



J. Serb. Chem. Soc. 80 (5) 717–729 (2015)
JSCS–4751

Modification of natural clinoptilolite and ZSM-5 with different oxides and a study of the obtained products in lignin pyrolysis

JELENA A. MILOVANOVIĆ^{1*}, RUTH ELISABETH STENSRØD², ELISABETH M. MYHRVOLD², ROMAN TSCHENTSCHER², MICHAEL STÖCKER², SLAVICA S. LAZAREVIĆ³ and NEVENKA Z. RAJIĆ³

¹Innovation Centre of the Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia, ²SINTEF, Forskningsveien 1, 0314 Oslo, Norway and

³Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

(Received 31 July, revised 17 October, accepted 6 November 2014)

Abstract: In this work, different metal oxides (MO) supported on two types of zeolites: 1) natural clinoptilolite (NZ) and 2) synthetic zeolite, ZSM-5 were prepared and tested as catalysts in the fast pyrolysis of hardwood lignin. NZ was modified with the CaO and MgO by a simple two steps procedure consisting of an ion exchange reaction and subsequent calcination at 773 K. The synthetic ZSM-5 was modified with several MO species (Ni, Cu, Ca, Mg) by wet impregnation and calcination at 873 K. The prepared catalysts were characterized by X-ray diffraction analysis (XRD), scanning electron microscopy and energy dispersive X-ray analysis (SEM/EDS), and measurement of their specific surface area (BET method). Acid sites were characterized and quantified by pyridine (py) absorption using Fourier transform infrared spectroscopy (FTIR). The catalysts exhibit catalytic activity depending on modification, reaction temperature and of the MO contents. The highest yield of useful phenol in bio-oil was obtained with NiO/ZSM-5 (34.8 wt. %) which exhibits the highest specific surface area and the highest concentration of Brönsted and Lewis acid sites. The studied catalysts did not increase significantly the content of polycyclic aromatic hydrocarbons (PAHs) and 'heavy' compounds (phenols with $M_r > 164 \text{ g mol}^{-1}$) compared to non-catalytic experiment.

Keywords: lignin; catalysts; natural zeolite; ZSM-5; bio-oil; phenol.

INTRODUCTION

Lignocellulose is the cheapest and most abundant source of biomass that is considered as a green and renewable energy source for potential replacement of fossil fuels. Lignin is the second most important component of lignocellulosic

* Corresponding author. E-mail: jmilovanovic@tmf.bg.ac.rs
doi: 10.2298/JSC310714109M

biomass, exceeded only by cellulose, representing about 4–35 wt. % of most biomass, 16–25 wt. % of hardwoods and 23–35 wt. % of softwoods.¹ Lignin is an amorphous, aromatic biopolymer that is a byproduct of the pulp and paper industries and is conventionally regarded as a waste material having low economic usage. However, its structural feature being comprised of variously linked phenylpropane units indicates that lignin could be considered as a potential source of some value-added chemicals, such as phenolic compounds.

In the last decade, fast pyrolysis is considered as the method of choice for biomass conversion to bio-oils.^{2–7} Pyrolysis is the thermal decomposition of biomass in the absence of oxygen performed at moderate temperatures (723–873 K) and at high heating rates. Since lignin is the most heat-resistant component in lignocellulosic biomass, its pyrolysis is regarded as a challenge because of the high amount of residual char. Accordingly, the aim of this study was to examine the direct conversion of hardwood lignin into useful chemicals by catalytic fast pyrolysis. For this purpose, two catalytic systems based on zeolites were explored.

Zeolites are open-framework aluminosilicates that are widely used in various applications. Their high concentration of active sites, high thermal/hydrothermal stability and enhanced shape selectivity make them perspective candidates for the design of catalysts for lignin pyrolysis. In a previous investigation, it was found that pyrolysis of hardwood lignin in the presence of natural clinoptilolite modified with nano-oxide particles (NiO and Cu₂O) yielded a pyrolysis oil with a high amount of phenols.⁸ This results suggest that natural clinoptilolite, as an important mineral resource in Serbia, could be used as a cheap, available and environmentally friendly precursor for the design of a catalytic system for lignin pyrolysis.

In the present study two types of zeolites were investigated for catalyst design: natural clinoptilolite (NZ) and synthetic ZSM-5. The natural clinoptilolite was modified with CaO and MgO (CaO–NZ and MgO–NZ, respectively) whereas ZSM-5 was modified with CaO, MgO, Cu₂O and NiO (CaO/ZSM-5, MgO/ZSM-5, Cu₂O/ZSM-5 and NiO/ZSM-5, respectively).

