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Heterogeneous catalytic reaction of microcrystalline cellulose in hydrothermal microwave-assisted decomposition: effect of modified zeolite Beta

José González-Rivera,[a] Ignacio R. Galindo-Esquivel,[a] Massimo Onor,[b] Emilia Bramanti,[b] Iginio Longo[c] and Carlo Ferrari*[c]

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Zeolite Beta, modified with some salts of alkali and alkaline earth metals (K, Zn, Sn), was tested in the hydrothermal heterogeneous catalytic decomposition of microcrystalline cellulose. The reactions were microwave-assisted, where the microwaves were issued by an *in situ* coaxial applicator. Zeolites were subjected to an ion-exchange process which determines the loss of crystallinity in the following order: Sn-Beta-IE > K-Beta > Zn-Beta > acid form H-Beta. The interaction between zeolites and microwaves was studied by irradiating zeolite powder under constant power and the heating response was in the following order: K-Beta > NH_4-Beta > Sn-Beta-IE ≈ Zn-Beta > H-Beta > alumina. These results show that the nature of the counterion strongly affects the absorption of microwaves. The catalytic activity of the different systems on the cellulose decomposition was studied, and resulted in the following order: H-Beta > K-Beta > Zn-Beta > Sn-Beta-IE > alumina, when the reaction medium contained 5 mM HCl. The most active catalyst was the acid zeolite Beta and the identified product distribution under the investigated conditions was (mol yield %): levulinic acid (22.3), glucose (12.1), lactic acid (4.1), formic acid (6.6), 5-(hydroxymethyl) furfural (14.6), acetic acid (15.2) and furfuraldehyde (3.1). The effect of temperature, time and the heterogeneous catalyst reuse (H-Beta) on the yields of different products was investigated. The use of MW radiation with a coaxial applicator instead of conventional heating gave clear advantages in the decrease of the reaction time (45 min) and in terms of yield enhancement (78.6% under the best conditions).

Introduction

The green chemical process design considers the biomass as the base for producing several value-added compounds for different applications, such as energy production and polymer processing.[1] Cellulose is the most abundant fraction of biomass, a partially crystalline, linear, unbranched, glucose-based homopolymer, with relatively high molecular weight, made up of β-1,4-glycosidic bonds. Cellulose can be transformed into several feedstock chemicals such as glucose, furfurals, levulinic acid and other compounds, mixtures or combinations thereof. Different approaches have been established for this purpose using enzymes,[2,3] strong acids,[4] and supercritical and subcritical water.[5]

Microwave (MW) technology is a powerful tool to optimize these processes because it significantly reduces the processing time, energy costs and equipment size with respect to conventional methods.[6] Therefore, in the last few years, special attention has been focused on biomass processing using MW radiation.[7–10] In addition, because of the synergy produced using MW and heterogeneous catalysts in the MW-assisted processes, this seems to be a promising environmentally friendly approach in cellulose chemical processing.[11]

Recently, several Brønsted and Lewis solid acids have been tested as heterogeneous catalysts in cellulose conversion using water as a solvent in conventional heating[11,12] or MW irradiation,[13] and ionic liquids with MW irradiation.[14] Aluminium and siliceous-based inorganic materials, such as alumina, zeolites and other similar frameworks, have shown some advantages due to their robust performance related to their high thermal stability (up to 600 °C), their strong acid sites (Lewis and Brønsted catalytic sites), and their well-known non-toxic and non-corrosive character.[15]

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[a] *Chemical Engineering Department, University of Guanajuato, Noria Alta s/n 36050, Guanajuato, Gto, Mexico*
[b] *Italian National Research Council, C.N.R., Istituto di Chimica dei Composti Organo Metallici (ICCOM) – UOS Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy*
[c] *National Research Council of Italy, C.N.R., Istituto Nazionale di Ottica, (INO) – UOS Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy. E-mail: carlo.ferrari@ino.it; Fax: +39-050-315-2247; Tel: +39-050-315-2245*

Glucose and some water soluble compounds are mainly obtained when zeolites are used as the catalysts, due to hydrolysis and dehydration reactions.[16] Moreover, the product distribution can be modulated if some salts of alkali and alkaline earth metals are used (biorefining).[17,18] High yield and high selectivity for some target products, such as lactic acid, levulinic acid or 5-hydroxymethylfurfural (5-HMF), can be achieved using metal salts of zinc, chromium, aluminium, iron, copper and so on, adopting two different approaches: conventional heating[17] and MW irradiation.[18] However, the use of metal salts involves other issues such as pollution, costs (reuse and product purification) and safety considerations.

Despite the advantages of using electromagnetic radiation and heterogeneous catalysts in carbohydrate chemistry, there are some significant drawbacks. First, several heterogeneous catalysts are not able to interact with MW because they are MW-transparent. In addition, the microwave devices usually used (microwave ovens) have a resonant behaviour and show configurations of non-homogeneous and unpredictable electromagnetic fields. This uneven electromagnetic field can lead to gradients in the reaction mixture temperature, which has a direct effect on the reaction product distribution. Lastly, these resonant devices cannot be easily scaled up to the industrial level. The main limit is represented by the small depth of penetration of MW power in reagents with high dielectric losses. At the typical working frequency of 2.45 GHz, MW power decreases to 1/e in less than two cm of water at 20 °C.

