

NATURAL ZEOLITE AS A CARRIER FOR NANO-OXIDE PARTICLES AND A POSSIBLE APPLICATION OF THE OXIDE/CLINOPTILOLITE COMPOSITE

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ABSTRACT

Nano-particles of NiO crystallize when the Ni-exchanged natural clinoptilolite is dehydrated by heating in air at 500 °C. Nano-NiO with an average size of about 5 nm has been found to be randomly dispersed in the clinoptilolite matrix. The NiO-containing clinoptilolite exhibits a good catalytic efficiency in lignin pyrolysis and produces bio-oil with a high content of phenols and low contents of acetic acid, furans and alcohols.

Key words: clinoptilolite, nano-particles, bio-fuels, lignin pyrolysis

INTRODUCTION

The traditional applications of zeolites have recently been extended to exploiting zeolite frameworks as hosts for the synthesis of novel nano-materials [1]. Nanometer-sized materials exhibit specific properties that differ significantly from their bulk counterparts. Different chemical methods have been reported for the synthesis of nano-materials, most of which suffer from complexity, low yield and high cost. Moreover, for most synthetic procedures a key requirement is usually the prevention of the agglomeration of the produced nano-particles.

Clinoptilolite is the most abundant natural zeolite and is characterized by large, intersecting, open channels of ten- and eight-membered tetrahedral rings. Recently, the channels occupied by ion-exchangeable cations have been explored for preparation of semiconductor particles of PbS at nanometric size (about 10 nm) [2].

Biomass has been considered as a green and renewable energy source for potential replacement of fossil fuels which depletion and impact on environment cause a serious concern. Heterogeneous catalysts, such as metal oxides, molecular sieves and activated carbon, play critical roles in the biomass catalytic conversion. Recently, it has been reported that the use of NiO particles could lower the decomposition temperature of biomass components, such as cellulose, xylan and lignin [3]. However, nano-sized metal particles are not thermodynamically stable, which results in the loss of catalytic activity of the catalysts. Employing porous materials as a matrix for nano-particles seem to be a suitable method to maintain catalyst activity for a longer period.

EXPERIMENTAL

The zeolitic tuff (Z) containing about 72 wt.% clinoptilolite was obtained from a large sedimentary Zlatokop deposit (Vranjska Banja, Serbia) and was used as-received in the experiments. The sample (with the grain size in the 0.063-0.1 mm range) was pretreated with 2.0 mol dm⁻³ solution of NaCl in order to improve the tuff's exchange ability. Prior to its further use, the Na-modified zeolite (NaZ) was filtered off from the suspension, washed with distilled water until it was free of chloride ions and dried at 105 °C. The ion-exchange was

performed at 35 °C using NaZ and 6-mmol dm⁻³ NiCl₂ solution in a ratio of 1g (solid)/100 cm³ (solution). The Ni-containing product (NiZ) was then recovered by filtration. All the treatments did not affect crystallinity of the clinoptilolite (checked by XRPD analysis).

The sample of NiZ was then thermally treated under air at about 500 °C at a heating rate of 10 °C min⁻¹. The calcined product was analysed by the transmission electron microscopy (TEM). Identification of the crystal phase formed during the thermal treatment of NiZ was done using the selected area electron diffraction (SAED) over multiple nano-crystals.

The BET surface areas (S_{BET}), the pore volumes and the pore diameter distributions of the calcined product were measured by N₂ adsorption at -196 °C. The BJH method was applied to determine the pore diameter distributions. The surface acidity was measured by NH₃-temperature programmed desorption (NH₃-TPD) using a Micromeritics AutoChem II 2920 catalyst characterization system.

Catalytic activity of the calcined NiZ (NiO-Z) was checked in a production of bio-oil by pyrolysis of hardwood lignin. The hardwood lignin used was a birch kraft lignin isolated according to the so-called LignoBoost technology developed and supplied by INNVENTiA AB in Sweden. In a fixed bed reactor the lignin (1.5 g) was treated with NiO-Z (0.7 g) and heated at 500 °C for about 15 min. The resulting liquid and gaseous phases were analyzed by using GC and GC/MS.

