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Review

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# Novel Process Options for the Application of Zeolites in Supercritical Fluids and Ionic Liquids

Supercritical fluids and ionic liquids offer attractive opportunities for modifying and applying zeolites as adsorbents and catalysts. After a brief introduction to the most important properties of these solvents, examples of zeolite applications in supercritical fluids and ionic liquids from the recent literature are discussed. Particular emphasis is put on the influence of reaction media on the processes occurring in the zeolitic pore systems, e.g., during shape-selective conversions in zeolite catalysts. The present potential and future challenges for the application of zeolites in supercritical fluids and ionic liquids are identified. Most attractive process options arise from a combined use of both ionic liquids and supercritical fluids in integrated reaction schemes.

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## 1 Introduction

Zeolites, i.e., microporous crystalline aluminosilicates, are an important class of high-tech materials for modern chemical technology. They are mainly used in ion exchange, adsorptive separations and heterogeneous catalysis [1–3]. The most important property of zeolites for these applications is their well-defined pore diameter lying in the same range as that of common chemical molecules. This gives rise to shape selectivity effects in adsorption and heterogeneous catalysis with zeolites. Molecules of adsorbents as well as reactants, products or transition states of chemical reactions can be selectively excluded from access to and/or egress from the zeolite pores due to the local constraints within the zeolite pore systems. These shape selectivity effects are the basis of the molecular sieve properties of zeolites.

The partly high densities of the phases adsorbed in zeolites lead to the so-called concentration effect. In the adsorbed state at saturation, the adsorbates or reactants experience, in addition to the electrostatic fields within the zeolite pores, forces similar to those in liquids at elevated pressures [3]. This effect allows the zeolite pore volume to be effectively used and, in some cases, it also influences the selectivity in a zeolite-catalyzed reaction. For a specific application in adsorption or in heterogeneous catalysis, active sites with a broad diversity of

chemical functionalities can be introduced into zeolites. These functionalities as well as the surface properties of zeolites can be modified by a large variety of postsynthetic treatment methods [4].

Since their first large-scale application in the refining industry in the 1960s, zeolites have been established as catalysts in a continuously increasing number of chemical conversions. This also includes the synthesis of fine and specialty chemicals [1, 5–7]. It is in these applications that liquid solvents are frequently used to contact reactants with a solid catalyst. In many instances, the solvent molecules are directly involved in the catalytic cycle and, thus, influence both conversion and selectivity of the reaction. Besides the effects of solvent on mass and heat transfer in industrial conversions, solvent separation from the reaction products, solvent recycling and the prevention of solvent emissions to the atmosphere often have a significant impact on the costs of a chemical production process. Against this background, it is an attractive goal to search for innovative and environmentally benign reaction media.

The present review focuses on the use of supercritical fluids and ionic liquids as alternative media for the modification and application of zeolites. Supercritical fluids have been intensively investigated for several years as media for adsorption and, in particular, for heterogeneous catalysis [8–10]. Therefore, here, only selected examples of zeolite applications in supercritical fluids can be considered. By contrast, the use of zeolites in and with ionic liquids is still in its infancy. Accordingly, an almost complete review of the literature currently available is presented. Particular emphasis is placed on whether and how the properties of supercritical fluids and ionic liquids

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affect the processes occurring within the pores of zeolites. Finally, the present potential and the future challenges for the application of these innovative media with zeolites as adsorbents or catalysts are briefly evaluated.

## 2 Application of Zeolites in Supercritical Fluids

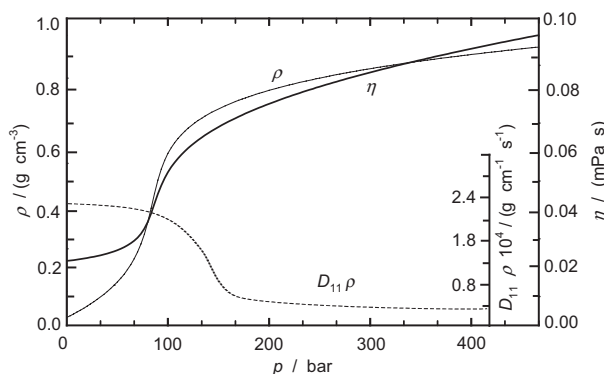
### 2.1 Properties of Supercritical Fluids

A supercritical fluid is defined as a substance beyond its critical point, i.e., critical temperature  $T_c$  and critical pressure  $p_c$ , but below the pressure required for condensation into the solid state. Supercritical fluids exhibit properties intermediate between those of typical liquids and gases (see Tab. 1). Thus, liquid-like solubilities can be combined with gas-like mass transfer rates. Most importantly, the decisive properties of these media for a given application can be varied over a broad range at temperatures near the critical point ( $T_{red} = 1.00$ – $1.30$ ) with only small changes in pressure. This is illustrated in Fig. 1 for carbon dioxide as an example. These strongly pressure-dependent properties also allow the products of a reaction mixture to be separated by an isothermal pressure decrease. In many cases, depressurizing the supercritical mixture is sufficient to isolate the products in a pure form.

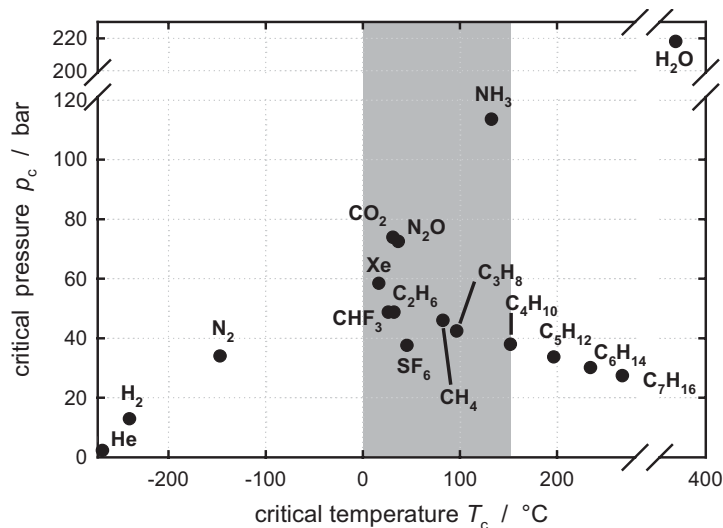
**Table 1.** Comparison of density  $\rho$ , dynamic viscosity  $\eta$  and self-diffusion coefficient  $D$  of gases, liquids and supercritical fluids.