In a previous study we described the set-up and application of a coaxial dipole antenna, a non-resonant microwave applicator.[19] An array of applicators can be utilized to activate uniformly a large volume of reagents with high MW power, each applicator emitting radiation without interfering with the others.

The present study describes the catalytic hydrothermal decomposition reaction of microcrystalline cellulose using the acid form of zeolite Beta and its modification with some alkaline metals (zinc, potassium and tin) as the heterogeneous catalyst. The reactions were microwave-assisted, where the MW were issued by a coaxial applicator. This "controlled" system allowed us to investigate the interaction between the electromagnetic field and the different components of the reaction system (solvent, reagents, catalyst, and products), which have been scarcely investigated.

The MW reactor configuration and the interaction of MW with the catalytic system are discussed. The product distribution observed in the hydrothermal decomposition of microcrystalline cellulose on the different catalytic systems is also presented and discussed.

Results and discussion

The first part of this study reports the characterization of the catalyst and its modified forms, including the interaction with the electromagnetic field. The second part reports the products and yields of the catalytic MW-assisted reaction of microcrystalline cellulose decomposition.

Modified zeolite Beta and its characterization

In order to tune the catalytic properties, zeolite Beta was modified with several metal salts using the conventional liquid ion exchange process. A combination of the acid surface properties (Lewis and Brønsted sites), the valency of extra-frame cation and/or metal oxide particles deposited on the surface can turn zeolites into special bifunctional catalysts.

Table 1 shows the results of elemental analysis using EDS. The Si/Al ratio is increased by the activation process of NH_4-Beta to the acid form H-Beta. This variation can be attributed to the loss of aluminium from the framework because the activation process was performed following a deep-bed high temperature calcination.[20]

In the case of Sn-Beta-IE, HCl and tin tetrachloride promote the isomorphic substitution of tetrahedral aluminium by Sn^{+4} into the zeolite framework.[21] We obtained a high concentration of tin, likely promoted by 0.3 M HCl (Table 1), although no tetrahedral Sn^{+4} form was found as revealed by the absence of the resonance shift at −450 ppm in the ^{119}Sn magic angle spinning NMR (results not shown).[22] This result suggests that tin is present in the form of SnO_2 particles deposited on the surface of the zeolite. A low concentration of chloride was also found and it might be attributed to $SnCl_4{\cdot}5H_2O$ partially precipitated at low pH.

Less incorporation of the cations K^+ and Zn^{+2} into the Beta framework were achieved when compared to the tin treatment. These cations show basic behaviour in catalysis[23] and were easily exchanged into the framework.

The Beta framework of the modified zeolites after the ion exchange process was further characterized using FTIR spectroscopy. The Beta framework shows two main bands associated with vibration of external linkages at 571 and 521 cm^{-1} (Fig. 1).[24] The band at 571 cm^{-1} is assigned to the vibration of five-membered rings and the band at 521 cm^{-1} to the presence of double four-membered rings. Changes in the intensity of these bands can be associated with changes in crystallinity.[25]

The relative crystallinity reported in Table 1 was calculated on the basis of the integrated area of the bands at 571 and 521 cm^{-1} of FTIR spectra normalized with respect to the band at 1095 cm^{-1} (100% crystallinity was assigned to the acid form H-Beta and it was used as the reference).

Zeolite Beta treated with the different cation metals showed loss of crystallinity as the intensity of both adsorption bands

Table 1 Composition of zeolite catalyst obtained from EDS analysis

Zeolite	Si (w/w)	Al (w/w)	M load (% w)	Si/Al ratio	Relative crystallinity[c] 571 cm^{-1}	Relative crystallinity[c] 521 cm^{-1}
H-Beta[a]	53	3	—	32	100	100
K-Beta	48	3	4	30	97	87
Zn-Beta	50	3	6	30	99	90
Sn-Beta-IE[b]	36	1	22	75	91	90

[a] NH_4-Beta (Si/Al = 25) data from the manufacturer. [b] 0.4 w/w of Cl was found. [c] Calculated from the integrated peak area of FTIR spectra.

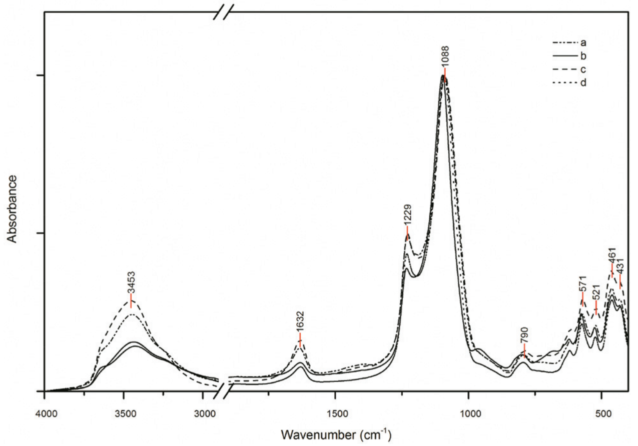


Fig. 1 FTIR spectra of modified zeolites: (a) K-Beta, (b) Sn-Beta-IE, (c) Zn-Beta, (d) H-Beta.

decreases. Regarding the Sn modified zeolite, the loss of crystallinity can be attributed to the dealumination promoted by HCl and the presence of SnO_2 particles in the structure (five and double four membered rings).

