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The development of the method of low-temperature peat pyrolysis on the basis of alumosilicate catalytic system

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Abstract

The catalytic pyrolysis of peat was investigated over several iron-containing zeolites of different structure (Beta, Y, Mordenite, ZSM-5) and SiO_2/Al_2O_3 molar ratios at 410 °C in a batch mode. The overall activity of iron-containing catalysts was similar, being however significantly higher than activity of parent materials. Additionally, iron-modified zeolites afforded higher ethene and propene selectivity than corresponding proton forms.

Keywords: Zeolites; Biomass; Pyrolysis

1. Introduction

Biomass is an important source of energy in the world, accounting for about 15% of the world's primary energy consumption. Thermochemical conversion technology, e.g. pyrolysis, gasification and combustion are studied extensively [1–10]. Application of biomass as a source of carbon and energy can be considered sustainable since biomass is a CO_2 neutral resource in the life cycle, causing almost zero net emissions of CO_2, which is a primary contributor to the global greenhouse effect. Pyrolysis is known to be an efficient way of converting biomass into gases, oil-like liquid products and char. Flash pyrolysis gives high oil yields, but is energy demanding.

In most biomass gasification processes, air is used as gasifying agent with the result, that a low calorific value gas is generated, which can be used after cleaning in gas-fired engines or gas turbines.

A range of feedstock is available for gasification and pyrolysis and varies from clean biomass to waste fuels containing different amounts of ash, alkaline and emission precursors like N, Cl and S.

Biomass may vary significantly in its physical and chemical properties due to its diverse origins and types. Overall biomass content on Earth is estimated to be around 1836 billion tonnes, which in terms of energy equivalent to 640 billion tonnes of oil. An interesting renewable feedstock is peat, deposits of which are found in many places around the world, notably in Russia and Scandinavia among other places covering a total of around 3% of global land mass.

In Russia ca. 20% of territories contain peat, corresponding to 186 billion tonnes or 37% of all global reserves. According to some estimates the amount of peat in Finland located on 26% of the land area is twice the size of North Sea oil reserves, corresponding to approximately 6.2% annual energy production of Finland.

Although peat has a relatively fast released CO_2 retake rate binding CO_2 on a similar levels to a growing forest, the total regrowth rate of a single peat bog could be slower than 1000 years, therefore peat is considered somewhere between truly renewable bio-fuels and fossilized fuels. Geologically, peat is the youngest and least altered member of the combustible rocks, with time turning into lignite coal. Compared to the other fossil fuels, peat is characterized by the lowest content of fixed carbon along with the highest content of volatile matter.

The use and selection of a suitable catalyst is of crucial importance for the pyrolysis process because it permits to operate at lower temperatures and can provide selectivity towards

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Table 1

Zeolites	Channel system structure description
ZSM-5	Three-dimensional pore system; straight 10 member-ring 5.2 × 5.7 Å channels connected by sinusoidal 5.3 × 5.6 Å channels. Intersection cavity: 9 Å
Mordenite	Two-dimensional pore system; straight 12-ring 7.0 × 6.5 Å channels connected by short alternating 8-ring channels (3 Å)
Beta	Three-dimensional pore system; 12-ring channel in c direction with pores 7.6 × 6.4 Å plus two 12-ring channels in a direction perpendicular to *c*-direction with pores 7.6 × 6.4 Å and 5.5 × 5.5 Å
Y	Three-dimensional pore structure; circular 12 member-ring 7.4 Å windows connecting spherical 11.8 Å cavities (super cages)

the desired products, avoiding any post-process upgrading, thus enhancing the benefit of the process and turning it economically feasible. Zeolites exhibit good activity and selectivity in the catalytic cracking of heavy oil feedstock to produce gasoline and gas-oil. Their success is based on the ability to prepare zeolitic materials with strong Brønsted acidity that can be controlled within a certain range, and which resist high reaction temperatures and catalyst regeneration conditions. The shape selectivity is due to the pore structure that can be controlled by synthesising the suitable zeolite type [11–15].

In this paper results from the catalytic pyrolysis of peat are reported. The zeolitic materials investigated as catalysts are H-Y, H-Beta, H-Mordenite-20, H-ZSM-5 and their iron-modified counterparts.