EXPERIMENTAL

Materials and methods

Natural clinoptilolite modified with oxide particles. Zeolitic tuff (from the Zlatokop deposit in Serbia) containing about 72 % of clinoptilolite, 13 % of quartz and 15 % of feldspars was previously investigated in detail.⁹ Samples with a grain size of 65–100 µm were modified into MgO- and CaO-containing catalysts by a procedure slightly altered from that described in the literature.¹⁰ Suspensions containing MCl₂ (M = Mg or Ca), NaOH and NZ were evaporated to dryness during approximately 5 h at 423 K on a sand bath. The obtained products were further calcined at 773 K for 3 h, cooled to room temperature and washed several times with distilled water until the filtrate was Cl-free.

ZSM-5 modified with oxide particles. ZSM-5 was synthesized using a procedure reported in the literature.¹¹ Aluminum sulfate octadecahydrate (Acros Organics), sodium hydroxide (Lach-Ner), and tetrapropylammonium bromide (TPABr, 98 %, Aldrich) were of analytical grade, whereas the colloidal SiO₂ solution (30 wt. %, Ludox AS, Aldrich) was of technical grade. From a reaction mixture containing reagents in the following molar oxide ratio: 7Na₂O–0.25Al₂O₃–100SiO₂–3TPABr–3500H₂O, a white highly crystalline product crystallized the XRD analysis of which confirmed it to be pure ZSM-5.

In order to prepare MgO/ZSM-5 and CaO/ZSM-5, a suspension containing MCl₂ (M = Mg or Ca), NaOH and ZSM-5 was heated to dryness on a sand bath. Cu₂O/ZSM-5 and NiO/ZSM-5 were prepared in a manner similar to that described in the literature¹² using CuSO₄·5H₂O (Aldrich) or NiSO₄·6H₂O (Aldrich), NaOH, NH₄OH (25 %) and ZSM-5. All the obtained products were calcined at 873 K for 2 h. All the used chemicals were of analytical grade.

Prior to catalytic test, the prepared catalysts were characterized by the XRD, SEM/EDS, FTIR and BET methods.

Pyrolysis test

The lignin pyrolysis experiments were carried out in a bench-scale, fixed-bed reactor under nitrogen atmosphere at different temperatures (723, 773 and 823 K) for about 15 min.

The body of the reactor, made of a beryllium–copper alloy, was filled in the following order with: 0.06 g of quartz wool (in order to hold the reactants), 0.70 g of the catalyst and 1.50 g of hardwood lignin (obtained from Innventia, Sweden)

The liquid products were collected in a liquid bath (256 K) and quantitatively measured in a pre-weighed glass receiver. The bio-oil consisted of two phases, *i.e.*, liquid-organic and aqueous phase. The organic fraction was separated by extraction with dichloromethane and the samples were stored immediately in a refrigerator. The gaseous products were collected and measured by water displacement, while the amount of the solid residue was measured by direct weighing.

The pyrolysis products were analyzed by GC, GC–MS and TG–MS.

Instrumentation

Elemental analyses of the parent and modified zeolitic samples were performed using an SEM/EDS microscope JEOL JSM-6610LV. Samples based on natural zeolite were prepared by embedding grains in an epoxy film, polishing the crystallites, cutting with a fine-grid diamond cut and coating with gold. The samples based on ZSM-5 were coated with gold. An average elemental composition of the samples was obtained by a data collection at 10 different mm²-sized windows on the pellet surface.

The XRD patterns of the samples were recorded using an Italcristal APD2000 diffractometer operating with CuK_α radiation in the 2θ range 5–65°. The Rietveld method¹³ was used for quantitative analysis of CaO–NZ and MgO–NZ. The estimated errors for the phase composition were under 5 % for clinoptilolite and feldspars, and under 2 % for the other phases.⁸

The BET specific surface areas (*S*_{BET}) of all samples were measured by a Micrometrics ASAP 2020. The samples were previously out-gassed under vacuum for 10 h at 423 K. The specific surface area was determined from the desorption isotherm at a relative pressure of 0.998.

The acid sites were characterized and quantified by pyridine (py) absorption using FTIR spectroscopy. The FTIR spectra were recorded with a resolution of 4 cm⁻¹ on a Nicolet

spectrometer equipped with a MCT detector. The samples were pulverized and pressed into self-supported disks (20 mg; area of 2 cm²) and placed in a quartz IR cell with KBr windows. Thermal treatment for 2 h at 673 K (277 K min⁻¹) was performed under vacuum in order to remove physisorbed water. After cooling to room temperature, an IR spectrum was recorded as the reference sample. Adsorption of py was then realized, dosing 0.133 kPa at equilibrium for 15 min followed by a thermal treatment at 373 K for 15 min to promote py diffusion. A second spectrum was recorded after removal of physisorbed py by out-gassing at 423 K for 15 min. The characterization of acid sites was effectuated on the difference spectrum obtained by subtraction of the background from the spectrum recorded after py adsorption.