SEM images of the different modified zeolites are shown in Fig. 2. The acid form H-Beta presents small particle aggregates (crystal size ≈ 0.5 μm) with wide shape morphology from irregular to round ball aggregates. Some influence on the aggregation pattern and changes in the shape were observed due to the variation in the Si/Al ratio and the cation exchanged. It is well established that the structure of zeolite Beta is intrinsically deformable by changing the aluminium content and the nature of the cation exchanged.[20]

Effects of MW on zeolites

The microwave interaction with a material is usually determined through the complex permittivity ε^*. The dielectric loss ε'' is a parameter representing the ability of the material to absorb microwaves and dissipate them into heat. It is a function of temperature, density and the microwave frequency, and usually decreases with a temperature increase.[9]

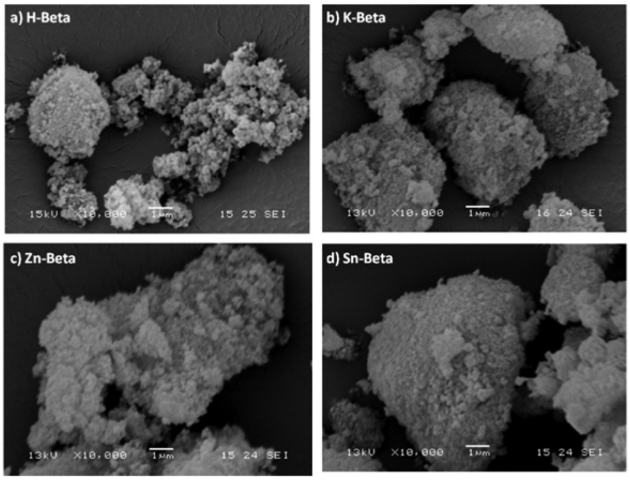


Fig. 2 SEM microphotographs of modified zeolites: (a) H-Beta, (b) K-Beta, (c) Zn-Beta, (d) Sn-Beta-IE.

Heterogeneous liquid phase reactions can benefit from MW technology in terms of energy demands, faster reaction rates, shorter residence times and space equipment saving.[26] Fig. 3 shows the temperature profile of modified powder zeolites under constant microwave power applied (100 W). Specific sites such as silanol groups (–Si–OH) and the metal oxides in the zeolite Beta framework have the ability to absorb microwaves.[26,27] The highest temperatures were achieved for K-Beta ≫ NH_4-Beta ≫ Sn-Beta-IE ≈ Zn-Beta ≫ H-Beta ≥ alumina. Therefore the highest response to MW application was obtained in the K-Beta system, while pure alumina showed the poorest interaction of the tested systems.

Few data have been reported in the literature regarding the interaction of microwaves with zeolites and the heterogeneous catalytic processing of cellulose. When cellulose is processed under hydrothermal conditions, a high temperature is required and the dielectric properties of the medium usually decrease. This is true if water is used as a solvent. In the reaction dispersion of this study, a small amount of HCl was introduced to promote the hydrolysis of microcrystalline cellulose. Thus, the hydronium ion presence contributes to increasing the permittivity of the medium, enhancing the heating rate.

Chromatographic analysis of the products of the MW-assisted catalyzed reaction

The products obtained from the hydrothermal MW-assisted catalysed-reaction of cellulose were analysed. Fig. 4–8 show the results of the analysis performed by liquid chromatography carried out on the reaction products. The effects on the reaction products of processing temperature and time are shown in Fig. 4 and 5 respectively.

Four different temperatures were tested ranging from 180 to 210 °C. The reaction medium was irradiated with MW constant

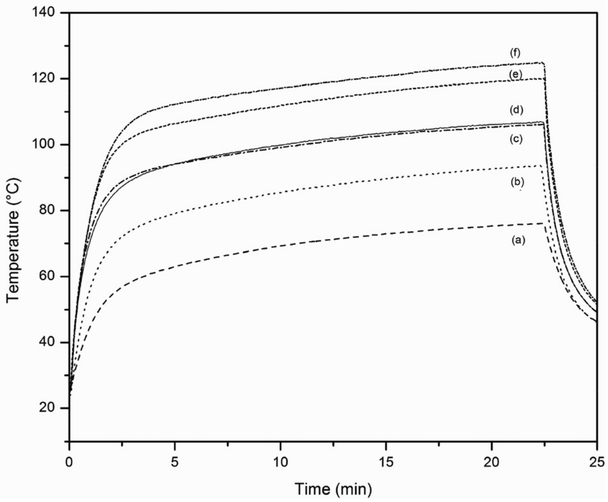


Fig. 3 Temperature profile of modified powder zeolites subjected to constant power applied of 100 W for 25 min: (a) alumina, (b) H-Beta, (c) Sn-Beta-IE, (d) Zn-Beta, (e) NH_4-Beta, (f) K-Beta.

