Acidic modifiying of natural zeolite as catalyst for etherification in green chemistry

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ABSTRACT

This work deals with the preparation, characterization and testing of a hierarchical porous clinoptilolite-based natural zeolite as a potential catalyst for the conversion of renewable glycerol feedstock to valuable fuel additives. The available natural zeolite clinoptilolite was ion exchanged with ammonium and activated atdifferent temperatures in order to obtain the acid form of the zeolite. The catalysts were characterized by XRD, FTIR,TG-DSC, TPD ofammonia, and nitrogen adsorption and desorption. The catalysts were tested in the acid catalyzed etherification of glycerol with tert-butanol. The acid catalyst$_S$ show high activity in the etherification reaction.

Introduction

Nowadays, the energy and environmental situation is a big problem for every country especially for developing countries, which are faced with limited fossil resources[1], CO_2 emission from fuel consumption for heating and transportation is a main sourceof air pollution and climate change due to global warming [2]. Therefore, the green synthesis of materialsand sustainable use of feedstock are very important issues. Catalysts play akey role for the environmental protection and development of green processes. Heterogeneous catalysts allow to improve the process efficiency by reducing the reaction time and temperature. They reduce the formation of by-products by improving the selectivity and enhance the productivity by increasing the conversion.

Glycerol is the main by-product of the biodiesel production from natural oils as vegetable oil, algae oil, microbial oil, and waste cooking oil [3, 4]. Glycerol is available in huge amounts. It can be catalytically converted to sustainable, valuable transportation fuel additives by etherification with alcohols, e.g. ethanol obtained from sugar. Because thisprocess uses renewable feedstock, it is environmental friendly and reduces the CO_2 emission. The CO_2 is cycled.

The present project aims to synthesize fuel additives by the etherification of glycerol with short chain alcohols like tert-butanol by using heterogeneouscatalysts based onnatural zeolite. The corresponding glycerol ethers can be catalytic synthesized by using acid or supported acid catalysts, i.e. strongly acidic sulfated zeolite, or ion-

exchangeresins [5]. Mostly, synthetic zeolites were used so far [6, 7].

Mineral acidssuch as H_2SO_4 and HClwere used as catalysts for the homogeneous catalytic etherification. Besidesits high activities; it is difficult to separate the acidsfrom the reaction products. Additionallythe mineral acidscausereactorcorrosion and environmentalpollution. Heterogeneous resin-based catalysts likeAmberlyst-15 arenot stable athigh temperature and the preparation of synthetic zeolites is less ecofriendly. For example, the synthesis of ZSM-5 and H-Y catalysts occursat elevated temperature, consumes energy for heating and produce hazardswaste chemicalsas NaOH and organic templateslike amines [8, 9].

The use of natural zeolitesas catalysts is, therefore, an interesting and environmental more benign alternative. Natural zeolitesarecrystalline orderedmicroporous aluminosilicate minerals. They are composed of SiO_4 and AlO_4tetrahedra, which are linked via the corners by sharing oxygen atoms.The zeoliteclinoptilolite contains elliptical oxygen-10-membered rings of 4.1× 7.5 Å size and two typesof oxygen-8-membered rings of 3.6× 4.6 Å and 2.81 × 4.7 Å size, respectively [10]. For example, the term "8-ring" of the channel aperture in zeolite refers to a closed loop that is built from eight tetrahedral coordinated silicon (or aluminum) atoms bridgedwith 8 oxygen atoms.The negative chargecreated by the isomorphous substitution of silicon by aluminumin the framework isneutralizedby cations like Na^+, K^+, Ca^{2+}, and Mg^{2+} which are located insidethe zeolite pore system. Additionally, the micropores contain adsorbed free water molecules. Zeolitescan be divided on the base of the different of Si/Al ratios. Clinoptilolite has medium pore size channels like zeolite ZSM-5 and has a medium aluminum content. The Si/Al ratio is *ca*. 5. The higher the aluminum contentin zeolitethe higher is ion exchange capacity and hence acid site concentration.But the stability will be decreased. Post-synthetic modifications improve the Brønsted acidity andincrease the glycerol conversion [7, 11].