Property	Gas <sup>a)</sup>	Supercritical fluid	Liquid
$\rho/\text{g dm}^{-3}$	0.6–2	200–500	600–1600
$\eta/\text{mPa s}$	0.01–0.3	0.01–0.03	0.2–3.0
$D/10^{-6}\text{m}^2\text{s}^{-1}$	10–40	0.07	0.0002–0.002

a) at  $p_{\text{gas}} = 1$  bar



**Figure 1.** Density  $\rho$ , dynamic viscosity  $\eta$  and product of self-diffusion coefficient  $D_{11}$  and density for carbon dioxide at  $40^\circ\text{C}$  ( $T_{red} = 1.03$ ) as a function of pressure.



**Figure 2.** Critical data ( $p_c$  and  $T_c$ ) for selected pure substances. Temperature range from 0 to  $150^\circ\text{C}$ , which is of interest for organic syntheses, is highlighted.

Fig. 2 shows the critical temperatures and pressures of selected pure substances. Evidently, the supercritical state can be reached for many substances in the temperature range of  $0$ – $150^\circ\text{C}$  that is of interest for the synthesis of organic compounds. Often, pressures  $< 100$  bar are sufficient. For ammonia and water, which both consist of strongly hydrogen-bonding molecules, the conditions at the critical point are significantly higher. The solvents mainly used in industrial applications at supercritical conditions are carbon dioxide, water as well as saturated hydrocarbons with up to six carbon atoms. This selection is predominantly governed by safety considerations (inertness under reaction conditions, toxicity, flammability, explosion limits, etc.), environmental benignity, availability and costs. Some other substances are used as supercritical fluids with a high polarity ( $\text{CHF}_3$ ,  $\text{N}_2\text{O}$ ) or a high polarizability ( $\text{Xe}$ ,  $\text{SF}_6$ ) for research purposes.

Another important property of supercritical reaction media is the lack of a gas/liquid phase boundary. This can, in particular, be beneficial to conversions which are conventionally performed in multiphase systems and where the rate is limited by mass transfer across such phase boundaries. Catalytic hydrogenations or oxidations in conventional multiphase systems are typical examples. The lack of a gas/liquid phase boundary is also important when using (micro)porous solids: the surface tension at this interface often hinders liquid phases from permeating into pores with too small diameters. The potential to use supercritical fluids capable of penetrating narrow pores with small diameters is discussed later in this study.

The properties important for the application of supercritical fluids in heterogeneous catalysis may be summarized as follows [9, 10]:

- Elimination of mass-transfer limitations both within the bulk fluid and across liquid/gas, solid/gas or solid/liquid phase boundaries.

- Extraction of reaction intermediates from the catalyst surface. This way, the deactivation of catalysts due to deposition of poisons such as coke can be reduced or even avoided. For consecutive reaction sequences such as partial hydrogenations or oxidations, the selectivity can be increased by rapidly removing a reaction intermediate from the catalyst surface before it undergoes a consecutive reaction. Additionally, the rate of mass transfer processes can be controlled by pressure. This way, in some cases, the selectivity of heterogeneously catalyzed conversions can be controlled by pressure variation [11].

- Improved heat transfer between a solid catalyst and the surrounding fluid with respect to gas-phase conversions.

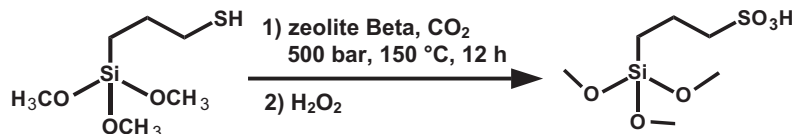
It should be emphasized that supercritical fluids as solvents or reaction media do not possess principally new properties. Their uniqueness rather lies in the combination of typically gas- and liquid-like properties as well as in the dependence of these properties on temperature and pressure near the critical point.

## 2.2 Modification of Zeolites and Related Materials

Supercritical fluids can be used to introduce guests into the pores of micro- or mesoporous molecular sieves or to chemically modify the walls within the pores of such materials. Due to the high diffusivity and the virtually negligible surface tension of supercritical fluids, these modifications can be achieved within short time and with a more controllable loading than with conventional liquids. These advantages are illustrated by way of three examples.

Holmes et al. [12] demonstrated that supercritical fluids can be used to prepare nanostructured metals and semiconductors within ordered mesoporous materials. So, for instance, nanowires of silicon or germanium can be introduced into MCM-41-type molecular sieves by controlled decomposition of metal organic precursors in supercritical *n*-hexane. Unlike conventional gas-phase procedures such as chemical vapor deposition (CVD), complete filling of the internal pore volume can be achieved. Moreover, metal deposition is completed within 15–30 min, whereas in liquid phase procedures it takes days. The resulting silicon-containing composite materials show a UV photoluminescence with an emission maximum depending on the pore diameter of the mesoporous host. They are, thus, attractive as sensors or for other optical applications.

The reactive deposition of metals from supercritical fluid solutions (chemical fluid deposition, CFD) is particularly attractive for the preparation of solid catalysts [13]. For this, a metal organic complex is dissolved, for instance, in supercritical carbon dioxide in the presence of a solid support material. By adding hydrogen to the supercritical complex solution the metal is deposited directly on the support. Thus, both the solubilizing power of supercritical fluids for high-boiling compounds and the miscibility with gases like hydrogen are used. First results for the deposition of platinum by reduction of the precursor complex cyclooctadienyldimethylplatinum(II) in



**Figure 3.** Schematic representation of surface functionalization of zeolite beta with sulfonyl groups by grafting of tris(methoxy)mercaptopropylsilane during treatment in supercritical carbon dioxide and subsequent oxidation after [15].

supercritical carbon dioxide indicate that CFD can be achieved in mesoporous materials such as MCM-41 ( $d_p = 2.3$  nm), but not in microporous zeolites like silicalite-1 or beta [14].

