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Elementary steps and reaction pathways in the aqueous phase alkylation of phenol with ethanol



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ABSTRACT

The hydronium ion normalized reaction rate in aqueous phase alkylation of phenol with ethanol on H-MFI zeolites increases with decreasing concentration of acid sites. Higher rates are caused by higher concentrations of phenol in the zeolite pores, as the concentration of hydronium ions generated by zeolite Brønsted acid sites decreases. Considering the different concentrations of reacting species, it is shown that the intrinsic rate constant for alkylation is independent of the concentration of hydronium ions in the zeolite pores. Alkylation at the aromatic ring of phenol and of toluene as well as O-alkylation of phenol have the same activation energy, 104 ± 5 kJ·mol⁻¹. This is the energetic barrier to form the ethyl carbenium ion from ethanol associated with the hydronium ion. Thus, in both the reaction pathways the catalyst involves a carbenium ion, which forms a bond to a nucleophilic oxygen (ether formation) or carbon (alkylation).

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1. Introduction

Alkylation is one of the key reactions in organic synthesis to form new carbon-carbon bonds [1–5]. The wide availability of bio-derived feedstocks and the quest for less demanding synthesis conditions require to conduct such reactions in the presence of water under conditions under which classic Friedel-Crafts alkylation is not possible [6–8]. Alkylation also enables to convert small functionalized (e.g., alcohols) or non-functionalized (e.g., alkenes) organic molecules to fuel range products, drastically increasing the carbon efficiency for both conventional petroleum and biorefinery conversion pathways [9–11].

In the presence of water, hydronium ions act as catalysts for alkylation, largely preventing the formation of (surface) esters as stable intermediates [6,12]. For both, molecular and solid acids, the low reaction rates in the presence of water hold a formidable challenge [12]. In aqueous solutions of mineral acids, the rate of alkylation of, e.g., functionalized aromatic molecules was hardly measurable, and by far slower than competing acid catalyzed reactions, such as dehydration [12].

Acidic zeolites, in contrast, have been reported to catalyze alkylation of phenol with short chain alcohols such as ethanol and propanol [13–15]. Products of these reactions are *ortho* and *para* substituted phenols and/or phenol ethers (see Fig. 1). The ether formation proceeds both via consecutive carbenium ion formation and nucleophilic attack by phenol (S_N 1) and bimolecular substitution reaction with simultaneous ether formation and water abstraction (S_N 2) [16–21]. On the other hand, C-alkylation can only proceed via a carbenium ion route in an electrophilic aromatic substitution formalism [22,23]. Because of the strong electron donating effect of the OH group, the *ortho*- and *para*-C in phenol are more electron rich than *meta*-C, thus the alkylation is preferred kinetically at *ortho*- and *para*-positions.

Preliminary experiments showed that both alkylation reactions, as well as multiple- and *trans*-alkylation are catalyzed by hydronium ions in aqueous phase, but that the constraints of zeolite pores are required to achieve reasonably high rates. Zeolite BEA showed, for example, promising results for C-C coupling of in situ generated cyclohexanol with phenol [6,12], while mesoporous and macroporous acids were not active. Zeolite BEA and USY were identified as promising candidates for the alkylation of phenol with *tert*-butanol in the condensed phase, and particularly zeolites with high Si/Al ratio showed higher activities, which was attributed to a higher hydrophobicity enhancing nonpolar reactant adsorption [24].

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Fig. 1. Reaction pathways of ethanol on a Brønsted acid site via carbenium ion. A: Dehydration to ethylene; B: Diethylether formation; C: Phenol ether formation; D: C-Alkylation forming *ortho*- or *para*-ethylphenol.

Here, we report a qualitative and quantitative study on reaction pathways and reaction kinetics of the alkylation of phenol with ethanol on zeolites with MFI structure with varying concentrations of Al, leading in aqueous phase to varying concentrations of hydronium ions. Using information from adsorption measurements and calorimetry together with detailed kinetics, we will show, how hydronium ions in confines are able to efficiently catalyze alkylation, in aqueous phase.

2. Experimental

Chemicals. The following chemicals were used: phenol (99% Sigma-Aldrich), toluene (99% Sigma-Aldrich), phenol-d₆, (99% Sigma-Aldrich), ethanol (99% Sigma-Aldrich), sodium sulfate (ACS reagent, >99%, Sigma-Aldrich), and ethyl acetate (Chromasolv, 99.9%, Sigma-Aldrich). Hydrogen gas was obtained from Westfalen (>99.999%). Deionized water was treated with an Easypure-II system from WERNER to obtain ultrapure water (18.2 M Ω cm).