The structure of Beta zeolite consists of polymorph A, which has straight channels of 7.3 × 6.0 Å and tortuous channels of 5.6 × 5.6 Å and polymorph B, which has straight channels of 7.3 × 6.8 Å and tortuous channels of 5.5 × 5.5 Å [16]. The structure of Mordenite zeolite consists of two channel systems: the perpendicular channel system has 12 MR pores with dimensions 6.7 × 7.0 Å and parallel channel systems have 8 MR pores with dimensions 2.9 × 5.7 Å. The channels are interconnected with small side pockets with diameter 2.9 Å [17]. Detail description of structures of zeolites investigated is given in Table 1.

For the sake of comparison data on non-catalytic pyrolysis and application of naturally occurred bentonite clay are presented.

2. Experimental

2.1. Catalyst synthesis and characterization

Bentonite clay (Armenia) was used as received. The NH_4-Beta-25, NH_4-Beta-150, NH_4-Beta-300, NH_4-Y and NH_4-Mordenite-20 were obtained from Zeolyst International. The numbers denote the SiO_2/Al_2O_3 molar ratios. The NH_4 forms of zeolites were transformed to corresponding proton forms using a step calcination procedure in a muffle oven at 773 K.

Na-ZSM-5 zeolite was synthesized in a 300 ml autoclave (Parr) using method as mentioned in Ref. [18]. Na-ZSM-5 zeolite was transferred to H-ZSM-5 catalyst by ion-exchange with ammonium chloride, followed by drying at 373 K and calcination.

H-Y, H-Beta-300, H-Beta-150, H-Beta-25, H-ZSM-5 and H-Mordenite-20 catalysts were modified with Fe using repeated ion-exchange method (Fluka). The precursor used for the ion-exchange was aqueous solution of ferric nitrate. After conventional repeated ion-exchange Fe zeolites were dried at 373 K and calcined at 773 K in a muffle oven.

The proton forms of the zeolite catalysts were characterized by X-ray powder diffraction and nitrogen adsorption. The acidity of the investigated samples was measured by infrared spectroscopy (ATI Mattson FTIR) using pyridine (≥99.5%, a.r.) as a probe molecule for qualitative and quantitative determination of both Brønsted and Lewis acid sites. The samples were pressed into thin self-supported wafers (10–12 mg/cm^2). Pyridine was first adsorbed for 30 min at 100 °C and then desorbed by evacuation at different temperatures (250 and 450 °C) to obtain a distribution of acid sites strengths. All spectra were recorded at 100 °C with a spectral resolution equal to 2 cm^{-1}. Spectral bands at 1545 and 1454 cm^{-1}, respectively, were used to identify Brønsted (BAS) and Lewis acid sites (LAS). The amounts of BAS and LAS were calculated from the intensities of corresponding spectral bands by using the molar extinction coefficients reported by Emeis [19].

2.2. Catalyst testing

Experiments were conducted in a tubular reactor (20 ml) operating in a batch mode. The reactor has a fitting for gas outlet connected to an auto sample. The amount of released gases was measured with an aid of an eudiometer. The heat of combustion of pyrolysis gases was determined by the method described in Ref. [20].

Amount of peat (from Tver region with 30% decomposition degree, C—53.61%, H—5.96%, N—0.79%, O—40.79%) was 2 g. The catalyst (below 100 μm) amount was typically 0.04 g. The experimental runs started with mechanical mixing thoroughly peat and a catalyst. Pyrolysis tests were conducted at 410 °C. The gaseous products were analyzed by GC (Model 3700) on a silica column (length 1 m, diameter 0.3–0.5 mm, carrier gas—nitrogen with the flow 120 ml/min, detector and column temperature 100 and 50 °C, respectively).

3. Results and discussions

3.1. Catalyst characterization results

The X-ray powder diffraction patterns of H-Beta-25, H-Mordenite-20 and Fe-H-Beta-25 catalysts are given in Figs. 1–3.

It was confirmed from the XRD patterns that modification by H and Fe did not influence the parent structures of zeolites. The surface area of H- and Fe-modified catalysts was determined by nitrogen adsorption using Dubinin method. Prior to the surface area measurements catalysts were outgassed at 473 K for 3 h. The surface area of proton and Fe-modified zeolite catalysts were very high (Table 2) indicating that introduction of Fe did not block the pores of zeolites.