The third example concerns the chemical functionalization of the internal surface of zeolite beta ( $d_p = 0.7$  nm). First, the zeolite is treated with tris(methoxy)mercaptopropylsilane (TMMPS) in supercritical carbon dioxide to obtain thiol groups attached to the internal surface. After subsequent oxidation of the thiol groups to sulfonyl groups (see Fig. 3), a strongly acidic catalyst with shape-selective properties is obtained [15]. The ketalization of cyclohexanone with ethylene glycol is catalyzed, whereas the bulkier pyrene aldehyde is not converted as it has no access to the zeolite pores. This example shows that molecular species can be transported even into microporous materials by using supercritical fluids.

## 2.3 Adsorption

In single-component adsorption at supercritical conditions, the adsorbed phase approaches a constant volume and a constant density with increasing pressures [16, 17]. This phenomenon is the basis of a method to determine the specific surface area of the adsorbent, independent of the space requirements of the adsorbate molecule [16]. This method is also applicable to zeolites such as Na-Y [17]. Interestingly, an adsorption maximum is found at conditions close to the critical point, which is more pronounced for zeolite Na-Y than for a microporous carbon [17]. This may be attributed to a higher density of the adsorbed phase due to the extremely high fluid compressibility at the critical point or to a higher fraction of adsorption on the external vs. the internal pore surface of the zeolite. The density of the carbon dioxide phase adsorbed on zeolite Na-Y at 32 °C is considerably higher than that of liquid carbon dioxide and close to that of solid carbon dioxide (see

**Table 2.** Density  $\rho$  of carbon dioxide adsorbed on zeolite Na-Y ( $p \gg p_c$ ) and at different conditions after [17].

Phase	$\rho / (\text{mmol cm}^{-3})$
Adsorbed phase (32 °C)	28.84
Critical density	10.63
Saturated liquid at 30.5 °C	12.78
Liquid at 30.5 °C, 200 bar	20.19
Dry ice (−74.8 °C, 1 bar)	34.16
Close-packed spheres	40.82

Tab. 2). Obviously, the interaction of the adsorbate with the pore wall has a much stronger effect on the adsorbed phase than the physical state of the fluid surrounding the adsorbent.

Only few investigations are available on the adsorption of substances from supercritical solutions on zeolites. Adsorption from supercritical carbon dioxide was applied to load the large-pore molecular sieve VPI-5 with benzoic, salicylic and acetylsalicylic acid within a short time [18]. The composite materials thus obtained might be of interest for the controlled release of pharmaceutically active compounds. In the adsorption of naphthalene on zeolite La,Na-Y at 200 °C and constant naphthalene mole fraction in the fluid phase, the same loading on the zeolite ( $m_{\text{Np}}/m_{\text{zeolite}} = 0.19$ ) was observed at pressures of 1 bar (gas phase) and 200 bar (supercritical phase) [19]. This may be considered an additional evidence that the density of the adsorbed phase in zeolites is virtually not affected by the physical state of the surrounding fluid.

Supercritical fluids can also be appropriate media for adsorptive separations. This was shown by Iwai et al. [20, 21] for the competitive adsorption of the isomers 2,6- and 2,7-dimethylnaphthalene (DM-Np) on zeolite Na-Y. With supercritical carbon dioxide as the solvent for both aromatic hydrocarbons, the separation factor  $K$  exhibits a strong pressure dependence (see Tab. 3). At higher pressures, more 2,7- than 2,6-DM-Np was adsorbed on the zeolite in supercritical carbon dioxide than in liquid n-octane. Pressure had only a slight influence on the diffusivity of the two isomers within the zeolite pores.

**Table 3.** Separation coefficient  $K = (m_{\text{ads},2,7\text{-DM-Np}}/y_{2,7\text{-DM-Np}})/(m_{\text{ads},2,6\text{-DM-Np}}/y_{2,6\text{-DM-Np}})$  and total loading  $Q = (m_{\text{ads},2,7\text{-DM-Np}} + m_{\text{ads},2,6\text{-DM-Np}})/m_{\text{zeolite}}$  for the competitive adsorption of 2,6- and 2,7-dimethylnaphthalene (DM-Np) on zeolite Na-Y at 35 °C and different pressures after [20, 21].

$p/\text{bar}$	$K$	$Q/(\text{g g}^{-1})$
120	1.6	0.120
148	2.1	0.049
198	2.2	0.076
Liq. octane	1.4	0.170

Another promising process option for zeolites is their application as a component of membranes for the separation of mixtures. With membranes containing zeolite Na-Y or silicalite-1, carbon dioxide could be successfully recovered from a supercritical solution of caffeine [22, 23]. Such solutions are obtained, for example, when extracting coffee beans with supercritical carbon dioxide. For cost reasons, an isobaric separation of carbon dioxide is to be preferred. At 35 °C and pressures below 120 bar, caffeine was completely retained by a silicalite-1 membrane and, thus, pure carbon dioxide was recovered [23].

## 2.4 Heterogeneous Catalysis

Several advantages of supercritical fluids as reaction media for heterogeneously catalyzed conversions have already been men-

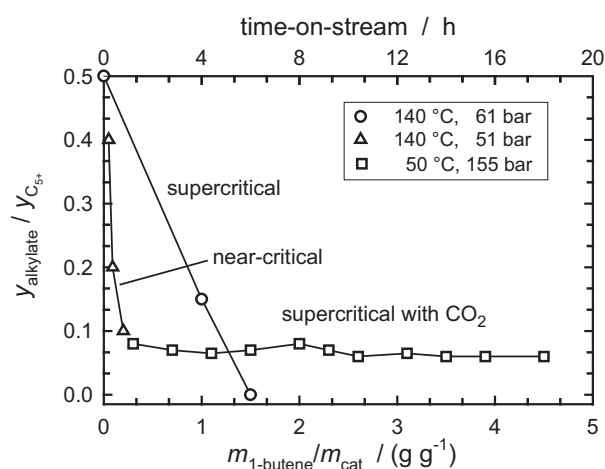
tioned above. In the following sections, some examples of heterogeneous catalysis by zeolites are discussed where the specific high-pressure phase behavior of supercritical fluids or the shape-selective properties of zeolites are exploited.