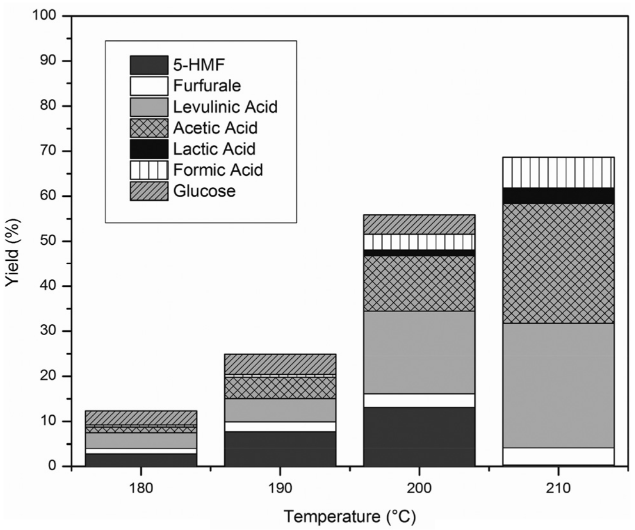


Fig. 4 The influence of reaction temperature on the yield of identified products. Reaction conditions: 5% of microcrystalline cellulose, 0.5 g of zeolite in 70 ml of water, 5 mM HCl, P = autogenous (P_0 = 1 bar, P_{max} = 18 bar), 500 RPM. Time: 30 min to achieve the target temperature (MW power = 240 W) and then kept for 30 min (MW at steady state ~100–120 W).

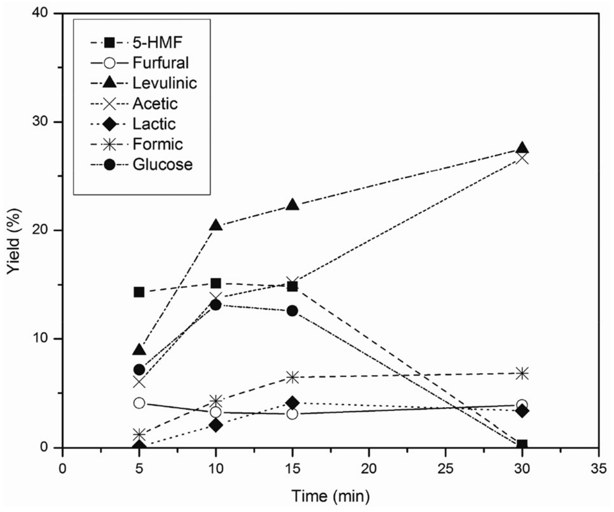


Fig. 5 The influence of the reaction time on the yield of different products. Reaction conditions: 5% of microcrystalline cellulose, 0.5 g of zeolite in 70 ml of water, 5 mM HCl, P = autogenous (P_0 = 1 bar, P_{max} = 18 bar), 500 RPM, T = 210 °C.

power for 30 min until the target temperature was reached. Then, isothermal conditions were kept for another 30 min. Fig. 4 shows the temperature influence on the total molar yield of the identified products, changing from 12.3% to 68.6% mol when the temperature is increased from 180 to 210 °C. The product distribution strongly depends on the temperature value. At high reaction temperature, the yield of levulinic acid benefits since it increases from 3.4% to 27.5%. Acetic acid shows a similar trend. The molar yields for glucose and 5-HMF suggest that at low temperatures these compounds are produced in good yield, whereas higher reaction temperatures produce a decrease in molar yield. The latter can be explained by consumption in subsequent side-reactions which results in the synthesis of smaller molecules. Lactic acid was not detected at temperatures below 190 °C.

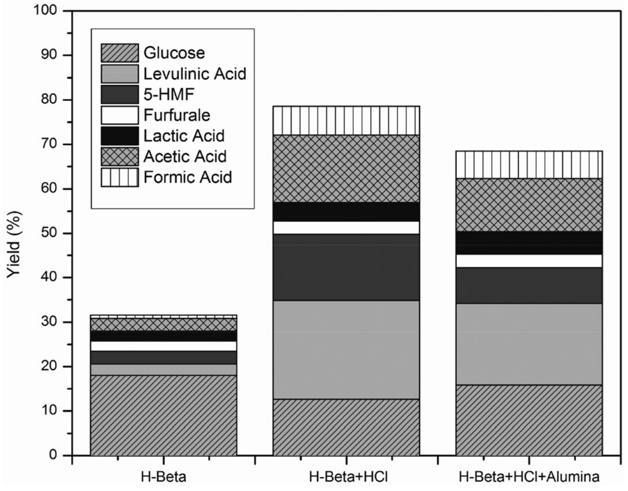


Fig. 6 Effect of different catalytic approaches on the hydrothermal reaction of microcrystalline cellulose. Reaction conditions: 5% (w/w) cellulose, 0.5 g of zeolite in 70 ml water, T = 210 °C, P = autogenous (P_0 = 1 bar, P_{max} = 18 bar), 500 RPM. Time: 30 min to achieve the target temperature (MW power = 240 W) and then kept for 15 min (MW at steady state ~100–120 W).