This workdeals with the preparation, characterization and testing of a hierarchical porous natural zeolite as a potential acid catalyst for the conversion of so far rarely used heavy feedstock to valuable fuel. It is also of high interest for the catalytic conversion of glycerol to fuel additive by its etherification with tert.-butanol [6, 12,13].

Because of steric hindrance and competition between 3 hydroxyl groups of the glycerol, the selectivity tomonoglycerol ether is the highest inthe etherification [13, 14], whereas the tri-ether is the most wished product. So activity and selectivity of the prepared natural catalysts wereevaluated and the reaction conditions were optimized in order to improve the catalytic performance.To the best of our knowledge, the etherification of glycerol with tert-butanol over natural zeolite was not reported so far in the literature.

Experimental

2.1 Catalyst preparation and characterization

A natural zeolite tuff containing clinoptilolite was used as starting material for the preparation of the acid catalyst. It may besome impurities such as quartz in small amount. The non-framework cations located in channels and open oxygen-rings of the zeolite undergo ion exchange and can be replaced by ammonium ions. Thermal decomposition of ammonium ions leaves Brønsted acid protonic (H*) sites (Scheme 1).
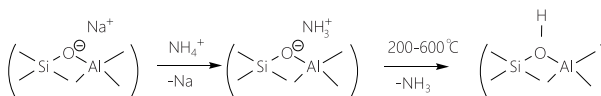
Scheme 1. Transfer of natural zeolite to acid form by ion exchange with NH_4^+ in aqueous solution and followed calcination

Procedure: 5,3 g clinoptilolite, 50mLof aqueous 0.5M NH_4NO_3solution and 100mLdeionized water was two times stirred at 65°C for 2 hours. The ion exchanged clinoptilolitewas separated by filtration and dried in an oven at 65°C.

Thereafter, the sampleswerecalcined at 200-600°C and tested in the etherification ofglycerol withtert-butanol. The obtained samples are denoted CL200, CL300, CL400, CL500, and CL600.

2.2 Characterization

The structural, textural and acidic properties of the catalysts were investigated by XRD analysis, FTIR spectroscopy, TG-DSC experiments as well as by temperature-programmed ammonia desorption (TPD) and nitrogen adsorption and desorption measurements.The catalyst activity was studied inphase using the acetalization of benzaldehyde with 1,3-butanediol as test reaction.

The X-ray diffraction pattern of the powdered clinoptilolite samples and catalysts were measured with a STOE-STADIP-P transmission diffraction spectrometer using mono chromized $Cu_{K\varnothing}$ radiation. The FTIR spectra were recorded on a Nicolet 380 FTIR spectrometer (Bruker Alpha) in reflection mode (ATR). The nitrogen adsorption and desorption isotherm measurements were carried out on a Thermal Sorptomatic 1990 system (Thermo Fisher). Prior to measurement,the samples were dehydrated under vacuum at elevated temperature. For differential thermal analysis (TG-DSC) the Setaram TGA Labsys 1000 device was used. Samples of *ca.* 30 mg weight were filled into in an alumina crucible and heated at a rate of 10K/minute under argon atmosphere. Temperature-programmed ammonium ion decomposition and ammonia desorption experiments (TPD) were done with a Thermo Fisher Scientific TPRO 1100 series device. Loosely adsorbed ammonia and water were removed by purging with helium at a temperature of 120°C.

2.3 Etherification of glycerol with tert-butanol

The following materials were used: for etherification experiments: 3.06g (~2.5mL)of glycerol (M=92, d=1.26g/mL), 9.86g(~12.5 mL)of tert-butanol (d=0.79 g/mL, M=74) and 0.225.g of the catalyst. The chemicals were added into a 50mL flask which was equipped with a condenser. Then the mixture was stirred and heated to the required temperature of 85°Cand stirred under refluxfor 15 minutes in order to obtain a homogeneous reaction solution. Then 0.225 g of activated catalyst was added to the reactionsolution. During the course of reaction, 0.5 mL aliquots of reaction solution were taken forgas chromatographic analysis.