### 2.4.1 Application of High-Pressure Phase Behavior

Both in the open and the patent literature, numerous examples are described in which deactivation of solid catalysts could be reduced or avoided by using supercritical fluids as reaction media [9, 10, 24]. Increased catalyst stability under supercritical conditions is predominantly due to the improved solubility (compared to conventional gases) and the accelerated removal (compared to conventional liquids) of higher boiling compounds from the catalyst surface. The deposition of such compounds would otherwise lead to poisoning and, hence, deactivation of the catalyst.

One important example where deactivation of a zeolite catalyst has, so far, prevented industrial application is the alkylation of isobutene with olefins [2, 3]. This conversion is of great importance for the production of high-quality gasoline blending components (alkylate). It is currently carried out by catalysis with liquid acids such as aqueous  $\text{H}_2\text{SO}_4$  or HF. The use of supercritical process conditions to extend zeolite catalyst life in isobutene alkylation was already described in a patent of 1994 [25]. However, at temperatures above 135 °C ( $T_c$  of isobutane) required to reach supercritical conditions, undesired side reactions, i.e., cracking and olefin oligomerization, lead to insufficient product quality.

Clark and Subramaniam [26] succeeded in reducing the critical temperature of an isobutane/1-butene feed mixture with a molar ratio of 9/1 to 40 °C by adding a 5-fold molar excess of carbon dioxide. Under supercritical conditions at 50 °C, no deactivation of an acidic USY-type zeolite was observed for more than two days on-stream (see Fig. 4). However, 1-butene



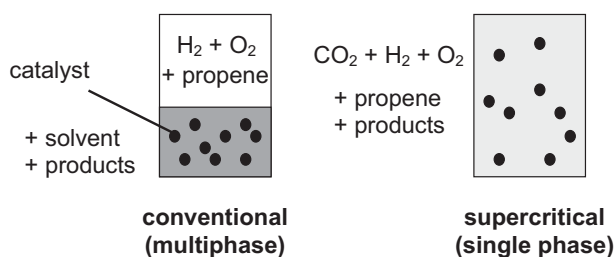
**Figure 4.** Alkylate fraction in  $\text{C}_{5+}$  products obtained in alkylation of isobutane with 1-butene over zeolite H-USY at near-critical conditions (140 °C, 51 bar), at supercritical conditions (140 °C, 61 bar) and at supercritical conditions in the presence of carbon dioxide (50 °C, 155 bar) after [26].

conversion was only 20 % and the fraction of the desired alkylate in the product was only 5–10 %. Moreover, the product is strongly diluted with carbon dioxide. At higher butane conversions, the catalyst is subject to a pronounced deactivation even under supercritical conditions [27]. A major part of coke deposits on a zeolite catalyst can be removed through cyclic regeneration in supercritical isobutane. Thus, a butene conversion >92 % can be maintained for more than 210 h on-stream [28]. Nevertheless, the composition of the alkylate product does not yet meet industrial requirements.

The effect of high-pressure phase behavior on conversion rate and catalyst stability was systematically studied for the Friedel-Crafts alkylation of benzene with ethane or propene over acidic zeolites. To obtain the reaction mixture benzene/ethane in different physical states, Shi et al. [29] varied composition, pressure and temperature in the range of 240–260 °C. In the conversion over zeolite H-beta, the authors observed a maximum reaction rate at pressures slightly above the critical point. With further increase in pressure at supercritical conditions, however, the conversion rate decreased. Also, an additional but less pronounced maximum of the reaction rate was found within the two-phase (liquid/gas) region of the feed mixture, again at near-critical pressure. These findings confirm that a given reaction can proceed faster in the vicinity of the critical point than in single gas or liquid phases. But, conducting the reaction in a single supercritical phase does not necessarily result in higher conversion rates.

Supercritical conditions close to the critical point are of advantage with regard to a long catalyst lifetime for the conversion of benzene with propene over zeolite H-beta. As recently shown by Tian et al. [30], this is especially true if, as the reaction proceeds, the reaction mixture undergoes a phase transition from the supercritical into the liquid state. By contrast, catalyst deactivation occurs very early if, initially, the reaction phase is present as a gas far from the critical point, and a liquid phase is formed in the course of conversion.

An innovative concept for the heterogeneously catalyzed propene epoxidation also relies on single-phase conditions with supercritical carbon dioxide as the reaction medium (see Fig. 5). Here, a bifunctional catalyst with microporous titanium silicalite-1 (TS-1) as a redoxactive component and with noble metals such as Pd, Pt as de-/hydrogenation components are first used for in-situ generation of hydrogen peroxide from



**Figure 5.** Schematic representation of the phases present during the heterogeneously catalyzed epoxidation of propene. Besides the solid catalyst, a multiphase system is present under conventional reaction conditions (left-hand side), whereas only one homogeneous phase exists under supercritical reaction conditions (right-hand side).

the elements. Hydrogen peroxide is then used for subsequent epoxidation of propene [31]. Here, supercritical carbon dioxide not only serves as a solvent for a homogeneous phase containing all reactants and products but, due to its chemical inertness and the high dilution of hydrogen and oxygen, allows the conversion process to be safely operated outside the explosion limits of the system. If methanol is used as a promoter for the titanium catalyst and as a co-solvent for the supercritical carbon dioxide, formic acid is formed as a by-product, poisoning the catalyst [31]. According to Beckmann et al. [32], the presence of methanol is not essential for the catalytic activity of TS-1 in supercritical carbon dioxide. Currently, the highest propene conversion achieved is less than 10 %, however, propene oxide selectivity is higher than 90 %.

## 2.4.2 Shape-Selective Catalysis in Supercritical Fluids

Shape selectivity effects in heterogeneous catalysis by zeolites are, naturally, based on the micropores of this catalyst class. The question whether or not the processes occurring in the zeolite pores are (or can be) affected by the physical state of the reaction phase surrounding the zeolite has been discussed controversially since the first reports on zeolite catalysis in supercritical fluids. The effects arising from the spatial constraints within the zeolite pores, especially transition-state and product shape selectivity, might be determined by the properties of the fluid surrounding the zeolite crystals. The question of how the properties of the outer phase affect the conditions in the zeolite pores has already been considered under Adsorption (see section 2.3). It is discussed further by way of some examples from zeolite catalysis.