Interaction of py with the Brønsted and Lewis acid sites in the samples gives rise to bands in the 1575–1525 cm⁻¹ and 1470–1435 cm⁻¹ range, respectively. Concentrations of the sites were calculated using the integrated absorbance of the bands and the molar extinction coefficients as measured by Emeis *et al.*, *i.e.*, 2.22 cm mol⁻¹ for Lewis sites and 1.67 cm mol⁻¹ for Brønsted sites. The weight and surface area of the disk was also considered.

The gaseous products of the pyrolysis test were analyzed using an Agilent 7890A instrument equipped with an FID and two TCD detectors, and an HP-PONA silica capillary column from Agilent, 50 m × 0.20 mm. The liquid products were analyzed by Agilent 5975C Inert MSD with a Triple-Axis detector. A combination of two silica capillary columns was used for the separation: a slightly polar DB-17 from J & W Scientific, 30 m × 0.32 mm, and a nonpolar HP-5 from Agilent, 30 m × 0.25 mm. Helium at a flow rate of 2.5 cm³ min⁻¹ was used as the gas carrier. Thermogravimetric analyses (TGA) were performed on the solid products in order to verify the inorganic carbon content. The outlet gas from the TGA was analyzed using a HPR-20 quadrupole mass spectrometer (Hiden Analytical) with regard to CO₂.

RESULTS AND DISCUSSION

Characterization of the obtained catalysts

Representative SEM micrographs of NZ and ZSM-5 are shown in Fig. 1. ZSM-5 consisted of prismatic, twinned crystals, typical for the MFI phase. Some of the crystals were sprinkled with small flower-shaped crystals (marked with “a” in Fig. 1a), which were reported to belong to ZSM-5 with a different Si/Al mole ratio than that of the bulk sample.¹⁵ The shape and color contrast in the SEM image of NZ indicates the presence of different mineral phases. The phase in which the Si/Al molar ratio was higher than 4 corresponds to the zeolite – clinoptilolite, which was examined in detail by EDS (Fig. 1b).

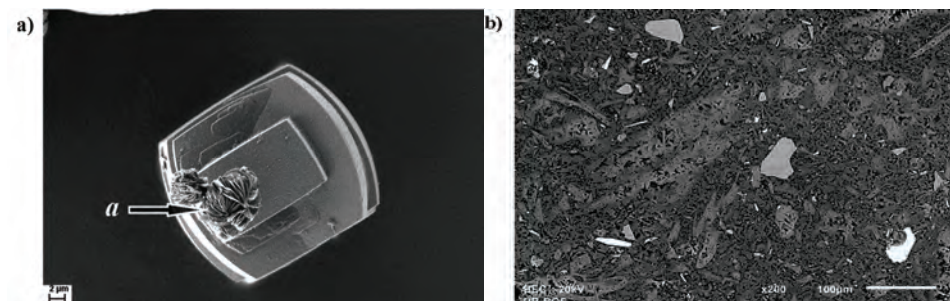


Fig. 1. SEM images of a) ZSM-5 and b) NZ.

The results of EDS analysis of the parent and the MO-loaded samples are given in Table I. The increase in the Ca and Mg content in CaO–NZ and MgO–NZ, respectively, in comparison to the parent sample (NZ) confirmed that the clinoptilolite was enriched with Ca, *i.e.*, Mg.

TABLE I. Average chemical composition of the parent (NZ and ZSM-5) and the MO-loaded zeolites obtained by EDS (wt. %)

Oxide	ZSM-5	CaO/ ZSM-5	MgO/ ZSM-5	NiO/ ZSM-5	Cu ₂ O/ ZSM-5	NZ	CaO–NZ	MgO–NZ
SiO ₂	97.8	85	54.6	96.8	95.8	72.2	61.2	66.0
Al ₂ O ₃	1.2	0.6	0.7	1.2	0.8	12.2	10.7	11.1
Na ₂ O	1	0.2	0.8	0.1	0.7	0.5	0.5	0.6
CaO		14.2				5.0	13.9	4.8
MgO			44			1.0	1.1	9.0
NiO				1.8				
Cu ₂ O					2.7			
Cl ₂ O						0.0	5.4	1.8
K ₂ O						2.5	1.6	2.1
TiO ₂						0.9	0.9	1.3
Fe ₂ O ₃						5.7	4.7	3.3

Decreases in the SiO₂, Al₂O₃ and Na₂O contents in favor of the metal oxide content, in comparison to the parent sample (ZSM-5), was observed for all modified samples.