The catalytic test runs at higher temperature underpressure werecarried out inautoclaves(Parr 5500)with Parr 4848 system (Scheme 2).The amount of catalyst and reactants was maintained constant, but the temperature and pressure were increased to 180°C and*ca.* 20 Bar, respectively.
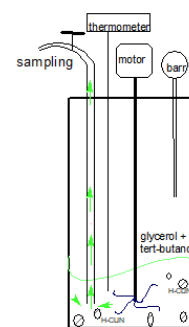
Scheme 2. Sampling and operating of etherification in autoclave

The reaction products were analysed by GC-MS (Agilent 6890/5973 GCMS). The GC-FID method with a 10 m DB wax 40/5-6-180/10-8-200/20column was used for analysis

Result and discussion.

3.1 Characterization
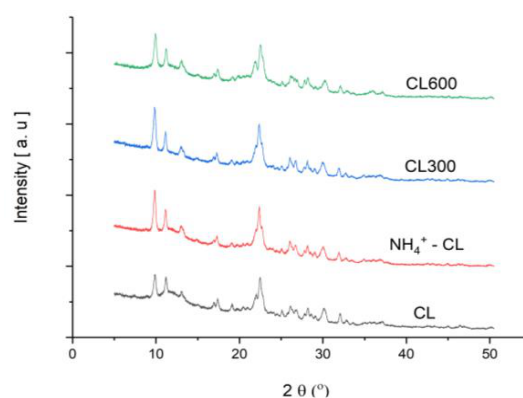
X-ray diffraction

Figure1.XRD patternof clinoptilolite CL after different treatment: CL- starting material, ammonium exchanged NH^+_4- CL, CL300 and 600 calcined at 300°C and 600°C

The X-ray diffraction pattern (Fig.1) show that the starting natural zeolite sample is mostly composed of clinoptilolite (*ca.*95% determined by XRD). Besides it contains some impurities originating from silica phasesshowing reflections at 2θ=21.9°and 26.4°. They are not catalytic active. Additionally, some mordenite is found.

After calcination of the ammonium exchanged clinoptilolite, the structure and crystallinity of the material is maintained during heating to 400°C.Heating to 600°C leads to somelossin the crystallinity. This is indicated by the increased background especially between 2θ=20-35°. Also the

intensities of the reflections of silica impurities at 2θ = 26.5° increase.
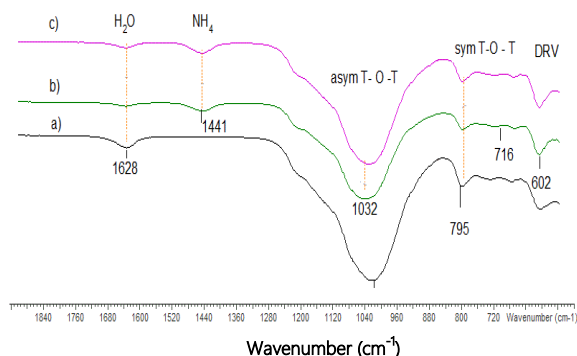
IR spectroscopy

Figure 2. FTIR lattice vibration spectra of clinoptilolite CL after different treatment: a) starting material CL b) ammonium exchanged NH_4^+- CL, and c) CL300 calcined at 300°C

The observed FTIR spectra in the range of lattice vibrations between *ca.* 500 and 2000 cm^{-1} are consistent with that of zeolite clinoptilolite (Fig.2). They show also the N-H stretching vibration band of the ammonium ions appearing at ca.1441 cm^{-1}[15]. The relative intensity of the vibration band of ammonium ions decreases somewhat after heating to 300°C. That mean, that a part of the ammonium ions is decomposed already at this temperature. Fully decomposition and, therefore, maximum formation of Brønsted acid sites is achieved after heating to 500°C or more.
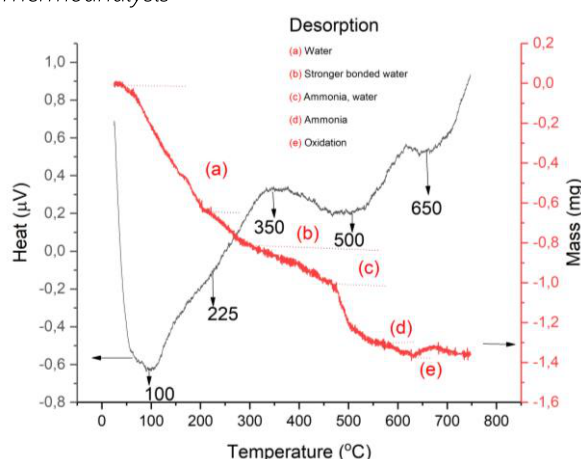
Thermoanalysis

