

MICROWAVE-ASSISTED DEPOLYMERISATION OF BIOLIGNIN™ IN THE PRESENCE OF ZEOLITE-BASED CATALYSTS

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ABSTRACT

In this work a microwave-assisted depolymerisation of lignin in the presence of zeolite-based catalysts was studied in order to obtain a valuable bio-oil. Catalytic activity of H-ZSM-5, H-Y, H-BETA and H-Mordenite containing nano-NiO particles was investigated in the depolymerisation of Biolignin™. The catalysts were prepared by mechanochemical dry milling (MCDM) method following by calcination under air at 400 °C. The highest bio-oil yield of 8.78 wt. %, was obtained in the presence of NiO-containing H-ZSM-5.

Keywords: lignin, depolymerisation, zeolite, microwave, nickel oxide

INTRODUCTION

Lignin is an amorphous, aromatic and the second most abundant natural polymer in the world, exceeded only by cellulose. It is composed of up to three different phenylpropane monomers (guaiacyl, syringyl and *p*-coumaryl alcohol) which are connected through a variety of alkyl, aryl and ether linkages via oxidative cross-coupling reactions making that lignin can be considered as a reservoir of variety of industrial useful chemicals. [1] However, the linkages in the lignin network can hardly be broken making its decomposition a challenging task.

Microwave-assisted depolymerisation has been considered as one of the promising methods for conversion of lignin to useful chemicals. Namely, certain strong chemical bonds in the lignin network can be fractured under microwave magnetic field. [2, 3].

Zeolites with their open-framework lattice, shape selectivity and acidity have proved to be effective catalysts and/or catalyst supports in lignin valorization. [4-6] It has been reported that temperature of lignin decomposition decreases in the presence of nano-sized NiO particles. [7] However, the activity of the nano-particles decreases by time due their thermodynamical instability which makes the nano-particles improper for the catalytic use. In order to stabilize nanoparticles different zeolites have been employed as nano-particles carrier. [4]

For the purpose of this study H-ZSM-5, H-BETA, H-Y and H-Mordenite were investigated as the matrix for nano-NiO. The MCDM has been used for the preparation of catalysts and the obtained products were checked in the microwave-assisted depolymerisation of Biolignin™. The effect of type of zeolite on yield of bio-oil was investigated.

EXPERIMENTAL

A series of the catalysts was prepared starting from nickel(II) chloride (Aldrich, p.a.). In a typical procedure zeolite sample in H-form (H-ZSM-5, H-BETA, H-Y and H-Mordenite, Zeolyst International) was grinded with the 2 wt. % of the Ni(II) salt in a Retsch PM-100 planetary ball mill using a 125 ml reaction chamber and 10 mm stainless steel balls. Milling conditions were 10 min at 350 rpm. The products were then calcined at 400 °C under air for 4 h. The obtained catalysts were characterized by different characterization techniques: powder X-ray Diffraction (PXRD, Bruker D8 Discover), N₂ physisorption (ASAP 2010 volumetric adsorption analyser from Micrometrics) and Transmission Electron Microscopy (TEM, FEI Tecnai G2 20 S-TWIN Scanning Transmission Electron Microscope System).

Depolymerisation of BioligninTM (supplied by CIMV, France) was carried out using a CEM Discover microwave reactor mode. Microwave power was set at 300 W over 1 h. Formic acid (FA) was used as a proton-donor solvent. The microwave vessel was filled with a lignin/catalyst ratio of 1/1 and a solid/liquid ratio of 1/12.5.

The products of the depolymerisation were separated using the procedure described by Toledano et al. [8] The product mixture was separated by filtration, liquid phase acidified to pH 1-2 and ethyl acetate was added until the solvent was colorless. In the next step Na₂SO₄ was added to remove any water remaining and separated by filtration. Finally, ethyl acetate was evaporated to obtain phenolic oil.

Yield of the obtained bio-oil was calculated gravimetrically as referred to the initial lignin content. The measurement was done with the precision of 0.001 g.

RESULTS AND DISCUSSION

Table 1 shows the textural properties of the prepared catalysts denoted as NiO/H-zeolite. It is evident that the MCDM procedure influence surface area of the zeolite, pore volumes and pore diameters in difference manner depending of the zeolite type.

Table 1. Textural properties of the prepared catalysts.

Catalyst	Si/Al	S _{BET} [m ² g ⁻¹]	Pore volume [mL g ⁻¹]	Pore diameter [nm]
H-ZSM-5	30	330	0.15	8.00
NiO/H-ZSM-5		322	0.20	9.90
H-BETA	75	650	0.90	9.40
NiO/H-BETA		537	0.83	9.50
H-Y	30	707	0.50	11.1
NiO/H-Y		642	0.30	9.10
H-Mordenite	20	552	0.80	18.0
NiO/H-Mordenite		412	0.16	13.6

The PXRD patterns given in Figure 1 show that the modification did not affect the parent zeolite frameworks. Due to a low nickel content in the catalyst the diffractions correspond to Ni phase are not evident.

