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Hardwood lignin pyrolysis in the presence of nano-oxide particles embedded onto natural clinoptilolite

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ABSTRACT

In this study the catalytic activity of Na-rich and MO-containing natural clinoptilolite (MO – nanoparticles of NiO, ZnO, or Cu_2O) was studied in the pyrolysis of hardwood lignin. The clinoptilolite samples exhibit different catalytic activities which depend mainly on the type of the nano-oxide. The presence of nano-oxides did not affect the porosity of the clinoptilolite framework but influenced its acidity. However, it seems that acidity of the lattice did not influence the catalytic activity of the clinoptilolite in the pyrolisis of hardwood lignin. The number of Lewis acid sites increased significantly for the ZnO- and Cu_2O-containing clinoptilolite whereas for the NiO-sample it did not change appreciably in comparison to the parent zeolite. The amount of phenols in the as-produced bio-oil varies from 39% for ZnO-clinoptilolite, 43% for Na-rich clinoptilolite, to 50 and 54% for Cu_2O- and NiO-containing samples, respectively. The highest yield of phenols obtained in the presence of NiO-containing clinoptilolite is ascribed to a synergetic interaction of the clinoptilolite lattice and nano-NiO particles.

1. Introduction

Lignocellulosic biomass is the most abundant renewable material which is a potential feedstock for producing chemicals, fuels and materials. It has recently been reported that between 40 and 50 million tons per year are produced in the world mostly as a non-commercialized product [1]. Although most research in the area of the potential uses of lignin is focused on the pyrolysis process for lignin treatment, investigations on the use of lignin in the production of phenols are rather scarce [1]. Phenol is an important industrial chemical which is mainly produced from fossil fuels. In the last decade great attempts have been made in obtaining phenol from cost-effective lignocellulosic materials [2].

Among various biomass conversion processes, pyrolysis has long been known to yield an oil-like liquid (i.e. "bio-oil") which can be used either directly or as an energy carrier product. In the biomass pyrolysis the presence of heterogeneous catalysts, such as metal oxides, molecular sieves and active carbon, plays a critical role [3,4]. Recently, it has been reported that the use of NiO particles decreases the decomposition temperature of biomass components, such as cellulose, xylan and lignin [5]. Since nano-sized particles are not thermodynamically stable, which results in the loss of catalytic activity of the catalysts, porous materials have been employed as a matrix for nano-oxides in order to maintain the catalyst's activity for a longer period [6].

On the other hand, clinoptilolite is one of the most abundant natural zeolites with intersecting, open channels occupied by hydrated ion-exchangeable cations which are potentially active catalytic sites [7]. The clinoptilolite lattice is thermally stable which enables its use in catalytic applications. Recently, we have found that a complete dehydration of the Ni(II)-, Cu(II)- and Zn(II)-loaded clinoptilolite leads to the formation of the corresponding oxides of nanometric size [8]. Therefore, clinoptilolite could be used as a good carrier of nano-oxides particles.

In this work we present the immobilization of several nano-oxides on the natural clinoptilolite surface, the characterization of the obtained materials using XRD, the N_2-sorption and IR spectroscopy and their catalytic activities in the lignin pyrolysis reaction.

2. Experimental

2.1. Preparation of catalysts

A natural zeolite (Z) obtained from the sedimentary Zlatokop deposit (Vranjska banja, Serbia) was used in the experiments. In

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order to improve the zeolite exchange capacity the zeolite tuff was first converted into the Na-form (NaZ) by treating Z with 2 mol dm^{-3} of NaCl solution at 25 °C for 48 h. Prior to its further use, the NaZ was filtered off from the suspension, washed with distilled water until it was free of chloride ions and dried at 105 °C. This conversion does not affect the crystallinity of the Z.

The ion-exchange was performed at 35 °C using NaZ and 6-mmol dm^{-3} MCl_2 (M – Ni, Cu, Zn) solution in a ratio of 1 g (solid)/100 cm^3 (solution). Metal-containing products were then recovered by filtration. XRPD analysis confirmed that the treatments did not affect crystallinity of the clinoptilolite lattice. Elemental analysis of the clinoptilolite phase of Z, NaZ, Ni–NaZ, Cu–NaZ and Zn–NaZ are given in Table 1.

The metal-loaded samples of Ni–NaZ, Cu–NaZ and Zn–NaZ containing (wt.%) 0.78 Ni^{2+}, 2.07 Cu^{2+} or 1.18 Zn^{2+} were heated at a heating rate of 10 °C min^{-1} to 550 °C and then were isothermally heated for 60 min in the air at 550 °C to be completely dehydrated. The obtained products were denoted NiO–NaZ, Cu_2O–NaZ and ZnO–NaZ.

2.2. Characterization methods

Elemental analysis of the natural and modified zeolite samples was performed using energy dispersive X-ray spectroscopy (EDS) by a scanning electron microscope JEOL JSM-6610LV. The samples were prepared by embedding grains in an epoxy film, polishing the crystallites, cutting with a fine-grid diamond cut and coating with carbon. This careful preparation provided an intersection view of the crystallite grains and allowed for a detailed elemental analysis of the major mineral phases. An average elemental composition of the samples was obtained by a data collection at 10 different mm^2-sized windows on the pellet surface.

Thermal analysis was performed using a SDT Q-600 simultaneous TGA-DSC instrument (TA Instruments). The sample (mass app. 10 mg) was heated in a standard alumina sample pan, the experiment being carried out under air with a flow rate of 0.1 dm^3 min^{-1} and a heating rate of 10 °C min^{-1}.