Figure3. Combined TG-DSC curves of ammonium exchanged NH_4^+ - CL

The combined (TG-DSC) curves of NH_4-CL are shown in Fig.3.A markedly endothermic weight loss is observed with heating the sample to *ca.* 200°C. It is assigned to desorption of weekly bound water as

indicated by the low temperature peak maximum at 100°Cin the DSC curve. Above 180°C strongly bound water, e.g. bound to cations is desorbed from the zeolite giving rise to an endothermic shoulder in the DSC curve with a maximum at 225°C. Starting from 280°C to 480°C desorption of water and possibly ammonia from Brønsted sites proceeds. The steep decrease of the weight loss curve between ca. 450 - 500°C is assigned to the decomposition of strongly bound ammonium ions with corresponding desorption of ammonia from strong Brønstedsites. It is also endothermic. Further enhancement of the temperature causes de-hydroxylation. And at high calcination temperature partial destruction of the zeolite occurs.
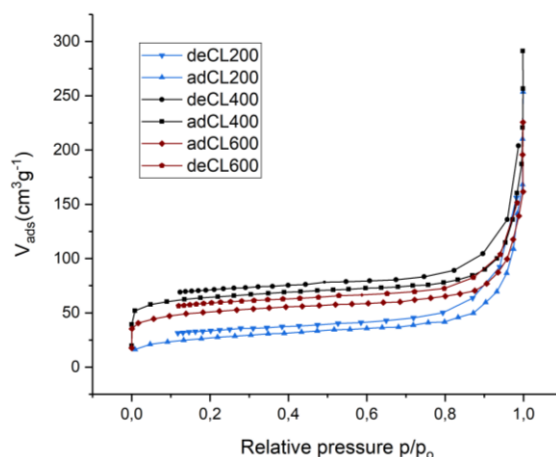
Nitrogen adsorption and desorption

Figure 4. Nitrogen adsorption and desorption isotherms of CL calcined at 200°C, 400°C, 600°C

Table 1: Effect of activation temperature (calcination) on the porosity of the catalysts

Sample	CL200	CL400	CL600
Pore Volume (cm^3/g)	0.1263	0.1723	0.1472
Surface area (m^2/g)	97,55	238.29	197.18

The nitrogen adsorption and desorption isotherms are shown in Fig. 4. They show only a small nitrogen up take at very low relative pressure (p/p$_0$=0.01) and correspondingly low specific surface area(Table 1). The small and medium sized pores are blocked by the cations. Starting with the decomposition of the ammonium ions at 300°C, the micro pore system is opened and acid catalytic BS sites are accessible for molecules. The size of microspores is>0.3 nm and mesoporous sizes range from 2 nm to 50 nm.

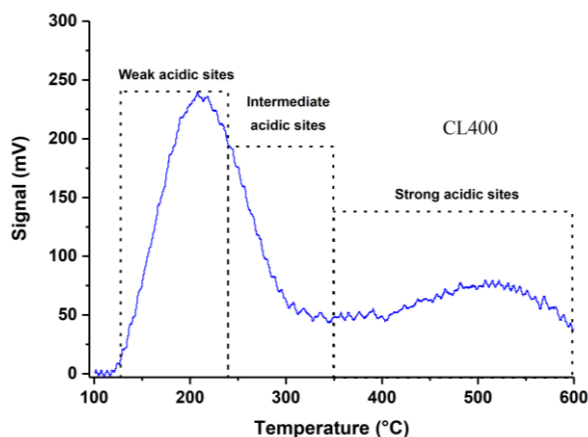*Temperature-programmed desorption of ammonia*

Figure5. Ammonia TPDcurve of ammonia loaded catalyst CL400

The NH$_3$-TPD curve of catalyst CL400 (Fig. 5) shows desorption of ammonia from weak and intermediate sites until *ca*. 280°C.This desorption peak is not observed with ammonium exchanged zeolite. Therefore, it cannot belong to Brønsted acid sites. Heating of ammonium ion exchanged zeolite samplesshows that desorption of ammonia from BS starts at *ca*. 280°C.A broad desorption peak of ammonia is observed between 350 and 600°Cwith a temperature maximum at *ca*. 520°C indicating the presence of strong and very strong acid sites. Heating to 400°C liberates mainly medium and strong acid sites. Above 400°C ammonia is desorbed from strong and very strong sites.This finding is confirmed by the FTIR spectra which show only a partial decrease of the intensity of the ammonium ion band after heating to 400°C(Fig. 2).