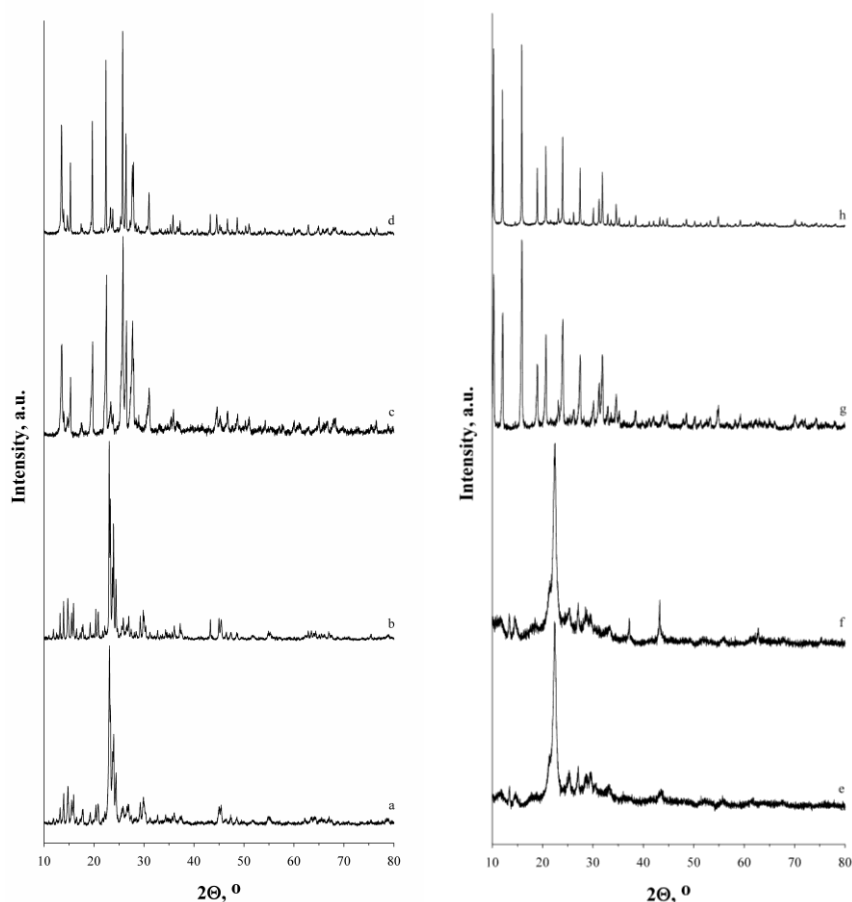


Figure 1. PXRD patterns of parent and Ni-containing zeolites: a) H-ZSM-5, b) NiO/H-ZSM-5, c) H-Mordenite, d) NiO/H-Mordenite, e) H-BETA, f) NiO/H-BETA, g) H-Y and h) NiO/H-Y.

An insight in the catalyst texture was obtained by a TEM analysis. TEM micrograph of NiO/H-ZSM-5 is given in Fig. 2. Electron diffraction pattern confirmed the presence of NiO bunsenite. A diameter of oxide particles is about 60 nm (Table 2).

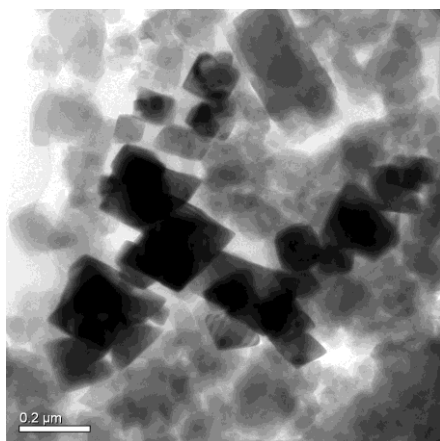


Figure 2. TEM micrograph of NiO/H-ZSM-5.

Table 2. Crystallite size of NiO phase.

Catalyst	Si/Al	Crystallite size [nm]
NiO/H-ZSM-5	30	66.5
NiO/H-BETA	75	*
NiO/H-Y	30	63.3
NiO/H-Mordenite	20	64.6

*Because of low crystallinity of NiO/H-BETA the analysis of NiO crystallite size was not possible.

Since the diameter of the particles exceed the pore diameter of the zeolite lattices, the nano-particles of NiO are formed at the surface of the zeolites.

Yields of obtained bio-oil are summarized in Table 3. The best bio-oil yield (8.78 wt.%) is obtained in the presence of NiO/H-ZSM-5.

Table 3. Effect of type of catalyst on bio-oil yield.

Catalyst	Si/Al	Bio-oil [wt.%]
NiO/H-ZSM-5	30	8.78
NiO/H-BETA	75	4.62
NiO/H-Y	30	5.42
NiO/H-Mordenite	20	2.12

Preliminary GC-MS analysis (not shown) indicated that not only yield but also composition of the bio-oil is influenced by zeolite type.

CONCLUSION

H-ZSM-5, H-BETA, H-Y and H-Mordenite were used as carrier for NiO nanoparticles obtained by MCDM method. The results show that the MCDM method can be used in the preparation of NiO-containing H-zeolite. The catalysts are active in the microwave-assisted depolymerisation of BioligninTM. The yield and composition of the bio-oil depends of zeolite type. The highest bio-oil yield was obtained in the presence of NiO/H-ZSM-5.

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