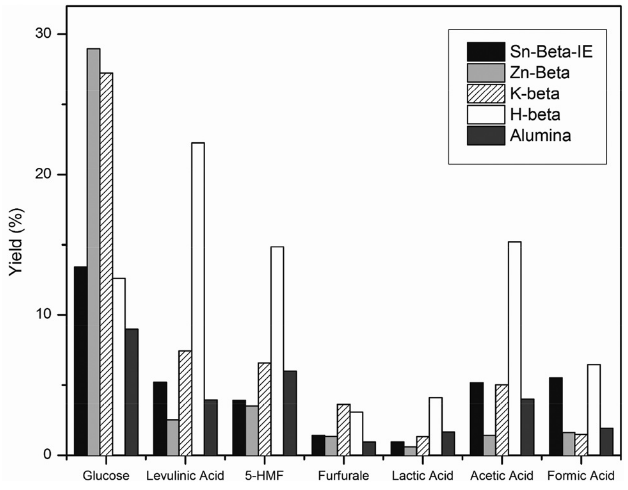


Fig. 7 Effect of Sn, Zn, K ion exchanged zeolites, activated neutral alumina and acid zeolite in the hydrothermal reaction of microcrystalline cellulose. Reaction conditions: 5% (w/w) cellulose, 0.5 g of zeolite in 70 ml water, 5 mM HCl, T = 210 °C, P = autogenous (P_0 = 1 bar, P_{max} = 18 bar), 500 RPM. Time: 30 min to achieve the target temperature (MW power = 240 W) and then kept for 15 min (MW at steady state ~100–120 W).

To further explore the yield behaviour and the product distribution, the reaction time was varied from 5 to 30 min when the reaction conditions were set at 210 °C and autogenous pressure (see Fig. 5). After 15 min of isothermal reaction, the

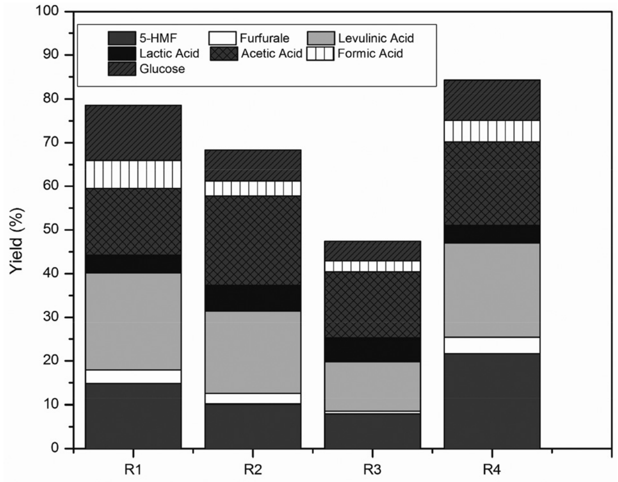


Fig. 8 Recycling catalytic reactions were performed following the procedure described elsewhere:[12] reaction conditions for R1 were the same as listed for Fig. 6. A second cycle R2 was carried out when fresh cellulose was added to the slurry dispersion and the same reaction conditions for R1 were applied. Likewise, a third cycle R3 was performed following the same procedure for R2. Solids from R3 were centrifuged, dried and calcined to 550 °C. A final R4 test was run using this H-Beta calcined powder and the starting conditions for R1.

yield of glucose and 5-HMF started to decrease and then after 30 min, both reached values close to zero. Conversely, the production of small acid molecules like levulinic acid and acetic acid follows a growing trend. The highest yield of lactic acid was achieved after 15 min of reaction. Increments in the reaction time seem to be harmful since the total yield of the identified products begins to decrease.

Chromatographic analysis of the products of reaction in acid medium and using ion exchanged zeolites

Once the optimum conditions of temperature and residence time were achieved, different catalytic schemes were investigated (see Fig. 6). For these experiments the temperature and time were fixed at 210 °C and 15 min of isothermal conditions. These conditions were chosen to avoid complete transformation of glucose and 5-HMF, and have the simultaneous presence of all the chemical species which can be synthesized. When H-Beta was used as a catalyst, a total yield of 31.6% was achieved, with glucose as the main product (18.5%).

The addition of 5 mM HCl in the reaction medium increased the solubility of cellulose and promoted its hydrolysis. Fig. 6 shows the enhancement in the total yield (78.6%) obtained combining the heterogeneous (H-Beta) and the homogeneous catalyst (HCl). Under these conditions levulinic acid was the main product and its yield increased from 2.5% to 22.3%.

The addition of 0.5 g alumina caused a decrease in the system activity leading to 68.5% yield, whereas the selectivity was modified to favour the production of lactic acid, at the expense of levulinic acid.