Selectivity changes due to varying the reaction pressure or due to the presence of a supercritical reaction phase as mentioned above were also described for several zeolite-catalyzed conversions. So, for instance, in the alkylation of toluene with propene over zeolite H-ZSM-5 under supercritical conditions, a higher selectivity for the para-substituted reaction product and a lower selectivity for propene cracking were observed, compared to the gas-phase conversion [33]. In toluene alkylation with ethene catalyzed by a USY-zeolite at supercritical conditions, Ginosar et al. [34] achieved a lower cracking and disproportionation selectivity and a correspondingly higher alkylation selectivity, compared to the conversion under liquid-phase reaction conditions. This result was rationalized in terms of a phase-dependent deactivation mechanism.

For the disproportionation of toluene over zeolite H-ZSM-5 at a temperature close to the critical point ( $T_{\text{red}} = 1.002$ ,  $T_c(\text{toluene}) = 318\text{ °C}$ ,  $p_c(\text{toluene}) = 41\text{ bar}$ ), a maximum in p-xylene selectivity was found at the critical pressure [35]. According to the authors, this finding is consistent with the formation of solvent clusters around the p-xylene molecules initially formed. Such a local density enhancement of the solvent at the critical point was proven for several dissolved solute molecule, e.g., by spectroscopy [36] or by organic test reactions [37]. In the present case of toluene disproportionation, solvent clustering around the p-xylene molecules might impede their readsorption on the catalyst and, thus, prevent their consecutive isomerization. This, however, is the only case

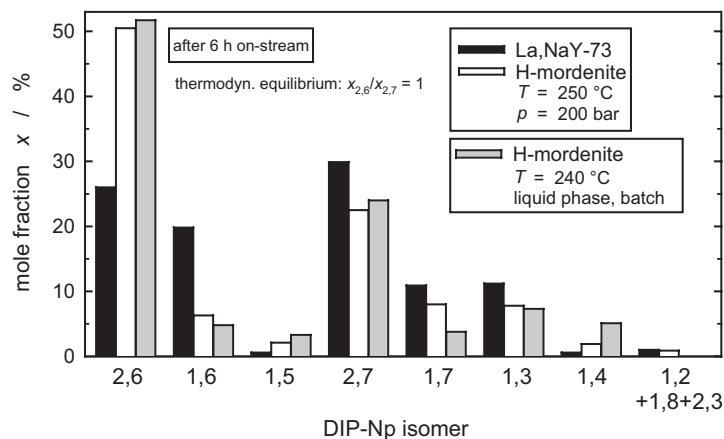


reported so far where the concept of local density enhancement at the critical point was invoked to explain the pressure effect on selectivity of a heterogeneously catalyzed conversion.

In the examples described above, it could not be clearly determined whether selectivity changes were caused by influence of the supercritical phase on the processes occurring within the pores of the zeolite catalysts. On the other hand, the pressure dependence of selectivity for the formation of 1- and 2-methylnaphthalene from naphthalene and methanol in supercritical carbon dioxide over zeolite La,Na-Y was attributed to the influence of the reaction phase on the processes on the outer catalyst surface [19].

In one of the first investigations on heterogeneous catalysis in supercritical fluids, a distinction was made between intra- and intercrystalline deactivation of a zeolite catalyst by coke deposits [38]. While intracrystalline deactivation leads to irreversible coke formation in the zeolitic pore system, the coke deposited on the outer surface of zeolite crystals can be reversibly removed by extraction under supercritical conditions. During a zeolite-catalyzed reaction under supercritical conditions, Niu and Hofmann [39] observed the extraction of polyaromatic coke precursors with slender molecules which were obviously formed due to shape selecting effects. Thus, the authors concluded that the supercritical fluid has access to the inner pore system of the zeolite. Wang and Li [40] found that coking in the disproportionation of toluene could be avoided for a macroporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst if supercritical conditions were used, whereas this was not possible for the microporous zeolite H-ZSM-5. During the acid-catalyzed cracking of n-heptane, Süer et al. [41] and Dardas et al. [42] observed a denser phase within the pores of zeolite Y than in its immediate surroundings, which was in accordance with the results of adsorption mentioned in section 2.3. The authors concluded that only coking within the zeolite pores can be reduced by using supercritical conditions, while this is not possible for coke laydown on the outer crystal surface of the zeolites. For the hydroxyalkylation of phenol on zeolite H-mordenite, the reaction rate was three times higher in supercritical carbon dioxide than in liquid toluene [43]. This was attributed to a faster diffusion of reactants and products in the zeolite pores at supercritical reaction conditions.

Alkylation of naphthalene with 2-propanol over zeolite H-mordenite, known to occur in a shape-selective manner under conventional gas or liquid-phase conditions, was investigated in different physical states of the reaction mixture under otherwise comparable conditions [44]. While the zeolite catalyst was almost completely deactivated after a few hours on-stream in the gas-phase conversion at 1 bar, the conversion in supercritical carbon dioxide at 200 bar was stable for at least ten hours on-stream. At comparable temperature, the distribution of the diisopropylnaphthalenes (DIP-Np) was virtually identical for the continuous conversion in supercritical carbon dioxide and the batch reaction in the liquid phase (see Fig. 6). In particular, the fraction of the more slender 2,6-DIP-Np formed on the mordenite-type zeolite was considerably higher than that of the slightly bulkier 2,7-DIP-Np. With zeolite



**Figure 6.** Distribution of diisopropylnaphthalene (DIP-Np) isomers for the conversion of naphthalene with 2-propanol over the zeolites H-mordenite and La,Na-Y-73 (exchange degree of Na<sup>+</sup> by La<sup>3+</sup>: 73 %) at 250 °C and 200 bar at supercritical conditions and at 240 °C in the liquid phase after [44].