3.2 Catalysis

The etherification of glycerol over solid catalysts leads to the formation of different mono, di, and tri glycerol tert-butyl ethers: two mono ethersM1(1-tert-butoxypropane-2,3-diol ether) and M2 (2-tert-butoxypropane-1,3-diol ether), two di ethers D1 (1,3-di-tert-butoxypropan-2-ol) and D2 (1,2-di-tert-butoxypropan-3-ol, and the tri ether T (1,2,3-tri-tert-butoxypropane) as shown in Scheme 3. The etherification of glycerol with tert-butanol was studied using natural zeolite catalysts activated at different temperature ranging from 200°C to 600°C,respectively. The reaction temperature was varied from 85°C to 180°C. The change of the conversion with reaction time, i.e. the ratio of the formed mono glycerol tert-butyl ether (M) to remaining starting material glycerol (Gly) is shown in Figure6. The M/Gly ratio increases nearly linearly with reaction time. The catalytic activity differs markedly with varying activation temperature (Fig.7). Highest activity is observed with the catalyst CL300although after activation at 300°C only a part of theBrønsted sitesare liberated by decomposition of the ammonium ions to ammonia and BS acidic protons. The ammonia is desorbed from weak to medium strong acid sites as shown by the NH$_3$-TPD curve(Fig. 5)[16]. In contrast, the sample activated at 200°C shows nearly no activity. It is not acidic because at that temperature Brønsted sites are not formed. Interestingly, a drop in activity is observed with further increase of the activation temperature to 500°C (Fig.7), although the acetalization experiments using benzaldehyde and butandiol-1,3 confirm the high catalytic activity of this sample. Hence, the loss in activity in the etherification of glycerol cannot be due to a lower intrinsic activity of these catalysts. Detailed inspection of the GS-MS data show that some di-glycerol is formed over higher acidic catalysts which were calcined at high temperature. Di-glycerol is a reactive molecule and rapidly polymerize. It is concluded that these by-products partially block (poison) the catalyst causing the observed activity drop. The markedly low activity observed with catalyst CL600 is in line with the partial amorphization and corresponding loss of acidity of this material at 600°C.

Undermildreaction conditions, i.e. reaction temperature up to 100°C, low conversion of glycerol (4% to 10% after 2h of reaction)is observed,and the main productsarethe mono glycerol tert-butylethers (M1 and M2). The better access of the two terminal hydroxyl groups in the glycerol compared to the only one internal hydroxyl group per molecule facilitates the formation M1ether with a selectivity of *ca*. 85%selectivity. The selectivity to the M2ether (Fig.8)is only 15%. Higher ethers like the two di ether D1 and D2 or the tri etherT are formed only at higher temperature starting with 100°C. The catalysts are very stable as indicated by the nearly linear increase of the conversion (M1+M2/Gly ratio) with reaction time (Fig.6).
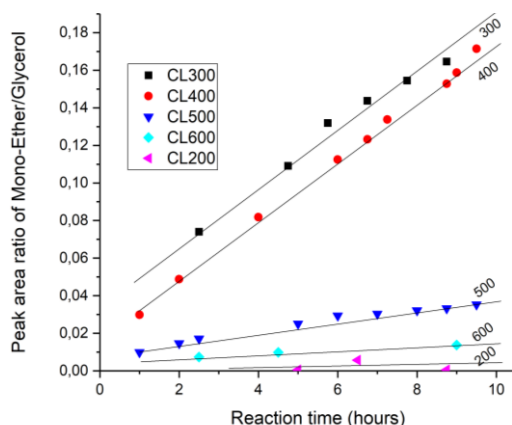
Figure 6. Conversion of glycerol over CL catalysts activated at 200°C to 600°C. M/Gly ratio vs. reaction time. Reaction temperature: 85°C