The dehydrated M–NaZ products (NiO–NaZ, Cu_2O–NaZ and ZnO–NaZ) were analyzed by transmission electron microscopy (TEM) and identification of the obtained oxides was performed using the selected area electron diffraction (SAED) over multiple nano-crystals. TEM studies were performed using a 200-kV TEM (JEM-2100 UHR, Jeol Inc., Tokyo, Japan) equipped with an ultra-high-resolution, objective-lens pole-piece having a point-to-point resolution of 0.19 nm, which is sufficient to resolve the lattice images of the oxide nanoparticles. For the TEM studies, the samples were crushed in an agate mortar, dispersed in absolute ethanol and applied to a Cu-holey carbon grid. From the TEM image, the diameter of the oxide nanoparticles was measured in order to determine their average size. Due to the relatively small size of the nanoparticles, the selected-area electron diffraction (SAED) was performed over multiple nanocrystals to obtain the characteristic diffraction rings and the structure-specific *d*-values.

Table 1
Average chemical compositions of the clinoptilolite phase of Z, NaZ and M–NaZ (M = Ni, Cu, Zn) obtained by EDS analysis.

Component	Wt.%				
	Z	NaZ	Ni–NaZ	Cu–NaZ	Zn–NaZ
SiO_2	65.7	66.6	66.5	65.7	65.6
Al_2O_3	13.0	12.9	12.7	12.4	12.5
Fe_2O_3	1.48	1.04	1.23	1.12	1.15
Na_2O	0.95	5.34	4.92	3.31	4.22
K_2O	1.33	0.14	0.13	0.12	0.15
CaO	3.08	1.40	1.33	1.28	1.27
MgO	1.41	1.21	1.19	1.08	1.11
MO*	–	–	0.99	2.60	1.47
Loss of ignition**	12.9	11.5	11.2	12.3	12.6

* M – Ni, Cu, or Zn.
** Obtained by thermal analysis.

The BET surface areas (S_{BET}), the pore volume and the average pore diameter of NaZ and the dehydrated M–NaZ samples were measured by N_2 adsorption at −196 °C using Hiden Isochema HTP1-V Volumetric Analyzer. The samples were previously outgassed in vacuum for 3 h at 350 °C. The BET specific surface areas were calculated from adsorption data in the relative pressure range p/p_0 from 0.04 to 0.18. The Dubinin–Astakhov analysis was applied to determine the pore size distributions.

The surface acidity of NaZ and the dehydrated M–NaZ samples were measured by NH_3-temperature programmed desorption (NH_3-TPD) using a Micromeritics AutoChem II 2920 catalyst characterization system. The samples [0.1550(4) g] were first heated to 390 °C (20 °C min^{-1}) and left at that temperature for 120 min. After cooling the material to 100 °C (15 °C min^{-1}), a mixture of 10% NH_3 and He (25 cm^3 (STP min^{-1}) was passed over the material for 30 min. Subsequently, the material was left under flowing He (25 cm^3 (STP) min^{-1}) for 60 min at 100 °C to remove physisorbed NH_3. NH_3-TPD was performed by ramping the material at 10 °C min^{-1} to 700 °C in He [(25.1 cm^3 (STP) min^{-1}, 10 °C min^{-1}, 30 min at 700 °C]. Ammonia content in the effluent was monitored using a TCD. The total amount of ammonia was quantified by integration of peaks with a Micromeritics' Peak Editor software.

Acid sites were characterized and quantified by pyridine absorption using FTIR spectroscopy. FTIR spectra were recorded with a resolution of 4 cm^{-1} on a Bruker IFS 6/S spectrophotometer equipped with a DTGS detector. The samples were pulverized and pressed into self-supported disks (15 mg; area of 2 cm^2) and placed in a quartz IR cell with KBr windows. A thermal treatment at 390 °C (20 °C min^{-1}) was carried out in vacuum for 2 h in order to remove physisorbed water. After cooling at room temperature an IR spectrum was recorded (it will be referred to as background). Adsorption of pyridine was then carried out, dosing 5 mbar at equilibrium over the disk for 10 min. A second spectrum was recorded after the removal of physisorbed pyridine by outgassing at 150 °C for 10 min. The characterization of acid sites was effectuated on a difference spectrum obtained by subtraction of the background from the spectrum recorded after the pyridine adsorption.

The interaction of pyridine with the Brønsted and Lewis acid sites of the samples gives rise to bands in the 1575–1525 cm^{-1} and 1470–1435 cm^{-1} range, respectively. The concentrations (C) of sites were calculated using the integrated absorbance A of the bands and the molar extinction coefficients ε as measured by Emeis, *i.e.* 2.22 cm μmol^{-1} for Lewis sites and 1.67 cm μmol^{-1} for Brønsted sites [9]. The formula used takes also into account the weight (w_d) and area (s_d) of the disk:

$$C = \frac{A}{\varepsilon}\frac{s_d}{w_d}$$

2.3. Catalytic test

The lignin pyrolysis experiments were carried out in a bench-scale fixed-bed reactor under nitrogen atmosphere. The reactor was filled with 0.7 g of catalyst or the sea send and covered with 1.5 g of lignin. For all experiments the as-received hardwood lignin (provided by Innventia) was used. The reactor temperature was kept constant at 500 °C, while the time of nitrogen introduction into the reactor was 45 min (flow rate of 100 cm^3 min^{-1} for 15 min and 30 cm^3 min^{-1} for 30 min). The liquid products were collected in a liquid bath (−17 °C) and quantitatively measured in a pre-weighted glass receiver. The bio-oil produced was initially in one phase, and two phases of the liquid – organic and aqueous –