La,Na-Y, exhibiting a more spacious pore system than H-mordenite, both DIP-Np isomers are formed in almost equal amounts according to the thermodynamic equilibrium also in the supercritical reaction medium. These findings can be considered as further evidence that, independent of the physical state of the media surrounding the zeolite crystals, the processes occurring within the zeolite pores are determined only by the spaciousness and the geometry of the pore system and by the chemical properties of the pore surfaces.

Shape-selectivity effects were also observed for the zeolite-catalyzed total oxidation of chlorinated organic compounds in supercritical water (supercritical water oxidation, SCWO). SCWO was developed as a process for the treatment of contaminated waste water to the stage of commercial applicability. However, wider use of the process has been limited so far by the high corrosiveness of supercritical water and the decomposition products formed during the oxidation reaction. Numerous solids have been evaluated as catalysts for SCWO [45]. Copper(I)oxide on zeolites with different pore systems was tested as catalyst for SCWO of 2-chlorophenol, a highly toxic and degradation-resistant model contaminant [46, 47]. Product shape selectivity observed during conversion over these zeolites was evident from the lower selectivities for polychlorinated and polyaromatic compounds compared to the noncatalytic reaction (see Tab. 4). The medium-pore zeolite

**Table 4.** Concentrations of by-products ( $m_{\text{product}}/m_{2\text{-CP}}$  in  $\mu\text{g g}^{-1}$ ) formed during oxidation of 2-chlorophenol (2-CP) in supercritical water at 400 °C over CuO supported on different zeolites ( $c_{2\text{-CP}} = 190\text{--}1500 \text{ mg L}^{-1}$ ) after [46, 47].

Product	No catalyst	CuO/ZSM-48	CuO/ZSM-5	CuO/Y
Phenol	1370	75	166	444
2,4-Dichlorophenol	2590	8.6	20.5	31.1
Naphthalene	25.6	3.4	6.4	17.5

ZSM-48 with a unidimensional pore system proved superior to the likewise medium-pore zeolite ZSM-5 with a three-dimensional pore system and the large-pore zeolite Y. This example shows that shape selectivity on zeolite catalysts can be exploited in supercritical fluids even at reactant concentrations as low as  $190 \text{ mg L}^{-1}$  ( $1.5 \text{ mmol L}^{-1}$ ).

The direct amination of isobutene with ammonia over acidic zeolites such as H-ZSM-5 or H-beta according to the *tert.*-butylamine process of BASF is performed under supercritical conditions at  $300^\circ\text{C}$  and 300 bar and with an ammonia excess of 1.3 to 1.5 [48]. At conversions of 12 to 15 %, the selectivity for the desired product is 99%. Under supercritical reaction conditions, the ammonia fraction in the feed can be kept sufficiently high to reach an acceptable conversion level while, at the same time, transformation of the Brønsted acid sites of the zeolite with ammonia to catalytically inactive ammonium ions can be avoided. In this application of zeolite catalysis under supercritical conditions, transition-state shape selectivity inhibits the dialkylation of ammonia.

## 2.5 Potential and Future Challenges

In view of possible process options, the potential to use supercritical fluids in zeolite applications may be summarized as follows:

- Micro- and mesoporous materials can be effectively modified by incorporating guests by means of supercritical fluids as transport media.
- Higher density of the supercritical phases allows process intensification, as against conventional gas-phase processes. For applications in continuous flow, adsorbers or reactors with lower overall volume can be used.
- Pressure can be used as an additional process parameter. Selectivity in adsorptive separations or in heterogeneous catalysis with zeolites can be controlled by pressure variation. Moreover, the pressure-dependent properties of supercritical fluids allow an integrated product separation, e.g., by an isothermal decrease in solubility by pressure reduction.
- Partly complex high-pressure phase behavior of mixtures near the critical point can lead to higher reaction rates or product selectivities. In many cases, catalyst deactivation due to coking can be reduced or even avoided. In order to fully exploit the potential of supercritical fluids for the application of zeolites in chemical technology and industry, several challenges lie ahead, including:
  - Obvious advantages of using supercritical fluids compete with the disadvantage of high process costs arising from the generation and maintenance of higher pressures. Therefore, applications need to be identified that allow an isobaric product separation without cyclic pressure changes.
  - Dilution of the reactants by the supercritical solvent may negatively affect the space-time yield. There are only few applications where the reactants in the supercritical state are used as the feed.
  - Application potential for some peculiarities at the critical point, e.g., local density enhancement, for zeolite-catalyzed reactions has not been sufficiently evaluated so far.

- Adsorption and diffusion within the zeolite micropores as well as their influence on zeolite-catalyzed conversions, in particular for multicomponent systems, is largely unknown.

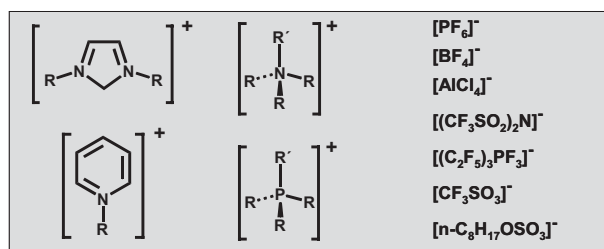
## 3 Application of Zeolites in Ionic Liquids

### 3.1 Properties of Ionic Liquids

Ionic liquids have been intensively studied as alternative solvents since the early 1980s. [49, 50]. They completely consist of ions and are liquid at temperatures below  $100^\circ\text{C}$ , often also at room temperature. Typical cations and anions as possible constituents of ionic liquids are shown in Fig. 7. It can be seen that a wide variety of ionic liquid solvents are accessible on the basis of a few fundamental chemical structures for cations, e.g., imidazolium, pyridinium or quaternary ammonium cations, by varying the alkyl rests bound to the N atoms or through different cation/anion combinations. This results in a broad spectrum of solvent properties for ionic liquids [51]. Because of their tuneable properties ionic liquids are sometimes referred to as “designer solvents” [52]. Moreover, the constituents of a ionic liquid may, by themselves, exhibit catalytic functionalities such as Brønsted or Lewis acidity.