Zeolite catalysts. All zeolites are referred to as MFIX, where "X" stands for the modulus Si/Al as determined by atomic absorption spectroscopy. Zeolite MFI45 (Si/Al ratio = 45) was obtained from CLARIANT AG in H-form. The MFI-zeolites CBV3024E (referred to MFI15) and CBV2314 (referred to as MFI12) were obtained from ZEOLYST in H-form. MFI32 is an AHFS treated MFI15 parent zeolite according to the method given below. All zeolites were treated at 823 K (rate: 10 K min⁻¹) for 6 h in 100 mL/min synthetic air (80% nitrogen, 20% oxygen; > 99%) before they were tested.

AHFS treatment procedure. Approximately 2 g of zeolite was added to a solution of $(NH_4)_2SiF_6$ (ca. 80 mL) and stirred in a polypropylene-bottle for 5 h. The solution contained a 4-fold excess of AHFS with respect to the Al content of the zeolite, in this case (CBV3024E; 2.76 wt.% Al corresponding to 2.1 mmol) 1.50 g (8.4 mmol) AHFS. After the treatment the sample was washed six times in hot deionized water (543 K) and calcined for 5 h in synthetic air (100 mL min⁻¹, heating rate: 10 K min⁻¹) at 823 K min⁻¹

Reaction procedure. All reactions were performed with the same molar amount of reactant, catalyst and solvent. In 100 mL ultrapure water 0.85 g of phenol (9 mmol), 9.5 g of ethanol (0.2 mol) and 500 mg of MFI were dissolved and suspended, respectively.

Catalytic reactions. The 300 mL-autoclave was loaded with 0.5 g zeolite catalyst (see above) and 0.85 g of phenol, 12 ml of ethanol and balanced with water to a total volume of 100 ml. The reactor was purged two times with hydrogen and pressurized with 50 bar of hydrogen. The reactor was heated to the desired temperature with a heating rate of approximately 10 K min⁻¹ without

stirring. As the reaction temperature was reached the stirring rate was set to 700 rpm. After the reaction time, the reactor was cooled down from reaction temperature to room temperature within two minutes using an ice bath. The pressure within the reactor was released at a temperature of 278 K to prevent the loss of volatile products. The reaction mixture was extracted with 3×20 mL ethyl acetate. To improve the phase separation of the organic and the aqueous phases, sodium chloride was added to the reaction mixture. After extraction, the organic phase was dried over sodium sulfate. The carbon balance was monitored by an internal standard (cyclohexanol).

Reactor. All reactions were performed in a 300-mL-autoclave from Parr Instruments Co. (type: PST FS, material: HASTELLOY C) with a temperature and stirring controlling device (Parr Instruments Co. 4848 Reactor Controller).

GC–MS. Quantification and qualification of the alkylation reactions were analyzed by GC/MS (Agilent Technologies 7890 B GC, column: Agilent 19091S-433UI INV02 (30 m × 250 μ m × 0.25 μ m), heating program: 10 K min⁻¹ from 353 K to 553 K). Gaseous products were analyzed by GC (Agilent Technologies, 3440 B GC, column: Agilent HP-Innowax 30 m × 250 μ m × 0.25 μ m), heating program: 10 K min⁻¹ from 333 K to 533 K.

AAS. The Si and Al contents of the zeolite samples were measured by atomic absorption spectroscopy (AAS) on a UNICAM 939 AA–Spectrometer.

 N_2 Physisorption. The BET specific surface area and pore volume of the zeolite were determined by nitrogen physisorption. The isotherms were measured at liquid nitrogen temperature (77 K) using a PMI Automatic Sorptometer. The catalyst was activated in vacuum at 473 K for 2 h before measurement. Apparent surface area was calculated by applying the Brunauer-Emmett-Teller (BET) theory, and the t-plot method was used to determine the pore volumes.

MAS ²⁷Al-NMR. Magic angle spinning spectra were recorded on a Bruker Avance AMX-500 spectrometer. Samples were packed after hydration at 42 m bar H₂O into ZrO₂-rotos, which were spun at 10 kHz. Al(NO₃) 9H₂O was used as reference. For measuring the 1D spectrum, an excitation pulse with power level of 7 dB and a length of 0.7 μ s was applied. Relaxation time was set to 2.0 s and 2000 scans were recorded. The data were processed after Fourier transformation using Bruker's software Topspin.

IR. Infrared (IR) spectroscopy of adsorbed pyridine was performed with a Nicolet 5700 IR-spectrometer (Thermo- Fisher) at a resolution of 4 cm^{-1} . The concentrations of acid sites were determined by IR spectroscopy of adsorbed pyridine at 423 K Download English Version:

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