



Durability improvements of H-ZSM-5 zeolite for ethanol conversion after treatment with chelating agents[☆]



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ABSTRACT

An H-ZSM-5 zeolite (Si/Al = 12) was treated with solutions of tartaric acid, citric acid and EDTA. The impact of this treatment on the durability in the conversion of ethanol was investigated and correlated with the extraction of small amounts of aluminium. M06-L/6-31G(d) was applied as level of theory for the quantum chemical part of this work. These investigations showed that all EFSPE can be regarded as solvable and hence also as removable. By solid state characterisations (NMR, IR, XRD) no changes in the bulk properties were observed, although catalytic testings of the treated samples showed significant durability improvements. This ostensible contradiction can be explained by a changed ethene supply to the hydrocarbon pool after the removal of EFSPE acting as active sites which catalyse only dehydration reactions.

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1. Introduction

1.1. Importance and properties of H-ZSM-5 catalysts

H-ZSM-5 is alongside zeolite Y well known from the FCC process for acid catalyzed conversion of high-molecular-weight hydrocarbons. It is characterised by a 3D microporous channel-system with strong Brønsted acid framework sites and weaker Brønsted and Lewis acid extra-framework sites [1,2]. An accurate discussion of its reactivity and catalytic behaviour has to account for its geometric and its chemical properties [3–5]. With respect to the zeolite framework both diffusional and shape selective effects are important and with respect to its chemical properties different possible acid sites have to be considered. This includes framework Brønsted acid sites, but also extra-framework species (EFSPE) such as extra-framework silicon species (EFSI), extra-framework aluminium species (EFAL) and extra-framework aluminium silicon species (EFALS). There is a huge repertoire of methods which can be applied to influence the framework and extra-framework

composition of zeolites after synthesis, e.g. steaming or extraction methods [2,6,7].

Among the multitude of known applications of H-ZSM-5 catalysts [8–12] the conversion of ethanol to hydrocarbons – the ETH process – is the theme of this article.

1.2. Mechanism of ethanol conversion over H-ZSM-5

There are still some uncertainties in drawing a complete picture of product formation during ethanol conversion, in spite of multiple efforts to clarify the conversion routes and reaction mechanisms in the ETH process [13,14]. Generally the conversion starts with ethanol dehydration either at acid sites or by thermal processes. The formed ethene may be consumed in different consecutive reactions in the hydrocarbonpool (HCP) at organic-inorganic hybrid catalytic sites, namely by polymerisation, cracking, hydride transfer or cyclisation reactions [3,14,15]. These catalytic sites are often discussed as cyclic or olefinic carbenium or radical organic species in vicinity to deprotonated zeolitic Brønsted acid sites [15]. Therefore ethene could be treated as feed for HCP-reactions in a proper sense, because dehydration of ethanol is an essential first step or it occurs simultaneously to the initial build-up reactions.

The geometric and chemical properties of the H-ZSM-5 zeolite influence the reaction routes in different ways [16]. Two general aspects to consider in this regard are the barrier heights of transition states and the relative quota of competitive reaction routes.

[☆] Dedicated to Prof. Dr. Joachim Sauer on the occasion of his 65th birthday.

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They can be influenced by confinement effects inside the pore system as well as by the balance between retardation and mobility of molecules and deposits inside cavities due to different molecule sizes. In addition there are specific aspects for each of the several routes, respectively.

- (i) The dehydration of ethanol can take place at almost all of the acid sites independent of their strength or location. Thermal dehydration is also possible.
- (ii) On the contrary, bond formation and bond cleavage (e.g. polymerisation, cracking or hydrogen transfer) strongly depend on the presence of strong Brønsted acid sites.
- (iii) Product formation arises mainly from the HCP at hybrid reaction sites. Therefore the formation of products aside from polymerisation depends on the integrity and accessibility of the pore system.

1.3. Deactivation routes over H-ZSM-5 zeolite

The process of catalyst deactivation is usually very complex and there are several sources which may account for deactivation. The scope of the deactivation sources is very broad and includes – but is not limited to – poisoning, thermal degradation, formation of gaseous compound, gas phase-solid or solid state reactions, mechanical degradation and fouling. However, the formation of organic species which are catalytically inactive and too large to leave the catalyst pore system – generally denoted as coke – seems to be the fastest deactivation source in ETH process over H-ZSM-5 and is therefore the main subject on the debate [3,17]. Coke deposits block the access to active sites inside the pore system and therefore promote the formation of ethene, which may also form independently of a surrounding pore system or by thermal dehydration at temperatures over 350 °C. Therefore ethene formation may be considered a measure of deactivation. The pore blocking character during the reaction is possibly correlated to the chemical nature of the deposits in the following order: olefins < aromatics with side chains < high-molecular-weight aromatic compounds [3].