Besides the relatively high thermal stability, typically up to  $200^\circ\text{C}$ , the nondetectable vapor pressure is a relevant property for the potential use of ionic liquids. Evaporation losses or emissions to the atmosphere encountered with many conventional organic solvents do not occur. Additionally, the negligible volatility of ionic liquids allows facilitated product removal by distillation. In many cases, simple product separation is possible due to the immiscibility of ionic liquids with organic or, partly, even with aqueous phases. Therefore, ionic liquids are also attractive solvents for multiphase reaction systems or liquid/liquid extractions. On the other hand, extraction with an additional liquid solvent may be required to isolate reaction products from ionic liquids or to purify an ionic liquid. An interesting approach to product removal from ionic liquids is extraction by supercritical fluids such as supercritical carbon dioxide. This approach can be similarly applied to transport reactants into an ionic liquid phase. It is particularly attractive for immobilizing molecular complex catalysts in ionic liquids [53, 54] or for biocatalysis with enzymes [55].

According to their ionic character, these solvents exhibit a high polarity, comparable to that of methanol or water [50]. This polarity can, however, be accompanied by low nucleophi-



**Figure 7.** Typical cations and anions as constituents of ionic liquids after [50].

licity, especially with weakly coordinating anions such as  $\text{PF}_6^-$  or  $\text{BF}_4^-$ . Advantages over conventional liquid solvents, therefore, arise when using electrophilic reagents or catalysts or, more generally, in reactions with strongly polar transition states or intermediates. While ionic liquids have a high density and a high solubilizing power for numerous organic compounds, the solubility of gases in ionic liquids is rather low. Furthermore, the partly high viscosity of ionic liquids can result in mass-transfer limitations of chemical conversions.

Interesting features for the use of zeolites in ionic liquids as solvents are their low surface tension (low capillary forces) and their pronounced capability of wetting inorganic solids. Moreover, the cation exchange properties of zeolites may lead to or be used to partially replace the cations of an ionic liquid by those initially present in the zeolite (see below).

Ionic liquids have also been used as media for the synthesis of some zeolite-related, microporous aluminophosphates or ordered mesoporous materials. In these applications, ionic liquids serve both as solvents and as structure-directing agents (“templates”) [56]. Unlike conventional hydrothermal synthesis performed at elevated pressures in autoclaves, preparation can be carried out at atmospheric pressure. For the synthesis of nanostructured mesoporous materials, self-assembly of the molecular species constituting the ionic liquids can be directly used [57].

In the meantime, a relatively wide variety of different ionic liquids is commercially available, also in larger quantities. However, their wider use is limited by the price being partly significantly higher than that of conventional liquid solvents. There were also concerns as to the potential toxicity of ionic liquids. First systematic investigations have shown, however, that toxicity of the ionic liquids tested so far is not higher than that of conventional organic solvents such as methanol, acetone or acetonitrile [51].

## 3.2 Heterogeneous Catalysis

### 3.2.1 Zeolite Catalyzed Conversions

Ionic liquids were used in zeolite catalysis as solvents for Friedel-Crafts alkylations and acylations as well as for selective oxidations. An overview of applications reported in the literature is presented in Tab. 5.

In the alkylation of phenol with *tert.*-butanol over the zeolites H-ZSM-5 and H-beta, a higher conversion was achieved in ionic liquids than in liquid *n*-hexane as the solvent [58]. However, the product distribution remained unaffected. With a selectivity for the *para*-substituted *tert.*-butylphenol of 50–99 %, this conversion shows that shape-selectivity effects of zeolite catalysts can also be exploited in ionic liquid media. A similar increase in the conversion level when using an ionic liquid rather than a conventional organic solvent has also been reported for the Prins cyclization of allyl alcohols with aldehydes on zeolite H-ZSM-5 [59].

A thorough study was conducted on the Friedel-Crafts acylation of anisol with benzoic anhydride over the zeolites H-USY, H-beta, H-mordenite and H-ZSM-5 in several different

ionic liquids [60]. Again, a higher conversion rate was observed in ionic liquids than in conventional liquid solvents. Activity and selectivity of the zeolite catalysts was strongly dependent on the nature and size of the ionic liquid cation. This was explained by an ion exchange of the cation of the ionic liquid with the protons of the zeolites. Instead of the zeolitic protons, the protonated anions of the ionic liquid formed as a result of this ion exchange act as the catalytically active sites. In ionic liquids with cations too large for an ion exchange within the zeolite micropores, only a low or no conversion at all occurred. The increasingly dark color of the ionic liquid reaction phase due to the formation of polyacylated aromatics in the course of conversion also supports the above explanation. Although the loss of zeolite protons leads to deactivation of the catalyst, deposition of higher molecular weight products on the zeolite surface could be avoided by carrying out the reaction in ionic liquids. Another consequence of proton exchange is the formation of hydrofluoric acid when ionic liquids with  $\text{PF}_6^-$  as the anion are used as reaction media. This leads to partial destruction of the zeolite framework.

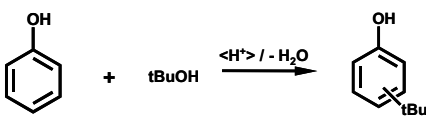
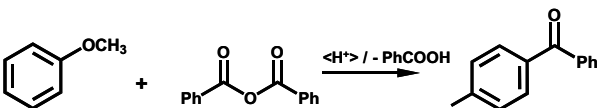
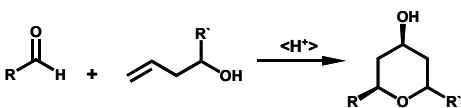
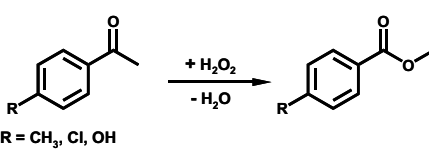
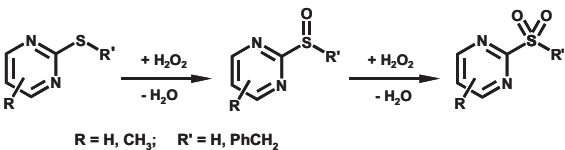
Corma et al. [61] first described the highly selective Baeyer-Villiger oxidation of ketones to esters with hydrogen peroxide over a tin-substituted aluminum-free zeolite beta ([Sn]beta) as the catalyst. The reaction was carried out at 80 °C in liquid dioxane. While the conversion of substituted acetophenones does not proceed at room temperature under these conditions, high yields of > 70 % are achieved in ionic liquids (see Tab. 5) [62]. In contrast, 4-methylacetophenone reacts neither at room temperature nor at 80 °C when using a titanium- or tin-substituted silicalite-1, a tin- and aluminum-free or a zinc-impregnated zeolite beta. Evidently, both the ionic liquid and the heteroatoms inserted in the zeolite framework are required for successful conversion. Another promising feature of this application is that the catalyst can be reused for at least three cycles without measurable yield loss.