XRD data were used for qualitative and quantitative analysis of CaO–NZ and MgO–NZ samples. Qualitative analysis showed the presence of anorthite, biotite, quartz, clinoptilolite, MgO in MgO–NZ, and CaO in CaO–NZ. The first three mineral phases are usually present in zeolitic tuffs.¹⁶ Quantitative analysis by the Rietveld method revealed 0.42 wt. % of CaO (JCPDS 37-1497) in CaO–NZ and 3.66 wt.% of MgO (JCPDS 89-7746) in MgO–NZ (Fig. 2).

On comparing the results of Rietveld and SEM/EDS analyses, it is evident that the Rietveld analysis gave lower values for the CaO and MgO contents in the MO-modified NZ samples than that obtained by elemental analysis (SEM/EDS). This could be explained by the facts that not only crystalline but also amorphous oxides form during the modification and/or by the incomplete transformation of Ca/Mg into the corresponding oxides. It seems likely that not all the crystallographic sites in the clinoptilolite lattice are available for the transformation of hydrous cations into oxide species.

Moreover, the XRD patterns of ZSM-5 samples (given in Fig. S-1 of the Supplementary material to this paper) showed that the modification affected the ZSM-5 crystal structure in different manner depending on the oxide type. Thus, the crystal structure of ZSM-5 collapsed during modification with CaO and MgO. The XRD patterns of CaO/ZSM-5 and MgO/ZSM-5 (not shown) display

only diffraction lines corresponding to CaO/MgO. The modification with NiO did not influence the crystallinity of ZSM-5, whereas the modification with Cu₂O led to a transformation of ZSM-5 into to a novel unknown crystal phase.

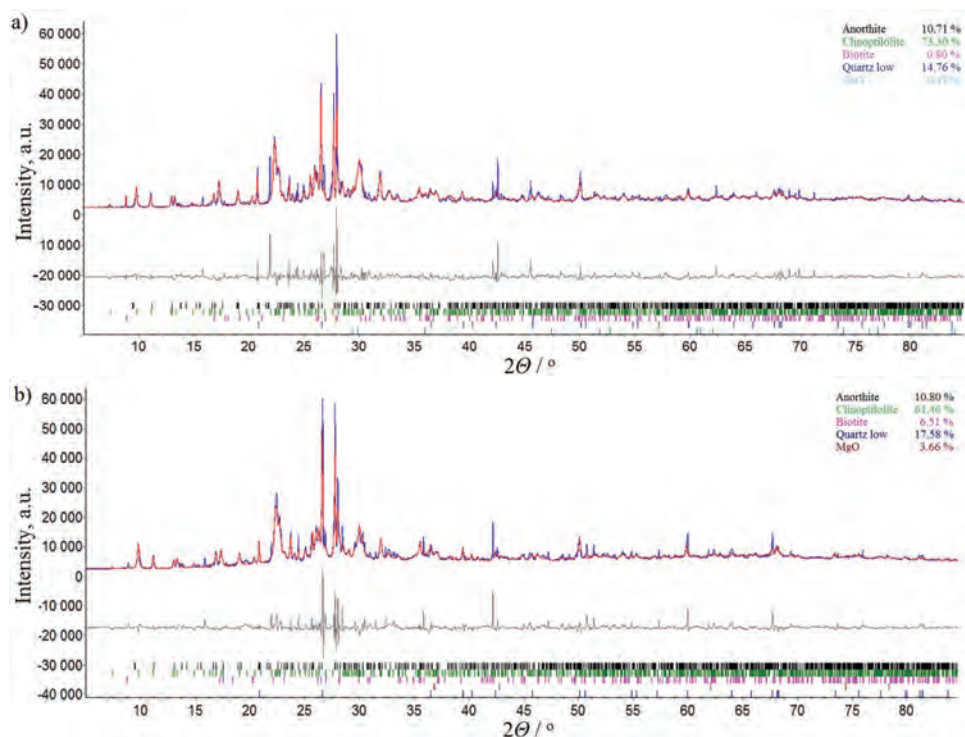


Fig. 2. Final Rietveld plot of: a) CaO–NZ and b) MgO–NZ. Observed – blue line; calculated – red crosses; difference – black line; calculated reflection positions for each phase are represented with different colored tick marks.

The results of specific surface area measurements are summarized in Table II. The results showed that the modification of NZ with CaO decreased the specific surface area of NZ, which could be attributed to the size of CaO particles that blocked the pore openings of the clinoptilolite lattice. On the other hand, the specific surface area of MgO–NZ was larger than that of NZ, indicating that MgO particles could be smaller than the CaO particles. Furthermore, the specific surface areas of CaO/ZSM-5 and MgO/ZSM-5 were significantly smaller than that of ZSM-5, confirming that the crystal structure of ZSM-5 had collapsed. The modification of ZSM-5 with NiO increased the specific surface area, indicating that the size of the NiO particles could be nano-metric.⁸ Finally, the specific surface area of Cu₂O/ZSM-5 was smaller than that of ZSM-5, which could be

explained by structural transformation of ZSM-5 and the formation of a novel crystalline product.