Coke formation occurs by growth and demobilisation of aromatic and olefinic precursor molecules, e.g. organic compounds of hybrid sites, until their centre of reaction is no longer accessible for feed molecules and other HCP species. With increasing time-on-stream the active HCP molecules are deactivated by intramolecular reactions such as hydride transfer, cyclisation or recombination with coke precursors which may diffuse inside the pore system [3]. Also, long time persistent radical-type sites of passivated polyaromatic compounds probably exist under high pressure [18].

The pore system dependent product formation routes and coke formation, which are consecutive to ethanol dehydration, occur simultaneously. Other than ethanol dehydration they are both strongly dependent on the nature of active sites, their local environment, their accessibility and diffusional limitations inside the catalyst pore system.

1.4. Impact and chemical nature of extra-lattice species

EFSPE are in general all charged and uncharged molecules and structures not belonging to the ideal crystal structure on the external and internal surface of catalyst samples. EFAL, EFSI and EFALSI are generated as residuals or side products during zeolite synthesis. Dealumination processes may lead to transformations between framework and non-framework species [2,7,19]. Catalytic activity is proposed to some, especially EFAL, e.g. as weak Brønsted

or Lewis acidic sites or adsorption sites, respectively [20]. Especially Lewis acidic sites are generated during processes such as dehydroxylation during thermal treatment or different postsynthetic dealumination techniques, compare below [21,22].

EFSPE can influence the geometric as well as the chemical properties of H-ZSM-5. Their steric influence may lead to pore blocking and diffusion limitations. However, their chemical impact on the zeolite as catalytic active sites is in most cases much more severe. EFAL often represent Lewis acid sites which are able to promote ethanol dehydration. In some cases also silanol groups and EFSI are considered as weak Brønsted acids. In that sense, different distributions, types and amounts of EFSPE inside catalytic materials could lead to a different local ethanol dehydration activity and thereby different water and ethene concentration inside the pore system. This can influence the catalyst structure and catalytic behaviour [23].

1.5. Exemplary methods for dealumination and desilication

Besides the mentioned dehydroxylation process during thermal treatment of zeolites, different techniques of dealumination, desilication of framework species as well as removal or transformation of EFSPE are state of the art [2,21]. The impact of methods to change the amount, distribution or nature of existing species on the catalyst behaviour is well documented in scientific literature [2,6,7,24]. In most cases efficiency of dealumination techniques by liquid phase transformation, e.g. by mineral acids or chelating agents such as EDTA varies until 50% or leads to non-negligible structural damages in case of more severe preparation conditions. Additional reinsertion of silica, e.g. by use of a $(\text{NH}_4)_2\text{SiF}_6$ solution, improves the stability of the framework but imposes the risk of pore blocking by hard removable fluoride species with alumina [2,21]. Gas phase dealumination techniques such as hydrothermal treatment or use of volatile SiCl_4 improves efficiency of dealumination processes. Also within these processes structural damages of zeolitic materials occur depending on post-synthetic preparation conditions such as temperature, pressure or duration. Formation of sticky species, e.g. Alumochlorine-oxo-species which are hard to remove by washing procedures afterwards, is often inevitable [2,21,22].

The impacts of these methods on catalyst samples have been proven by ^{27}Al -MAS-NMR. However, the applicability of the observed changes to EFSPE and their distribution is very limited. Often they do not support further correlations to catalyst behaviour [25].

1.6. Scope of this work

Balancing dealumination efficiency, chemical composition and catalytic activity of EFSPE inside the channels, diffusional conditions inside the pores on the one hand and structural integrity to protect desirable shape selective catalytic effects on the other hand is a complex task which has to be handled stepwise.

Although the main goal of this work is to improve the durability of H-ZSM-5 during the conversion of ethanol, we further try to correlate the increased durability to changes on the catalyst surface and especially to changes in the composition of EFSPE by applying solid-state characterisations, quantum chemical modelling and catalytic testing.

2. Experimental

2.1. Calculations

Transition state calculations were performed using the software suite Gaussian version 09 [26]. The M06-L functional [27] with the

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