



# How zeolitic acid strength and composition alter the reactivity of alkenes and aromatics towards methanol



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## ABSTRACT

This work encompasses a combined experimental and theoretical assessment of how zeolitic acid strength and composition affects acid-catalysed methylation reactions. Overall, higher methylation rates were observed over the material with higher acid strength. Co-reactions of methanol with benzene at 250 °C over the two isostructural AFI materials H-SSZ-24 and H-SAPO-5 revealed large differences in selectivity. While the stronger acidic H-SSZ-24 mainly produced toluene and polymethylbenzenes, high yields of C<sub>4+</sub> aliphatics were observed over H-SAPO-5. These results strongly suggest that alkene methylation was preferred over H-SAPO-5 even at very low conversion during methanol/benzene co-reactions. Furthermore, a comparison of benzene and propene methylation at 350–400 °C revealed a significantly faster rate of benzene than propene methylation in H-SSZ-24, whereas the rates of benzene and propene methylation were similar in H-SAPO-5. The observed difference in reactivity of the two hydrocarbons in both catalysts could be understood by careful analysis of various molecular dynamics simulations of the co-adsorbed complexes. The probability to form protonated methanol was, as expected, higher in the more acidic material. However, in H-SSZ-24, the probability for methanol protonation was higher when co-adsorbed with benzene than when co-adsorbed with propene, while the same was not observed in H-SAPO-5. Furthermore, it was found that benzene and methanol are more likely to form a reactive co-adsorbed complex in H-SSZ-24 compared to propene and methanol, while the opposite was observed for H-SAPO-5. This work shows that molecular dynamics simulations provide insights into the adsorption behaviour of guest molecules in large pore AFI materials. The obtained insights correlate with the experimentally observed reactivities.

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## 1. Introduction

Acid catalysis is of importance in numerous chemical reactions, not least in the petrochemical industry, where zeolitic acid catalysts are used in several major processes [1]. For this reason, fundamental understanding of the effect of acid strength on reactions is a topic of major interest. The most important acid sites for catalysis over zeolitic materials are the Brønsted acidic sites formed when the negative charge resulting from a substitutional defect is balanced by a proton [2]. The strength of an isolated Brønsted acid site is most rigorously defined by the deprotonation energy of the framework. However, deprotonation energies are not easily

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measured for zeolites. They can be calculated by a number of theoretical methods, but accurate values are challenging to compute as different methods can give contradictory results [3]. Furthermore, deprotonation energy is an incomplete descriptor for reactivity in zeolites, as solvation effects and interactions between positively charged species and the framework contribute to the observed reactivity [4–7]. Another common measure of acid strength is the interaction of the acidic OH group with basic probe molecules, monitored by, e.g., vibrational spectroscopy [8] or NMR [9]. In recent studies, it has been observed that while reaction rates globally increase when a stronger acidic catalyst is employed, the extent of the increase is not uniform for all individual reactions [10–12].

During the last decades, conversion of methanol to hydrocarbons (MTH) has received significant attention due to its attractiveness in processes where natural gas, coal or biomass is converted to fuels and chemicals. By tuning the catalyst and reaction

conditions, a wide variety of hydrocarbons can be produced [13]. The MTH reaction is catalysed by Brønsted acidic zeolitic catalysts. It proceeds through a complex network of reactions, referred to as the hydrocarbon pool mechanism [13–17]. The hydrocarbon pool mechanism was initially proposed by Dahl and Kolboe [18–20] and has been the subject of numerous other studies [13,14,16]. The hydrocarbon pool mechanism mainly consists of two interrelated reaction cycles in which polymethylbenzenes (polyMBs) and alkenes are sequentially methylated and cracked or de-alkylated to form light alkenes (see Scheme 1). These two cycles are often simply referred to as the arene and alkene cycles, respectively. The relative importance of each cycle is determined mainly by three factors: (1) catalyst topology, (2) reaction conditions and (3) acid strength. Both cycles operate simultaneously in the medium pore catalyst H-ZSM-5 [21,22], but the arene cycle can be suppressed in the narrow channels of H-ZSM-22 [23,24]. At similar conditions, methanol conversion over large-pore zeolites proceeds mainly via the arene cycle [25–28]. However, the reaction conditions are of great importance, as the alkene cycle can be promoted in large-pore zeolites when low temperatures and high pressures are employed [29,30]. Some of the present authors recently demonstrated that the relative importance of the arene and alkene cycle is influenced by the zeolitic acid strength [31,32].

In this work, the influence of zeolitic acid strength on the methylation of arenes and alkenes was studied over the isostructural, but compositionally different, materials H-SSZ-24 and H-SAPO-5 (AFI structure). H-SSZ-24 is an aluminosilicate zeolite, while H-SAPO-5 is a silicoaluminophosphate. This difference in composition leads to a difference in Brønsted acid strength [33–35], with H-SAPO-5 containing weaker acid sites than H-SSZ-24 [32]. The AFI framework is composed of columns of twisted four- and six-rings, together forming one-dimensional twelve ring channels running parallel to the *c*-axis. These channels are nearly circular and measure 7.3 Å in diameter. Previous studies on this structure demonstrated that the largest observed major product during methanol conversion is the same as during homogeneous methanol conversion, i.e. hexamethylbenzene (hexaMB) [36,37]. Thus, the AFI topology apparently provides limited, if any, product shape selectivity. The acid strength of isolated sites is the main difference between H-SSZ-24 and H-SAPO-5. However, the difference in composition may also lead to different interaction behaviour between molecules and the framework.