TABLE II. BET specific surface area of the zeolite materials

Sample	$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$
NZ	30.9
CaO–NZ	17.5
MgO–NZ	45.4
ZSM-5	229.8
CaO/ZSM-5	99.8
MgO/ZSM-5	53.4
NiO/ZSM-5	311.4
Cu ₂ O/ZSM-5	135.8

The acid sites of the zeolite samples were characterized and quantified by py absorption using FTIR spectroscopy. Interaction of py with the Brönsted and Lewis acid sites of the samples gave rise to bands in the 1575–1525 cm^{-1} and 1470–1435 cm^{-1} range, respectively. For CaO– and MgO–NZ, the concentration of Brönsted sites was practically negligible (1 $\mu\text{mol g}^{-1}$). Both the samples showed the presence of the Lewis acid sites with concentrations that were higher on MgO–NZ than on both CaO–NZ and NZ. Two IR vibration bands at 1449 and 1456 cm^{-1} , marked in Fig. S-2a of the Supplementary material, can be clearly observed and assigned to the interaction of lattice Al^{3+} and py.

The concentrations of the acid sites on the catalysts are summarized in Table III. It is evident that the unmodified NZ contained both Brönsted and Lewis sites, which were ascribed to the presence of extra-framework cations (Lewis sites) or to silanol groups (Si–OH) (Brönsted sites) formed on the surface of the zeolites.¹⁷ The presence of MgO (MgO–NZ) significantly increased the concentration of Lewis acid sites on clinoptilolite, whereas the presence of CaO generally decreased the acidity (CaO–NZ).

TABLE III. Quantitative evaluation ($\mu\text{mol g}^{-1}$) of the Lewis and Brönsted acid sites on the zeolite samples; n.d. – no data

Sample	Brönsted sites	Lewis sites (1456–1448 cm^{-1})
ZSM-5	n.d.	65
CaO/ZSM-5	n.d.	51
NiO/ZSM-5	17	53
Cu ₂ O/ZSM-5	n.d.	33
NZ ⁸	7.9	14.2
MgO–NZ	1.6	38
CaO–NZ	1.4	11

It can be noticed that the modification of ZSM-5 with the metal oxides changed the acidity (Fig. S-2b of the Supplementary material). The presence of

NiO introduced Brønsted acid sites on ZSM-5. These sites were referred to as the bridging hydroxyl groups consisting of protons bonded to the zeolite lattice in the micropores (Si–O(H)–Al).¹⁷ The modification of ZSM-5 with the other oxides decreased the acidity of ZSM-5.

Results of the catalytic test

The prepared catalysts were tested in the fast pyrolysis of hardwood lignin using the pyrolysis unit schematically shown in Fig. S-3 of the Supplementary material.

The pyrolysis products consist of a liquid product (*i.e.*, bio-oil), a gas mixture and a solid residue. Since the bio-oil has the highest industrial impact, this product was analyzed in detail in the present work.

The compounds identified in the bio-oil were classified into eight groups: hydrocarbons, phenols, acids/esters, alcohols/ethers, carbonyls/aldehydes, polycyclic aromatic hydrocarbons (PAHs), phenylpropanoid and heavy compounds (phenols with $M_r > 164$). These groups were then classified into desirable and undesirable,¹⁸ according to their impact on the effective and the environmentally friendly use of the bio-oil. For example, phenols and hydrocarbons are desirable fractions as they have a high commercial value as industrial chemicals. Acids are undesirable since acidic bio-oils are corrosive for engines. Furthermore, carbonyls and heavy compounds are undesirable since they reduce the chemical stability of the bio-oil. PAHs are hazardous for the environment due to their mutagenic and carcinogenic properties.

The effects of the type of catalysts, the reaction temperature and the metal-oxide content on the yield and composition of the bio-oil were investigated.

The types of the catalysts had different influences on the yield of bio-oil as can be seen from Table IV. In the table, the results from the pyrolysis experiments (under similar conditions) using an inert solid material (silica) and system without catalysts are also given. In this manner, the results of the catalytic pyrolysis process with the prepared catalysts could be compared with those from a conventional (non-catalytic) pyrolysis process.