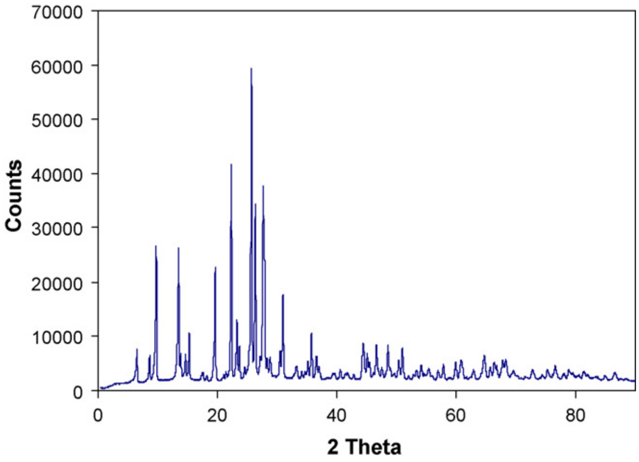

Fig. 1. X-ray powder diffraction pattern of H-Mordenite-20.

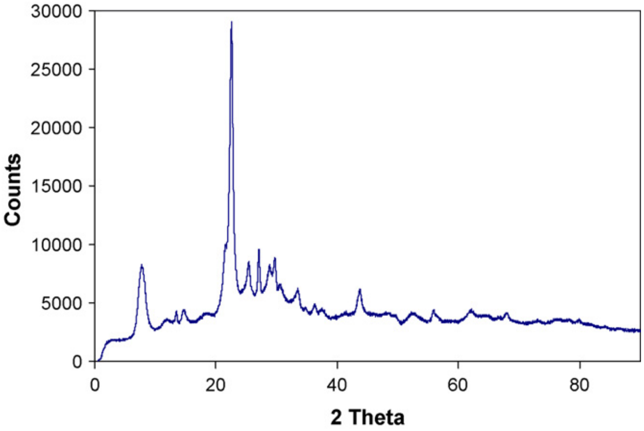

Fig. 2. X-ray powder diffraction pattern of H-Beta-25.

Table 2
Surface area measurements using nitrogen adsorption (Sorptometer 1900, Carlo Erba Instruments)

Catalysts	Surface area (m^2/g) (Dubinin)	Fe content (wt%)
H-Beta-25	807	–
H-Beta-150	664	–
H-Beta-300	805	–
H-Mordenite-20	605	–
H-Y	1218	–
Fe-H-Beta-25	784	2.3
Fe-H-Beta-150	779	1.1
Fe-H-Beta-300	917	ca. 0.1
Fe-H-Mordenite-20	758	2.7
Fe-H-Y	1035	Not determined
Fe-ZSM-5	461	0.2
H-ZSM-5	477	–
Bentonite	Not determined	2.5

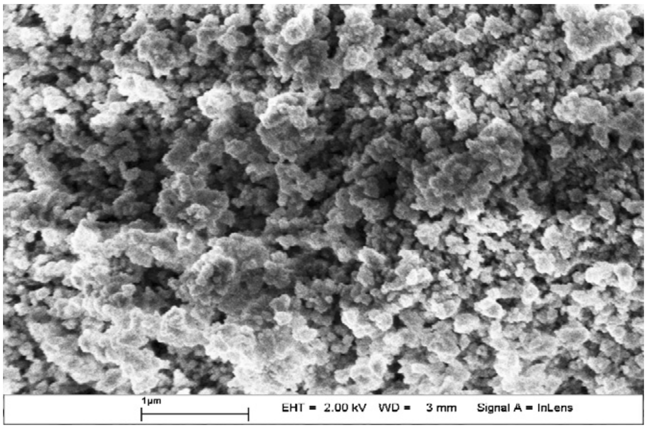

Fig. 4. Scanning electron micrograph of Fe-H-Beta-25.

Increase of surface area in iron-containing zeolites can be attributed to increase of micropores during calcinations procedure.

The H-Y zeolite catalyst exhibited the highest surface area of the proton form catalysts tested and H-ZSM-5 the lowest one.