RESULTS AND DISCUSSION

The EDS analysis of the NiZ showed that Ni(II) replaced only the Na⁺ ions in the clinoptilolite phase. The chemical composition of the NiZ expressed by oxide mass % is as follows: SiO₂ – 66.5, Al₂O₃ – 12.7, Fe₂O₃ – 1.23, Na₂O – 4.62, K₂O – 0.13, NiO – 0.82, CaO – 1.33 and MgO – 1.19, loss of ignition - 11.40.

TEM analysis of the NiZ before and after calcination is illustrated in Figure 1. The clinoptilolite phase appears in the form of monoclinic crystalline sheets with well-defined crystal faces. Calcination affects the surface of the clinoptilolite crystal clusters which become populated with spherical nano-crystalline particles.

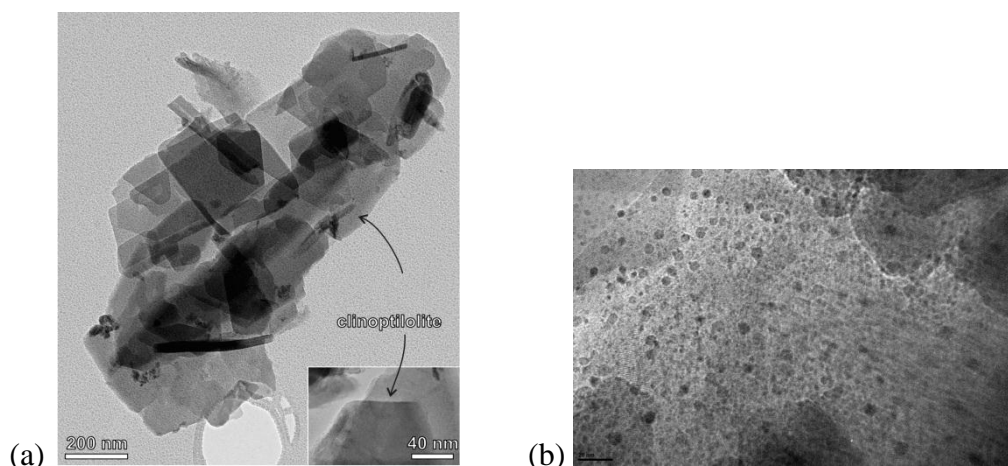


Figure 1. TEM image of NiZ and the calcined NiZ. a) The clinoptilolite phase appears in the form of hexagonal plates, b) clinoptilolite crystals sprinkled with NiO (dark spots).

The SEAD analysis revealed that the formed particles belong to NiO. The size of the NiO crystallites is between 2 and 7 nm with an average particle size of about 5 nm in diameter. The SAED pattern recorded over multiple NiO particles showed that they belong to the cubic NiO structure (JCPDF # 78-0643). No preferential faceting of the cubic NiO crystals can be observed, which implies a rapid crystallization.

Table 1. Comparison of the measured d-values of NiO nano-particles from SEAD pattern and the NiO reference.

Distance, nm	d ₁	d ₂	d ₃	d ₄
Measured distance, nm	0.246	0.206	0.145	0.126
Distance in NiO (JCPDF # 78-0643)	0.24113	0.20883	0.14766	0.12592
Crystallographic plane	{222}	{400}	{440}	{622}

The surface area (S_{BET}), the pore volume and the average pore diameter of the NiO-Z are summarized in Table 2. The S_{BET} is $32 \text{ m}^2 \text{ g}^{-1}$, similar to that of the untreated natural clinoptilolite (Z) [4]. The average pore diameter is slightly increased showing that the crystallization of NiO affected the clinoptilolite pore openings (being approx. 0.4 nm). It is quite expectable since the formation of NiO (which diameter exceeds the aperture of the clinoptilolite channel) proceeds through dehydration and movement of Ni(II) ions from interior towards the surface of the crystals.

Table 2. S_{BET} , pore volume and average pore diameter of NiO-Z

$S_{\text{BET}}, \text{m}^2 \text{ g}^{-1}$	Pore volume $\text{cm}^3 \text{ g}^{-1}$	Average pore diameter, nm
32	0.004	0.51

The TPD curve for NH_3 evolution from NiO-Z is shown in Figure 2. The curve was deconvoluted by fitting to Gauss functions (using Origin 7.0). The first two peaks centered at 180 and 250 °C could be attributed to weak acid sites. These acid sites are represented mainly by Lewis-type sites and are considered to be the relevant extra-framework ions [4]. The peaks at 400 and 620 °C both correspond to strong acid sites, which are mostly attributed to Brönsted-type sites containing protonated active groups [4]. Since calcination led to a complete water removal (checked by thermal analysis), not only nano-NiO but also Si-O(H)-Al was formed by dehydration of NiZ.