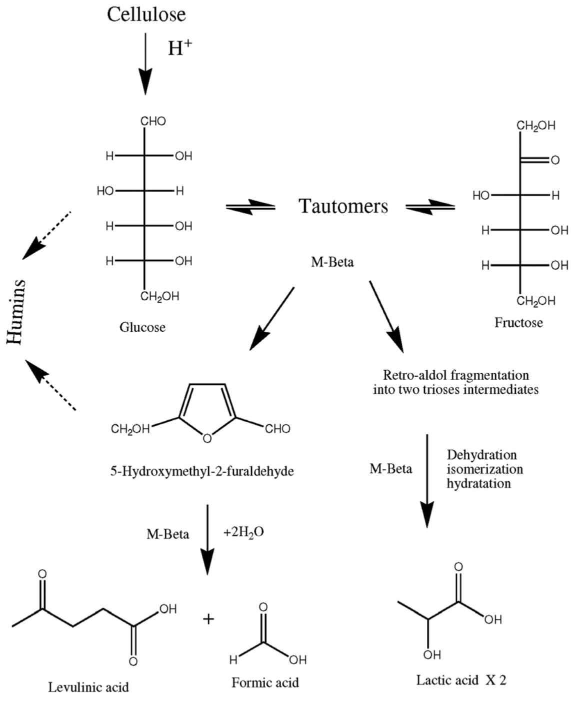
The use of a small concentration of HCl (5 mM) is not harmful to the zeolite framework, as it is generally accepted that an amorphous phase may appear for acid concentrations above 1 M, due to structure breaking. Moreover, low leaching of extra framework aluminium and no leaching of aluminium framework occurs at concentrations below 0.1 M under mild treatment conditions.[28]

Zeolite Beta and Sn-Beta have shown high activity in the isomerization of glucose to fructose at low pH = 1.0.[29] The pH of the reaction precursors was between 3.0 and 4.0. Thus, an improvement in the yield due to leaching of some aluminium species is not expected in these reactions.

In all the catalytic systems examined in this study the yield of 5-HMF was relatively low (≤14.9%), probably due to the rehydration to levulinic acid and formic acid, other side reactions or humins production.[30]

The cellulose reaction seems to follow the generally accepted pathway reported for acid processing of carbohydrates (Scheme 1).[30–32] First, the cellulose depolymerizes to glucose in acid medium. Glucose isomerizes to fructose due to the synergy between the different catalytic sites present in the reaction system (H^+, Lewis and Brønsted sites).[33] From the isomerisation intermediate (1,2 enediol) some dehydration reactions occur with the formation of 5-HMF.[32] The rehydration of 5-HMF leads to levulinic acid and formic acid or humins formation.[34] Humins were macroscopically detected at the end of the reaction.

Fig. 7 shows the distribution of the main products obtained from the hydrothermal MW-assisted reaction of cellulose catalyzed using ion exchanged zeolites. The catalytic activity was



Scheme 1 Microcrystalline cellulose decomposition pathway catalyzed by metal zeolites.

Table 2 Comparison between MW and conventional heating

	Experimental conditions		% Yield (mol)			
Heating method	Heating time (min)	Temp. (°C)	Glucose	Levulinic acid	5-HMF	Formic acid
Conventional	360	180	4.0	1.6	—	1.0
MW	60	180	3.2	3.4	2.8	0.5

found in the following order: acid form H-Beta > K-Beta > Zn-Beta > Sn-Beta-IE > alumina, with the following total yields: 78.6% > 52.7% > 39.9% > 35.5% > 27.5% mol.

The acid form of zeolite Beta was the most active catalyst. The highest yield of glucose (29.0%) was achieved when Zn-Beta was used. This catalyst also promoted the lowest formation of the other by-products, which implies a high rate associated with the hydrolysis reaction of microcrystalline cellulose and the inhibition of subsequent reactions.

Sn-Beta-IE shows the lowest activity of all the exchanged zeolites, probably due to the dealuminization process induced during the catalyst synthesis (Table 1). The fact that the dealuminization process decreases the amount of acid sites, as mentioned before, supports the idea that the systems under study follow the acid processing of the carbohydrate pathway.

The acid form H-Beta promoted the highest formation of levulinic acid (and formic acid) and an appreciable amount of lactic acid. The latter is probably the product of a secondary reaction that does not involve the 5-HMF and the well known capability of zeolites to perform isomerisation/dehydration reactions (see Scheme 1).[35]

Trace amounts of acrylic acid (41.6 and 69.4 μM) were also detected when H-Beta and K-Beta were used. Acrylic acid is a very desirable product due to its versatility for the production of water soluble polymers. For comparison purposes, activated alumina was tested under the same conditions. We found that it presented the lowest activity and did not favour the formation of any specific product.

Reuse of the catalyst

The use of zeolites in different reactions has been demonstrated and due to its good thermal properties their reuse is very feasible.[12] Fig. 8 shows the results of the reuse of the solid catalyst in the MW-assisted reaction of microcrystalline cellulose. The successive reactions were performed without addition of fresh HCl. Good yields were achieved after 3 cycles.

The first approach was carried out adding fresh cellulose to the slurry dispersion obtained from a reaction carried out under standard conditions (5% (w/w) cellulose, 0.5 g of zeolite in 70 ml water, T = 210 °C, P = autogenous, 500 RPM, 30 min to achieve the target temperature, then kept for 15 min).[12] Two processes are shown in Fig. 8 (R1 to R3). In these processes the system started to saturate due to the production of unknown products or humins and the total yield tends to decrease. Interestingly, for lactic acid, in whose synthesis the 5-HMF is not involved, the yield increased.

To completely restore catalytic abilities, the zeolite must be recovered by centrifugation and calcined again at 550 °C. Accordingly, the reused H-Beta of reaction R3 was recovered, calcined and used under the same reaction conditions (reaction R4 in Fig. 8), getting high levels of the total yield (84%). Thus, the feasibility of the catalysts reuse in the heterogeneous microcrystalline cellulose decomposition was demonstrated.