The scanning electron micrographs of Fe-H-Beta-25 and Fe-H-ZSM-5 showed that the morphology was similar to that of parent Beta and ZSM-5 zeolites. It was inferred from this observation that introduction of Fe did not change the crystal structure of parent zeolites. Scanning electron micrographs of Fe-H-Beta-25 and Fe-H-ZSM-5 are given in Figs. 4 and 5.

The acidity investigation results by FTIR using pyridine as a probe molecule are given in Table 3.

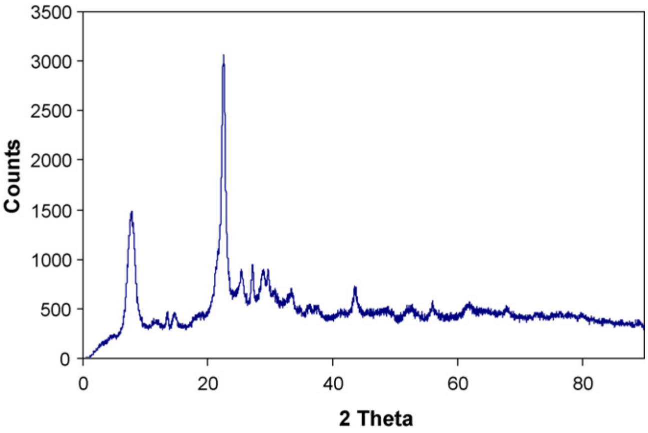

Fig. 3. X-ray powder diffraction patterns of Fe-H-Beta-25 zeolite catalyst.

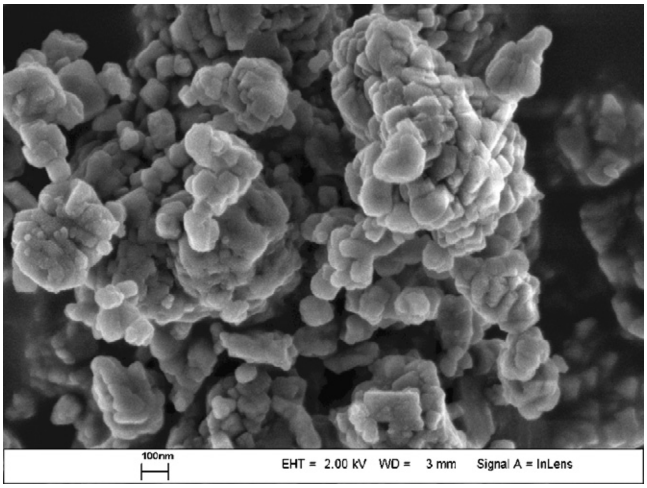

Fig. 5. Scanning electron micrograph of Fe-ZSM-5.

Table 3
Brønsted and Lewis acidity of fresh catalysts

Catalysts	Brønsted acid sites (μmol/g)		Lewis acid sites (μmol/g)	
	250 °C	450 °C	250 °C	450 °C
H-Y	326	62	78	13
H-Mordenite-20	331	212	71	39
H-Beta-25	269	120	162	113
H-Beta-150	176	72	43	10
H-Beta-300	82	10	30	4
Fe-H-Y	292	0	81	0
Fe-H-Mordenite-20	543	90	37	0
Fe-H-Beta-25	221	0	157	0
Fe-H-Beta-150	212	20	145	22
Fe-H-Beta-300	90	0	67	0

H-Mordenite-20 was observed to have the highest Brønsted acidity followed by Fe-H-Y zeolite catalyst at temperatures of 250 and 350 °C.

Among proton forms the H-Mordenite-20 zeolite catalysts exhibited the highest Brønsted acid sites concentration, followed by H-Y catalyst. H-Beta-300 with the highest SiO_2/Al_2O_3 ratio, i.e. with least Al content showed the lowest acidity. H-Beta-25 showed the highest concentration of LAS sites, followed by H-Mordenite-20 and H-Beta-150.

Introduction of Fe resulted in decrease or even disappearance of strong acid sites (e.g. those which retain the probe molecule at 450 °C. Previously similar observations were reported for platinum modifies zeolites [21] and were explained by the interactions between the metal and zeolite supports. Interestingly after iron modification the total concentration of Brønsted sites increased for Fe-H-Beta-150 and Fe-H-Mordenite-20 compared to their proton form counterparts.