The conversion increases markedly with higher reaction temperature (Fig. 7). Also at higher temperature the catalyst CL300 shows highest activity (conversion) and high selectivity to the M ethers. At high temperatures, 140°C and 180°C, the conversion of glycerol is increased to *ca.* 50-70% (Fig. 8).
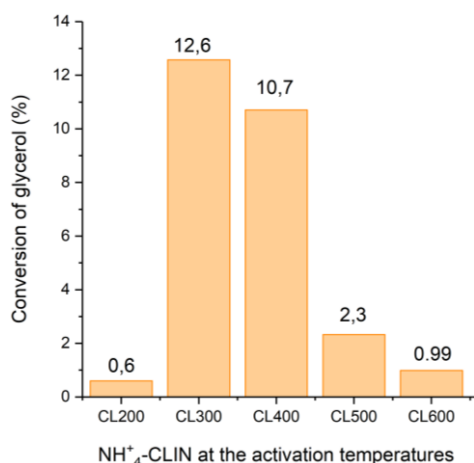

Figure 7. Conversion of glycerol over CL catalysts activated at 200°C to 600°C after 7h of reaction at 85°C

Additionally, formation of di- and tri tert-butyl glycerol ethers beside of the mono ethers is observed. The yields of M1 and M2 reach 47% and 23%, respectively, already after 1h of reaction.Also the formation of some tri ether is observed (1%). Other conditions as the catalyst loading were the same as with the experiments performed under normal pressure inorder to find the best reaction condition. Side products asthe di-tert-butyl etherwere not observed. Some indication was found for the formation of small amounts di-glycerol ether at high temperature. Among the products, D and T

ethers are excellent additives for diesel re-formulation, which are formed over the acidic natural zeolite catalyst CL300 with a selectivity of *ca.* 34% after 1h of reaction at 180°C(Fig.8). The catalytic results show high activity of acid natural zeolite catalyst in the etherification of glycerol to the correspondingtert-butyl ether. The enhancement of the reaction temperature markedly increases the conversion of glycerol and the selectivity to mono and di ether.
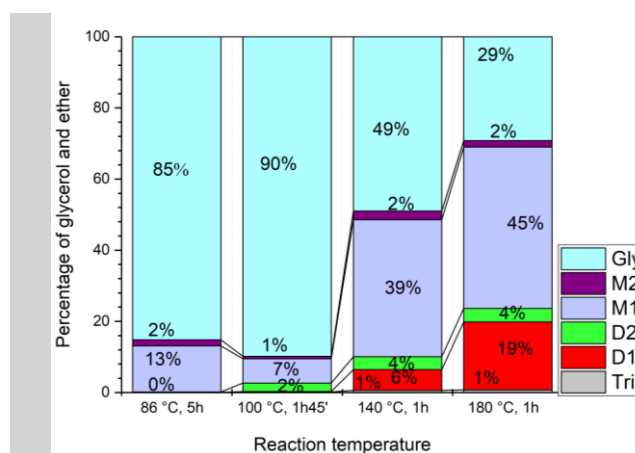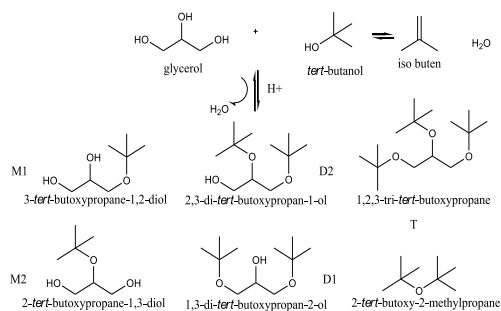

Figure8. Influence of the reaction temperature on the selectivityto ethersof etherification ofglycerol overCL300 catalyst

Scheme 3. Etherification reaction between glycerol and tert-butanol

Conclusion

Acidified natural zeolite is an attractive catalyst and shows high activity in the etherification of glycerol to mono and di glycerol tert-butyl ether. The catalyst shows good long time stability under reflux conditions. The conversion and the selectivity are strongly influenced by the reaction temperature. Specifically, the formation of di and some glycerol tri tert-butyl ether is enhanced.

Acknowledgement

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