Comparison with conventional heating

In this study we also investigated the hydrothermal reaction of microcellulose with 0.5 g of H-Beta and 5 mM HCl using conventional heating for longer reaction times (360 min), achieving only yields below 7% mol while only 60 min are required to achieve a total yield of more than 12% using microwaves at low temperature. Table 2 summarizes the comparison of the results.

The data in the table demonstrate the advantages of the MW-assisted approach from every point of view: treatment time, energy consumption and efficiency of the reaction.

The reactor used in this work is promising also because it allows an effortless scale-up.[36] Moreover, due to the fast heating of the electromagnetic field, the homogeneously applied electromagnetic field and the magnetic stirring, the pressure and temperature inside the vessel can be carefully controlled.

Experimental section

Materials

Microcrystalline cellulose (Sigmacell type 50, particle size 50 μm, S5504) purchased from Sigma-Aldrich (Milan, Italy) was employed as a substrate and used without further treatment. Ammonium form commercial zeolite Beta (NH_4-Beta, CP814E) was supplied by Zeolyst International (USA) (SiO_2/Al_2O_3 = 25, surface area = 680 $m^2\ g^{-1}$). Activated neutral alumina (150 mesh, 58 Å, 267 740) was purchased from Sigma-Aldrich (Milan, Italy). HCl (37%, m/m) was purchased from Carlo Erba (Rodano, Milan, Italy). Deionized water obtained with a Milli-Q system (Millipore, Bedford, MA, USA) was used as the solvent and the reactant in all reactions.

Catalysts preparation

The heterogeneous catalysts were prepared using NH_4-Beta as the starting material. The acid form H-Beta was obtained after controlled heating of NH_4-Beta for four hours at 550 °C under an air atmosphere. Potassium Beta (K-Beta) and zinc Beta

(Zn-Beta) were prepared using the corresponding 0.15 M aqueous solutions of potassium sulfate (Merck, 99%) and zinc acetate (Merck, 99.5%). Tin Beta (Sn-Beta) was prepared using a solution of 0.3 M HCl and 0.15 M tin tetrachloride pentahydrate (Sigma-Aldrich, 98%).

The liquid ion exchange process was carried out using 10 g of NH_4-Beta in 100 ml of the corresponding salt solution. The dispersions were stirred at 600 RPM for 15 h at 85 °C. After this process the zeolites were filtered, washed several times (redispersed in water, centrifuged and decanted, until near neutral pH) and dried at 80 °C for 24 h and finally calcined for four hours at 550 °C in a deep-bed under an air atmosphere.

Catalyst characterization

The morphology and particle size were analyzed using a Joel 5600 LVS Scanning Electron Microscope (SEM). The Si/Al ratio and the metal loaded into the zeolite framework were determined using an energy-dispersive X-ray spectroscope (EDX) mounted on the Jeol SEM detector.

The crystallinity of the zeolite Beta framework after the ion exchange process was determined using FTIR spectrophotometry, pelletting the samples with KBr. Spectra were recorded in the range 4000–400 cm^{-1} using a Spectrum 100 FTIR spectrophotometer (PerkinElmer Inc., USA). The FTIR spectra were baseline-corrected and normalized at 1095 cm^{-1}.

The interaction between the solid catalysts and microwaves was evaluated by the determination of the temperature profile of a weighted quantity of zeolite powder under constant applied MW power (100 W) for 25 min. For these experiments, the solid catalyst was loaded in a quartz tube and held in a microstrip line. The temperature was measured using an optical fiber thermometer placed in the middle of the catalyst powder.

Heterogeneous catalytic reaction: equipment and procedure

The catalytic reactions were carried out in a 250 ml homemade stainless steel pressurized reactor, equipped with a coaxial antenna as a microwave applicator (Fig. 9). The reactor consists of a cylindrical chamber of stainless steel with two circular caps closed with several bolts. The cap above presents a deep recess accomplished by a tube of quartz. The seal between the cap of stainless steel and the quartz tube is ensured by an O-ring. The recess is used to introduce the coaxial antenna providing the MW power. The reactor has two other connections for the introduction of the temperature probe (type K thermocouple) and for connection to a cylinder of nitrogen with a relative pressure meter (DS Europe, Mod. LP 652-100). The sample holder of 100 ml was made with Teflon and shaped to reduce the transmission of heat to the steel walls of the reactor. The magnetic stirrer is placed under the base of the reactor.

The source of microwave is a magnetron oscillator equipped with forward and reflected power indicators (SAIREM, Mod. GMP 03 K/SM, up to 300 W of continuous MW irradiation power at a frequency of 2.45 GHz). A satisfying MW impedance matching between the reactor and the MW source was obtained with suitable selection of the configuration of the active section of the applicator, as a function of the permittivity of the reagents. The exposed applicator tip is provided with a threaded metal cap whose position is a function of the dielectric permittivity of the reagents. It was therefore possible to reduce to zero the reflected power from the reactor to the microwave source.

