/redox properties (IR, XPS, EPR spectroscopies) (Śrębowata A *et al.*). Synthesis of the Ni loaded zeolites FAU led to the formation of the catalysts with different textural parameters (total surface area, pore volume, etc.), nickel particles size and acidic properties. Both partial dealumination (Ni@USY_DeAl) and open mesoporous structure (Ni@SDUSY) allowed for suppressing of metallic particles agglomeration leading to their uniform dispersion through the crystal (Fig. 1). Finally, the zeolite of the highest Si/Al (=31) ratio offers the best dispersion of metallic particles, indicating that acid sites

density of supports differentiates the strength of their interaction with metal particles. Each of the catalysts studied showed activity in the continuous-flow hydrodechlorination of 1,2-dichloroethane providing very high selectivity towards environmentally friendly ethylene or economically valuable product i.e. vinyl chloride (Fig. 2).

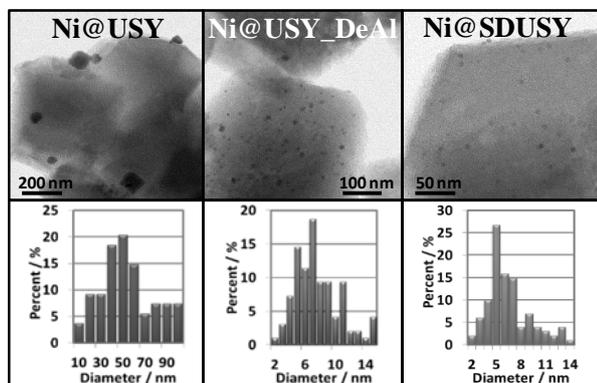


Fig 1. STEM micrographs of the catalysts studied.

Table 1. Nickel loading, textural, and acidic characteristic of studied zeolites.

Zeolite	S_{BET}	Ni	Si/Al	Al ^a	B ^b	L ^b
	m ² /g	wt. %		μmol/g		
Ni@USY	501	2.59	2.7	3764	652	661
Ni@USY_DeAl	506	1.54	3.5	3095	846	898
Ni@SDUSY	532	0.79	31	435	242	337

^a Concentration of Al obtained from chemical analysis in Ni-zeolites.

^b Concentration of Brønsted (B) and Lewis (L) acid sites derived from quantitative Py-sorption IR.

^c Acid strength of B and L sites derived from Py-thermodesorption studies.

Correlation of the catalytic properties of nickel catalysts in 1,2-DCA HDC with their textural parameters clearly shows that the differentiation in the metallic particles size do not provide important changes in catalytic activity, but the selectivity is significantly affected. The zeolite Ni@USY with the biggest particles showed the highest activity than the other Ni loaded zeolites. The latter catalysts Ni@SDUSY and Ni@USY_DeAl being somewhat less active provided ethene and ethane as the only products. (Fig. 2). The formation of vinyl chloride was inhibited. It provides an argument for facilitated hydrogenation of ethane over the nickel sites of the highest dispersion. Besides, the role of the acidic feature cannot be neglected. The 1,2-dichloroethane transformation over Ni@SDUSY and Ni@USY_DeAl accommodating a high number of Brønsted acid sites is associated with the vinyl chloride formation, while a reduced number of protonic sites facilitates the formation of hydrogen transfer product, i.e. ethane. The ethane formation becomes not trivial for Ni@USY_DeAl which provides dramatic difference in nickel particles size and only moderate in the amount of Brønsted acid sites if comparing with Ni@USY. It allows anticipating that the interaction of 1,2-DCA molecules with the catalyst surface is affected by nickel moieties size but not acidic property. The latter one, however, affects catalytic performance in by ruling metal dispersion.

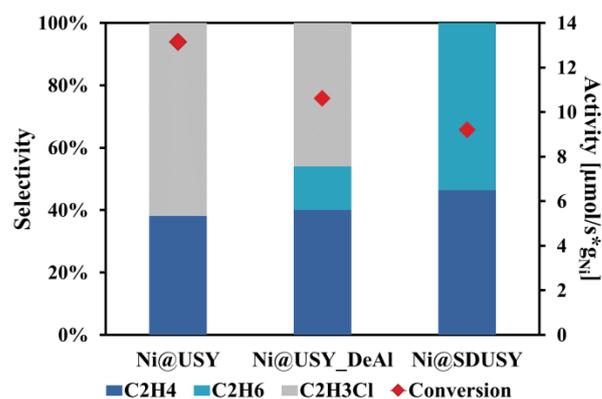


Fig 2. Catalytic behaviour of Ni loaded zeolites in 1,2-DCA hydrodechlorination.

Conclusions

We have shown that catalytic behaviour of Ni-loaded faujasites depends on their textural and acidic features. Nickel in the form of small (~ 2- 10 nm) and uniformly dispersed nanoparticles was found to be very active in 1,2-DCE transformation to ethane. When increasing nickel particle size (~ 10- 100 nm) vinyl chloride appeared as the main reaction product.

Acknowledgements

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