3.2. Catalytic activity

Comparison of thermal and catalytic pyrolysis of peat (Fig. 6) shows that in the presence of alumosilicates of either natural (bentonite) or synthetic origin (H-form of zeolites) the heat of combustion of the produced pyrolysis gases increases in two-fold, and the use of the Fe-Beta-300 zeolite leads to the five-fold increase of the heat of combustion.

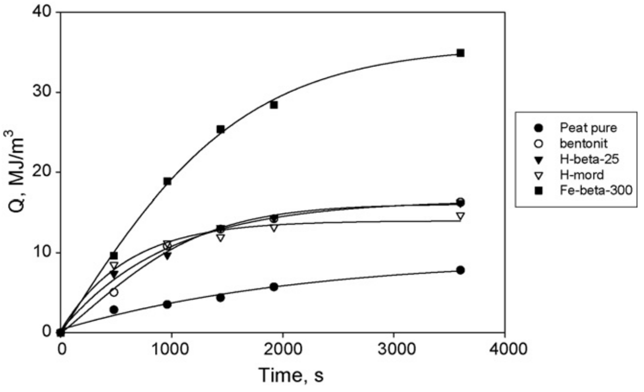

Fig. 6. Dependence of the heats of combustion of the pyrolysis gases with time at 410 °C.

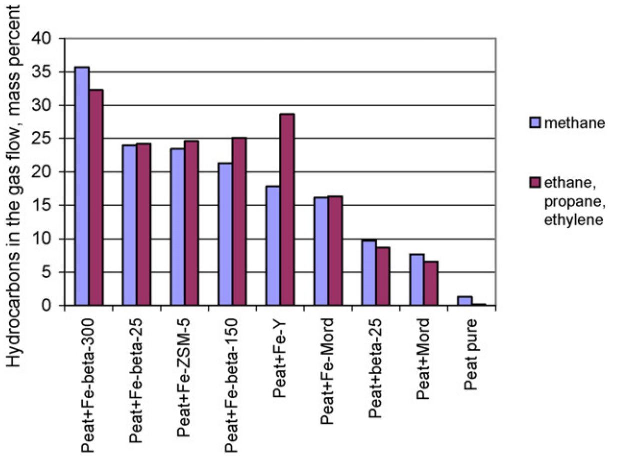

Fig. 7. Content of released gases with time at 410 °C for different H-zeolites and ion-exchanged with Fe.

It was shown previously [22], that bentonite displayed one of the highest activities among tested mineral clays, which was explained by the presence of iron in this sample. To elucidate further the potential impact of iron on catalytic pyrolysis of peat, in Fig. 7 experimental data showing the released amount of gases after ca. 1 h are given.

It is known, that thermochemical conversion of biomass at 400–450 °C does not lead to the noticeable formation of oxygen containing organic products [23], therefore the effectiveness of the pyrolysis catalysts can be estimated by the use of the produced light hydrocarbons (C_1–C_3) profiles, shown in Fig. 7. In the case of the pure peat pyrolysis the minimal amounts of gases were obtained. The introduction of the catalysts led to the essentially increase of the light hydrocarbons amount, mainly methane: comparable results were obtained in the cases of H-Mordenite-20 and beta-25 (7.68 and 9.75% CH_4, respectively) and in the series of Fe-Beta-150, Fe-ZSM-5 and Fe-Beta-25 (21.26, 23.45 and 24.03% CH_4, respectively) modified with iron. It can be seen from the data, that modification with iron essentially decreases the acidity of the catalytic systems (Table 3) and increases the produced light hydrocarbons amount in two to three-fold, compared to the catalysts without any modification (Fig. 7). The maximum of CH_4 (35.65%) and C_2–C_3 (32.24%) content was obtained by the use of Fe-Beta-300,

Table 4
Selectivity data in peat pyrolysis at 410 °C after 1 h

	$(C_{2=}+C_3)/(C_1+C_2)$	Selectivity to methane among light hydrocarbons
Non-catalytic	0	0.64
Bentonite	0.49	0.45
H-Beta-25	0.36	0.53
H-Mordenite-20	0.33	0.50
Fe-H-Beta-300	0.43	0.53
Fe-H-Beta-150	0.61	0.46
Fe-H-ZSM-5	0.56	0.49
Fe-H-Y	0.698	0.38
Fe-H-Beta–25	0.51	0.50
Fe-H-Mordenite-20	0.47	0.50