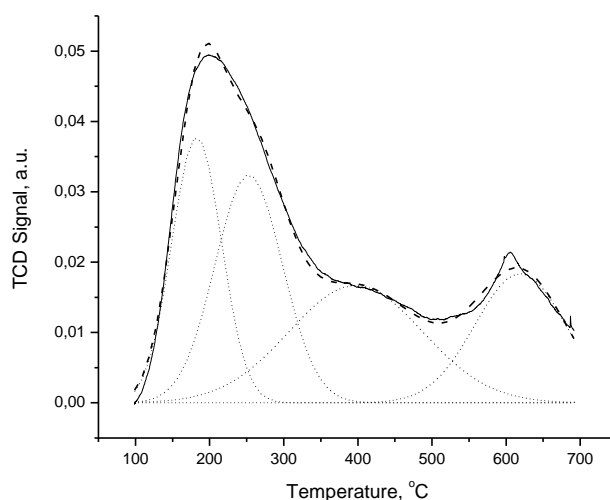


Figure 2. NH_3 -TPD profile: bold – experimental, dash – fit, dot – resolved peaks.

The NiO-Z exhibited a good catalytic performance in hardwood lignin pyrolysis and the production of bio-oil. A promising catalyst is expected to produce more desirable and fewer

undesirable fractions. Phenols and hydrocarbons are desirable fractions since they are chemicals of a high commercial value, while oxygen-containing compounds, such as acids and carbonyls, as well as heavy compounds are considered as undesirable fractions. The presence of NiO-Z alters the quality of the pyrolysis products in comparison to non-catalytic degradation [5]. The solid residue, liquid and gas yields in the catalytic reaction are as follows (wt.-%): ash: 28.3 ± 1.0 , liquid phase: 53.2 ± 5.0 and gaseous phase: 18.5 ± 4.0 . A wide range of organic compounds was found in liquid phase, most of them being based on benzene or phenol. The identified compounds were grouped into eight groups (Table 3).

Table 3. Liquid components from the catalytic pyrolysis of lignin

Components	wt. %	Components	wt. %
Hydrocarbons	0.60	Carbonyls and aldehyds	11.07
Phenols	43.87	Polycyclic aromatic hydrocarbons	2.75
Furans	0.13	Heavy compounds	33.18
Acids and esters	7.25	Unknown compounds	3.87
Alcohols and ethers	0.35	Average molar weight: $164.81 \text{ g mol}^{-1}$	

It can be noticed that the phenols concentration in the produced bio-oil (about 44 wt.%) is similar to that found in the bio-oil produced by catalytic pyrolysis of lignin using mesoporous MCM-41 catalyst [5].

CONCLUSION

Calcination of the Ni(II)-containing natural clinoptilolite under air at 500 °C could serve as a suitable method for the generation of the nano-sized NiO. The present work has shown that the clinoptilolite lattice is a suitable crystalline carrier to prevent agglomeration of small oxide nano-particles. The NiO-containing clinoptilolite exhibits a good catalytic performance with a high liquid yield and excellent selectivity to phenols in the pyrolysis of hardwood lignin. The nano-sized NiO might be responsible for the good performance.

REFERENCES

- [1] A. Nezamzadeh-Ejehieh and Z. Salimi, *Appl. Catal. A-Gen.* 2010, **390**, 110-118.
- [2] J.F. Roman-Zamorano, M. Flores-Acosta, H. Arizpe-Chavez, F.F. Castillon-Barraza, M.H. Farias, R. Ramirez-Bon, *J. Mater. Sci.* 2009, **44**, 4781-4788.
- [3] J.F. Li, Yan R, B. Xiao, D.T. Liang, and D.H. Lee, *Energ. Fuel*, 2008, **22**, 16–23.
- [4] A. Godelitsas, D. Charistos, A. Tsipis, C. Tsipis, A. Filippidis, C. Triantafyllidis, G. Manos, and D. Siapkias, *Chem. Eur. J.*, 2001, **7**, 3706-3721.
- [5] M. Stöcker, *Angew. Chem.* 2008, **47**, 9200-9211.