TABLE IV. Product yields (wt. %) from the pyrolysis of hardwood lignin

Sample	Solid phase	Liquid phase	Gas phase
Without catalyst	62.2	27.2	10.6
Inert	70.5	21.4	8.2
MgO–NZ	59.3	27.7	12.9
CaO–NZ	59.2	26.7	14.1
MgO/ZSM-5	61.4	23.8	14.9
CaO/ZSM-5	60.8	25.5	13.6
Cu ₂ O/ZSM-5	57.4	25.0	17.6
NiO/ZSM-5	55.1	34.8	10.1

The highest yield was obtained in the presence of NiO/ZSM-5 (34.8 wt. %) whereas other catalysts gave lower liquid yield than that obtained for the non-catalytic pyrolysis (27.2 wt. %). On the other hand, all catalysts except NiO/ZSM-5 led to an increase in the gas production, which reached 17.6 wt. % for Cu₂O/ZSM-5. The results are given in Table V and shown in Fig. 3.

TABLE V. Composition of the organic phase (wt. % of the organic fraction) in bio-oil; $M > 164 \text{ g mol}^{-1}$ phenols were not found

Catalyst	Phenol	HC	Acids/ esters	Alcohols/ ethers	Carbonyls/ aldehydes	PAHs	Phenyl- propanoid
Without catalyst	66.6	11.5	0.0	12.9	1.3	0.0	0.0
Inert	66.8	2.4	0.0	21.6	0.0	0.0	0.0
MgO-NZ	77.6	14.5	0.0	6.2	0.0	0.0	0.0
CaO-NZ	77.8	14.8	0.5	5.7	1.2	0.0	0.0
MgO/ZSM-5	79.7	0.5	1.8	15.4	0.0	0.6	0.0
CaO/ZSM-5	84.1	4.2	4.9	1.9	0.0	1.2	0.5
Cu ₂ O/ZSM-5	77.2	15.0	0.0	7.2	0.0	0.0	0.0
NiO/ZSM-5	68.7	12.2	7.4	3.5	2.3	0.0	0.0

The results in Table V and Fig. 3 clearly indicate that the presence of the catalysts led to an increase in the yield of phenol and the increase was most noticeable in the presence of CaO/ZSM-5 (84.1 wt. %). Moreover, the catalysts did not increase significantly the content of PAHs and heavy compounds compared to the non-catalytic experiment. The catalysts exhibited small changes in the acids/esters and carbonyls/aldehydes production with the exception of CaO/ and NiO/ZSM-5, which produced a significant amount of acids/esters (4.9 and 7.4 wt. %, respectively).

The influence of the reaction temperature on the liquid yield was examined for catalysts that gave the highest liquid yield (NiO/ZSM-5) and the highest amount of phenols (CaO/ZSM-5). The results are summarized in Table S-I of the Supplementary material.

An increase in the temperature also affected the yield of bio-oil. Both catalysts gave the highest amount of bio-oil at 773 K. In addition, an increase in temperature affected the composition of the bio-oil. The results are summarized in Table S-II of the Supplementary material.

It is evident that the influence depends on the catalyst type. The presence of CaO/ZSM-5 led to an increase of the desirable and a decrease of the undesirable fractions at higher temperatures, whereas the trend was opposite in the presence of NiO/ZSM-5.

The influences of the MO content on the liquid yields are summarized in Table S-III of the Supplementary material.

It is evident that an increase in the CaO amount on ZSM-5 slightly decreased the yield of bio-oil. On the other hand, an increase in the NiO amount on ZSM-5