Table 5
Evolution of methane over Fe-modified zeolites at 410 °C after 1 h

	Mass %						
	Fe-H-Beta-300	Fe-H-Beta-150	Fe-H-ZSM-5	Fe-H-Y	Fe-H-Beta–25	Fe-H-Mord-20	H-Mord-20
Methane	35.65	21.26	23.45	17.81	24.03	16.13	7.68
Ethane	11.80	7.48	7.33	9.54	7.95	5.92	3.06
Ethene	14.68	13.95	13.68	15.58	12.37	3.68	1.63
Propane	5.77	3.65	3.58	3.50	3.89	6.74	1.92
Σ light/Σ all	0.679	0.4634	0.4804	0.4643	0.4824	0.3247	0.1429

and the effectiveness of the catalytic system increased in order Fe-Beta-150 → Fe-Beta-25 → Fe-Beta-300, which is in accordance with the increase of the total surface area 779, 784 and 917 m^2, respectively (Table 2).

Hydrocarbons C_2–C_3 (28.62%) were prevailing in gaseous products of peat pyrolysis over with Fe-Y catalyst in comparison with CH_4 (17.8%), which is probably connected to the super cages structure of Y-zeolites and also to the absence of acid sites (Table 3).

Previously [24] several H-form of zeolites, employed also in the present study, were tested in the catalytic degradation of LDPE. Contrary to our present observation the catalytic activity of different zeolites in catalytic pyrolysis of this polymer differed very much. This effect was explained taking into account the different structures of each zeolite, in particular small pore ferrierite produced a poor performance compared with large pore Beta with Mordenite being an intermediate case.

It is interesting, however, to compare the gas compositions in peat pyrolysis depending on the catalyst nature. It was already noticed before [22] that application of bentonite results in higher amount of hydrocarbons, in particular ethene and propane. In fact the selectivity towards these hydrocarbons is essential in evaluating the catalyst performance, since they have higher heat value compared to ethane and methane. Interestingly that over bentonite (Table 4) the formation of ethene/propane is enhanced.

The difference in behavior of bentonite and H-forms of synthetic zeolites could be explained by the presence of Fe in the natural clay, which is well known to be efficient Fischer-Tropsch synthesis catalyst. The high methane content in H-Mordenite-20 is most probably associated with high Brønsted acidity.

The evolution of light hydrocarbons after 1 h of reaction time over iron-containing samples is presented in Table 5.

As follows from Fig. 6a and Table 5, the methane release is much higher over iron-modified zeolites, than over proton forms. At the same time (Table 4) the product distribution among light hydrocarbons is shifted towards higher than methane products. The lowest selectivity to methane was achieved with bentonite. Note that the natural clay contains 2.5 wt% of iron, possessing at the same time low acidity. Slightly higher $(C_{2=} + C_3)/(C_1 + C_2)$ ratio for bentonite is then coming at the expense of low activity in pyrolysis.

Besides hydrocarbons (Table 5), CO in amount of 0–67.5%, CO_2 from 0 to 89.1%, H_2 from 0.1 to 29% and H_2O from 0 to 24 mol/l were formed as a result of pyrolysis. The degree of peat conversion to pyrolysis gases changed (from 10 to 60%) depending on the conditions and the catalysts used.

4. Conclusions

Catalytic pyrolysis of peat was tested over several iron-containing zeolites. Introduction of Fe in Beta, Mordenite, Y and ZSM-5 zeolites influences the parent structures. It was demonstrated that presence of iron strongly influences catalytic activity and selectivity, e.g. formation of light hydrocarbons (methane, ethane, ethene and propane). Introduction of iron enhances in particular production of ethane and propane, i.e. hydrocarbons with higher than methane heating value.

Application of catalytic pyrolysis in the processing of biogenic fuel (peat) allows obtaining combustible gas (with high heat of combustion) at lower temperatures than in non-catalytic process that solves ecological and technological problems without the reduction of heat-generators efficiency.

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