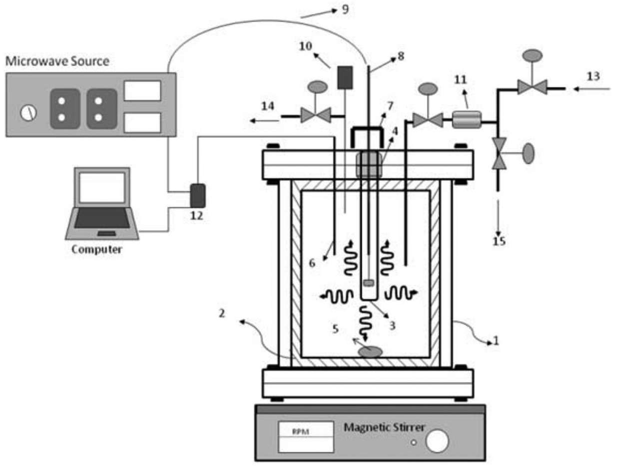


Fig. 9 Schematic diagram of the microwave reactor: (1) stainless steel vessel, (2) Teflon vessel, (3) quartz tube, (4) O-ring, (5) magnetic stir bar, (6) thermocouple, (7) choke, (8) antenna, (9) coaxial cable, (10) pressure sensor, (11) in-line filter, (12) data acquisition, (13) gas pressure inlet, (14) pressure release, and (15) sampling valve.

The reactor is provided with pressure and temperature sensors. A versatile PID control approach is used since the system may operate in two ways: isothermally when the power is regulated or adiabatically when the power is kept constant. The latter causes a constant temperature increase, within limits, until the power is switched off.

A typical reaction was performed loading into the reactor microcrystalline cellulose (5% w/w) in 70 mL water and different substrate/catalyst ratios (HCl, H-Beta, K-Beta, Zn-Beta, Sn-Beta-IE or alumina or combinations thereof). The reactor was closed and the pressure adjusted. The mixture was stirred at 500 RPM, irradiated by MW at the desired power or temperature and time. After the reaction time was established, the power supplied was switched off and the reactor was quenched in a cool water bath to avoid further reaction.

Catalytic reaction product analysis

The reaction products in aqueous solution were analyzed using an HPLC gradient pump (P4000, ThermoQuest) equipped with a Rheodyne 7125 injector (Rheodyne, Cotati, CA, USA), a 50 μL injection loop, coupled with a mechanical degassing system (SC1000, ThermoFinningan) and a UV6000 diode array and pulse amperometric (Au) detectors. Levulinic acid, 5-HMF, lactic acid, furfuraldehyde, acetic acid, formic acid and acrylic acid were separated using a reversed-phase HPLC column Hydra RP C18 (Phenomenex) 250 × 4.6 mm (silica particle size 4 mm), with an isocratic elution in 100% 0.05 M PBS, pH = 2.50, and 16% methanol flowing at

0.8 mL min^{-1} and final rinsing of 100% methanol to clean the column. Chromatograms were recorded at 210 nm. Calibration curves of analytical standards were used for the quantitation of the reaction products. Glucose was quantified using the amperometric detector and post-column derivatization with 0.1 M NaOH flowing at 1 mL min^{-1}. All the solutions were filtered and diluted 10 times in water before analysis.

The molar yields of glucose and the products determined by HPLC were calculated using the following equation:[37]

$$\text{Yield mol\%} = 100\left(\frac{\#c_i}{6}\right) \times \left(\frac{V \times C_i}{n_{\text{cellulose}}}\right) \qquad (1)$$

where $\#c_i$ = number of carbon atoms in the product i, C_i = molar concentration of the product i (HPLC), v = volume of aqueous dispersion precursors and $n_{\text{cellulose}} = \frac{\text{initial g of cellulose}}{162}$.

Conclusions

The use of a microwave reactor and a heterogeneous catalyst allowed us to obtain short reaction times and yields much higher than reactions carried out using conventional heating. Zeolites interact with MW, decreasing the energy consumption and the time required for heating the reaction systems. The heterogeneous catalyst can be easily recovered by filtration and reused with good yield.

The addition of minimal amounts of HCl to the reagents enhances the catalytic activity observed on the microcrystalline cellulose hydrothermal decomposition reaction, probably due to an enhanced permittivity of the reaction medium.

Acid form H-Beta and K-, Sn-, Zn-modified zeolite Beta are capable of effectively catalyzing the reaction in the presence of MW, due to their capacity to absorb MW. Moreover, it has been demonstrated that the nature of the exchanged cation is a key factor that affects the absorption of MW in the zeolites. Thus, the different exchanged cations induce changes in the product selectivity, Zn-Beta favours glucose formation, while H-Beta favours the production of levulinic acid. Furthermore, an increase in the amount of zeolite added to the reaction system favours the formation of by-products through the conversion of glucose.

Zeolite-Beta coupled with MW seems to be a promising approach in the development of new green processes for cellulose processing.

The use of the coaxial applicator developed to introduce the MW into the reaction system allowed for a precise control of the temperature and pressure of the system, avoiding hot spots, and permitting to activate with MW power a chemical reaction inside a metal vessel. The MW reactor can be easily scaled up and can be adapted for continuous operation, using an array of applicators along a tube, also made of metallic material, without giving rise to electromagnetic resonance, without loss of radiation and therefore with great energy efficiency. The high pressure MW-assisted chemical reactor proved to be very useful especially to perform hydrothermal reactions.

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