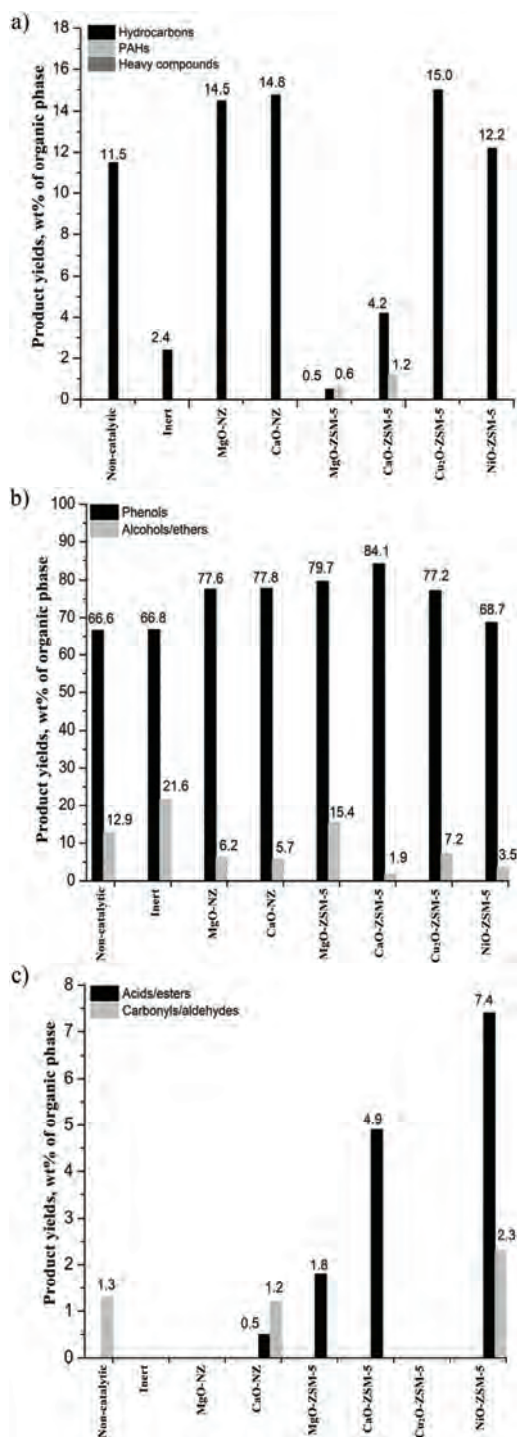


Fig. 3. Product yields (wt. % of the organic phase): a) hydrocarbons, PAHs and heavy compounds; b) phenols and alcohols/ethers and c) acids/esters and carbonyls/aldehydes.

increased the yield of the bio-oil. At this moment, an explanation for the opposite trend could not be offered since the structure of ZSM-5 collapsed during the modification with CaO. However, it seems likely that the type of metal oxide affects the mechanism of pyrolysis and it could not be excluded that the oxide carrier (*i.e.*, ZSM-5) also influenced the pyrolysis process.

Table S-IV of the Supplementary material shows that not only the yield, but also composition of the bio-oil was influenced by the MO amount. An increase of the MO content increases the amounts of phenols and undesirable acids/esters, and decreases the amounts of both hydrocarbons (HCs) and alcohols/ethers.

Preliminary analysis of solid residues analyzed by GC-MS showed that the residues are C-rich and that amount of liberated CO₂ depended on the catalyst (31.7 wt. % CO₂ was obtained with CaO/ZSM-5 and 52.3 wt. % with NiO/ZSM-5).

Finally, the GC analysis of the gas products indicated that there was no significant difference between catalytic and non-catalytic experiments.

CONCLUSIONS

Natural clinoptilolite and synthetic ZSM-5 were studied as carriers for several metal oxides in order to test their catalytic activity in fast pyrolysis of hardwood lignin. The studied catalysts affected the pyrolysis mechanism in different manners depending on the zeolite type and type and amount of metal oxide. The highest bio-oil yield was obtained in the presence of NiO/ZSM-5 (34.8 wt. %), while the highest content of phenols in bio-oil was obtained in the presence of CaO/ZSM-5 (84.1 wt. %). For CaO/ZSM-5, it was found that the crystal structure of ZSM-5 collapsed during the modification with CaO.

Increasing the amount of NiO on ZSM-5 increased the yield of the bio-oil while increasing the CaO amount decreased it. This was explained by acidity and specific surface area, considering that the presence of NiO on ZSM-5 changed the concentration and type of the acid sites on the ZSM-5, and increased its specific surface area. The reaction temperature also influenced the pyrolysis mechanism, showing the highest bio-oil and phenol yields at 773 K.

All the obtained results indicated that NiO/ZSM-5 could be considered as a perspective catalyst for further optimization and use in fast pyrolysis of hardwood lignin. Since the crystallinity of the catalyst did not change during the catalytic test, one of the important objectives of future investigation would be performing long-term stability tests.

SUPPLEMENTARY MATERIAL

XRD patterns, FTIR spectra, the scheme of experimental pyrolysis unit, the influence of temperature and the MO content on bio-oil yield and composition of the organic phases are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

Acknowledgments. The authors gratefully acknowledge BRISK- Biofuels Research Infrastructure for sharing knowledge, Innventia AB, SINTEF and the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172018).

ИЗВОД

ПИРОЛИЗА ЛИГНИНА У ПРИСУСТВУ КАТАЛИЗАТОРА НА БАЗИ ПРИРОДНОГ
ЗЕОЛИТА И ZSM-5

ЈЕЛЕНА А. МИЛОВАНОВИЋ¹, RUTH ELISABETH STENSRØD², ELISABETH M. MYHRVOLD²,
ROMAN TSCHENTSCHER², МИХАЕЛ СТÖCKER², СЛАВИЦА С. ЛАЗАРЕВИЋ³ и НЕВЕНКА З. РАЈИЋ³