The main emphasis of this work was on the reaction between methanol and benzene. Methanol/benzene co-reactions have been performed previously over the same catalysts [31,32], but the focus of those studies was on formation of light alkenes and not on arene methylation. In the current study, experiments were performed at very low benzene conversion (<0.3%) in order to limit the extent of secondary reactions. Even so, significant by-product formation was

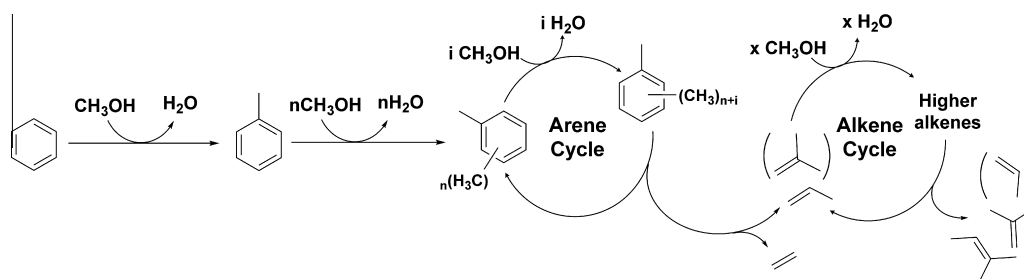
observed (*vide infra*). A schematic overview of reactions that may occur during this co-reaction, based on the current understanding of the dual-cycle mechanism, is shown in Scheme 1. The conditions employed here were expected to strongly favour the reactions to the left in Scheme 1. In addition to monitoring product selectivity, isotopic labelling was employed to distinguish primary from secondary products.

Additional experiments were performed to directly compare rates of benzene and propene methylation over the two catalysts. These experiments were complemented with a theoretical study on the dynamical adsorption behaviour, formation of pre-reactive complexes and reactivity of methanol and the hydrocarbons in both materials. Density functional theory (DFT)-based molecular dynamics and metadynamics simulations were found to illuminate the fundamental causes of the experimentally observed differences in reactivity. Recently, some of the present authors performed a molecular dynamics study on the methylation of benzene in H-ZSM-5 and discovered that prior to reaction various protonated methanol clusters can be formed. These methanol clusters seemed to have a lower reactivity towards benzene methylation as compared to single methanol molecules [38]. In this work, dynamical adsorption behaviour is for the first time linked with experimentally observed reactivities.

## 2. Materials and methods

### 2.1. Experimental details

The synthesis of H-SSZ-24 and H-SAPO-5 has been described previously [32]. Both samples were characterised by powder X-ray diffraction, scanning electron microscopy, N<sub>2</sub> adsorption, n-propylamine TPD and CO-adsorption monitored by FT-Infrared spectroscopy (FTIR). More details on catalyst characterisation are available in Supporting Information (Section S1). FTIR-monitored adsorption of CO confirmed that H-SSZ-24 contained stronger Brønsted acidic sites than H-SAPO-5. The largest shift in O–H stretching frequency upon adsorption of CO observed in H-SSZ-24 was  $\Delta\nu_{\text{OH}} = -317 \text{ cm}^{-1}$ , while the shift in H-SAPO-5 was  $\Delta\nu_{\text{OH}} = -265 \text{ cm}^{-1}$ . Both samples were highly crystalline and exhibited similar BET surface areas (360 m<sup>2</sup>/g and 340 m<sup>2</sup>/g, respectively). Acid site densities were determined to be 0.11 mmol/g (Si/Al ~ 150) and 0.068 mmol/g (Al + P/Si ~ 240), respectively, from TPD of n-propylamine performed in a manner similar to that described by Gorte et al. [6,39,40]. After pre-treatment in a flow of oxygen at 550 °C, the catalyst was cooled to 150 °C. 80 ml/min (all flows are at SATP) of N<sub>2</sub> bubbled through a saturator containing n-propylamine at room temperature was then fed over the catalyst for 20 min. Subsequently, the catalyst was left



**Scheme 1.** Reactions expected to occur during co-reactions between benzene and methanol according to the generally accepted dual-cycle mechanism [13,31]. The reactions to the left of the scheme are expected to dominate at the chosen conditions. Benzene is first methylated to form toluene, which may be further methylated to form polymethylbenzenes. These polymethylbenzenes may de-alkylate as part of the arene cycle to yield lower alkenes. The alkenes may react further in an alkene cycle, where they are methylated to higher alkenes, and crack to form mainly branched C<sub>4</sub> and C<sub>5</sub> alkenes. It is assumed that ethene leaves the catalyst without further reaction due to its low methylation rate [75,85,86].

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