¹Иновациони центар Технолошко–металуршког факултета, Универзитета у Београду, Карнегијева 4, 11000 Београд, ²SINTEF, Forskningsveien 1, 0314 Oslo, Norway и ³Технолошко–металуршког факултета, Универзитета у Београду, Карнегијева 4, 11000 Београд

Припремљени су и тестирани различити оксиди метала везани за две врсте зеолита: 1) природни клиноптилолит (NZ) и 2) синтетички зеолит, ZSM-5, као катализатори у брзој пиролизи тврдог лигнина. NZ је једноставним двостепеним поступком који се састојао од јонске измене и накнадне калцинације на 773 К модификован оксидима калцијума и магнезијума. Претходно синтетисан ZSM-5 је такође модификован са неколико врста оксида (Ni, Cu, Ca и Mg) коришћењем влажне импрегнације и калцинације на 873 К. Припремљени катализатори су окарактерисани рендгенском дифракционом анализом, скенирајућом електронском микроскопијом спрегнутом са симултаном енерго-дисперзивним спектрометријом (SEM/EDS) и мерењем специфичне површине (ВЕТ методом). Кисела места на катализаторима окарактерисана су и квантификована адсорпцијом пиридина уз инфрацрвену спектроскопију са Фуријевом трансформацијом (FTIR). Припремљени катализатори испољавају каталитичку активност у зависности од начина модификације зеолита, реакционе температуре и садржаја оксида на зеолиту. Највећи принос корисног фенола у био-уљу добијен је са NiO/ZSM-5 (34,8 мас. %) који има највећу специфичну површину и највећу концентрацију Бренштедових и Луисових киселих места. Присуство испитиваних катализатора током пиролизе не доприноси значајно повећању садржаја полицикличних ароматичних угљоводоника нити једињења са великом моларном масом у односу на не-катализован процес.

(Примљено 31. јула, ревидирано 17. октобра, прихваћено 6. новембра 2014)

REFERENCES

1. A. V. Bridgwater, *Therm. Sci.* **8** (2004) 21
2. Sh. Li, Sh. Xu, Sh. Liu, Ch. Yang, Q. Lu, *Fuel Process. Technol.* **85** (2004) 1201
3. B. S. Kang, K. H. Lee, H. J. Park, Y. K. Park, J. S. Kim, *J. Anal. Appl. Pyrolysis* **76** (2006) 32
4. J. Lédé, F. Broust, F. T. Ndiaye, M. Ferrer, *Fuel* **86** (2007) 1800
5. J. Du, P. Liu, Z. Liu, D. Sun, Ch. Tao, *J. Fuel Chem. Technol.* **38** (2010) 554
6. A. Pattiya, *Bioresource Technol.* **102** (2011) 1959
7. D. Mourant, C. Lievens, R. Gunawan, Y. Wang, X. Hu, L. Wu, S. Sh. A. Syed-Hassan, Ch. Z. Li, *Fuel* **108** (2013) 400
8. N. Rajić, N. Zabukovec Logar, A. Rečnik, M. El-Roz, F. Thibault-Starzyk, P. Sprenger, L. Hannevold, A. Andersen, M. Stöcker, *Micropor. Mesopor. Mater.* **176** (2013) 162
9. Dj. Stojakovic, J. Milenkovic, N. Daneu, N. Rajic, *Clay Clay Miner.* **59** (2011) 277
10. L. M. Camacho, R. R. Parra, S. Deng, *J. Hazard. Mater.* **189** (2011) 286
11. W. J. Kim, M. Ch. Lee, D. T. Hayhurst, *Micropor. Mesopor. Mat.* **26** (1998) 133

12. A. Masalska, *Catal. Today* **65** (2001) 271
13. A. X. S. Bruker, TOPAS V2.1, *General profile and structure analysis software for powder diffraction data – User's Manual*, Bruker AXS, Karlsruhe, 2003
14. C. A. Emeis, *J. Catal.* **141** (1993) 347
15. S. Sang, F. Chang, Z. Liu, Ch. He, Y. He, L. Xu, *Catal. Today* **93–95** (2004) 729
16. Š. Cerjan Stefanović, N. Zabukovec Logar, K. Margaret, N. Novak Tušar, I. Arčon, K. Maver, J. Kovač, V. Kaučič, *Micropor. Mesopor. Mater.* **105** (2007) 251
17. A. Godelitsas, D. Charistos, A. Tsipis, C. Tsipis, A. Filippidis, C. Triantafyllidis, G. Manos, D. Siapkias, *Chem. Eur. J.* **7** (2001) 3705
18. K. S. Triantafyllidis, E. F. Iliopoulou, E. V. Antonakou, A. A. Lappas, H. Wang, Th. J. Pinnavaia, *Micropor. Mesopor. Mat.* **99** (2007) 132.