Higher reaction rates in ionic liquids than in liquid dioxane were also reported for the selective oxidation of pyrimidine alkyl thioethers to the corresponding sulfoxides and sulfones at 40 °C over titanium- and germanium-substituted MCM-41 materials (see Tab. 5) [63]. Most attractively, the loss of titanium due to leaching from the solid catalyst was much less pronounced in ethylmethylimidazoliumtetrafluoroborate [emim][ $\text{BF}_4$ ] as an ionic liquid, compared to liquid ethanol as a conventional solvent (titanium loss with regard to the initial amount in the fresh catalyst: [emim][ $\text{BF}_4$ ]: 18 %, ethanol: 40 %).

In this conversion, similar to the anisol acylation mentioned above, an influence of the cation of the ionic liquid was observed: with increasing cation size, i.e., with increasing alkyl chain length at the imidazolium N atom, the thioether conversion was lower, while the sulfoxide selectivity remained unchanged (see Tab. 6). An increasing viscosity of the ionic liquid or an increasingly hindered access of the ionic liquid to the catalyst mesopores with increasing cation size were discussed as possible reasons. However, the anion of the ionic liquid, too, can have a strong effect on the catalytic activity (see Tab. 6). This effect was attributed to a coordination of the anion to the catalytically active titanium site and, thus, to an influence on the transition state of the rate-limiting step of the reaction. The coordination is particularly strong, for instance,



**Table 5.** Overview of conversions over zeolites and ordered mesoporous materials in ionic liquids.

Reaction	Catalyst	Ionic liquid(s) <sup>1)</sup>	T <sub>R</sub> /°C	Ref.
	H-ZSM-5 H-Beta H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /MCM-41	[bmim][PF <sub>6</sub> ] [C <sub>6</sub> mim][BF <sub>4</sub> ] [C <sub>8</sub> mim][BF <sub>4</sub> ]	60	[58]
1) Friedel-Crafts alkylation				
	H-ZSM-5 H-mordenite H-USY H-Beta	combinations of the cations [emim], [bmim], [edmim], [C <sub>4</sub> mpip], [C <sub>8</sub> py], [N <sub>8881</sub> ], [P <sub>66614</sub> ] and the anions [BF <sub>4</sub> ], [PF <sub>6</sub> ], [OTf], [NTf <sub>2</sub> ]	80	[60]
2) Friedel-Crafts acylation				
	H-ZSM-5	[bmim][PF <sub>6</sub> ] [C <sub>6</sub> mim]Cl [n-Bu <sub>4</sub> N][BF <sub>4</sub> ]	25	[59]
3) Prins cyclization				
 R = CH <sub>3</sub> , Cl, OH	[Ti], [Sn]Silicalite-1	[bmim][BF <sub>4</sub> ]	25	[62]
4) Baeyer-Villiger oxidation				
 R = H, CH <sub>3</sub> ; R' = H, PhCH <sub>2</sub>	[Ti,Ge]MCM-41	combinations of the cations [emim], [bmim], [bdmim], [C <sub>8</sub> mim], [C <sub>n</sub> py] (n = 4,6,8), [bmpyr] and the anions [BF <sub>4</sub> ], [PF <sub>6</sub> ], [OTf], [NTf <sub>2</sub> ], [EtOSO <sub>3</sub> ]	40	[63]
5) selective oxidation of thioethers				

cations: [bdmim]: 1-butyl-2,3-dimethylimidazolium, [bmim]: 1-butyl-3-methylimidazolium, [bmpyr]: 1-butyl-3-methylpyrrolidinium, [n-Bu<sub>4</sub>N]: tetrabutylammonium, [C<sub>n</sub>mim]: 1-alkyl-3-methylimidazolium, [C<sub>4</sub>mpip]: N-butyl-N-methylpiperidinium, [C<sub>n</sub>py]: 1-alkylpyridinium, [emim]: 1-ethyl-3-methylimidazolium, [N<sub>8881</sub>]: methyltrioctylammonium, [P<sub>66614</sub>]: trihexyltetradecylphosphonium; anions: [BF<sub>4</sub>]: tetrafluoroborate, Cl: chloride, [PF<sub>6</sub>]: hexafluorophosphate, [EtOSO<sub>3</sub>]: ethylsulfate, [NTf<sub>2</sub>]: bis(trifluoromethanesulfonyl)imid, [OTf]: triflate

**Table 6.** Conversion and sulfoxide selectivity in the conversion of 2-thiobenzylpyrimidine over [Ti,Ge]MCM-41 in ionic liquids after [63].

Ionic liquid <sup>1)</sup>	X <sub>2</sub> -thiobenzylpyrimidine/%	S <sub>sulfoxide</sub> /%
[emim] [BF <sub>4</sub> ]	77	95
[bmim] [BF <sub>4</sub> ]	73	96
[C <sub>8</sub> mim] [BF <sub>4</sub> ]	27	100
[emim] [OTf]	49	98
[emim] [EtOSO <sub>3</sub> ]	25	100

<sup>1)</sup> abbreviations as in Tab. 5

for the ethyl sulfate anion. This example clearly shows that the complex interactions between the molecular species as constituents of ionic liquids, on the one hand, and the catalytically active sites on the surface of a porous catalyst, on the other hand, can be exploited to achieve higher rates of chemical conversions.

### 3.2.2 Ionic Liquids on Porous Supports (Supported Ionic Liquid Phases, SILP)

Recently, the concept of immobilization of liquids on porous supports for heterogenization of liquid or liquid-soluble mo-

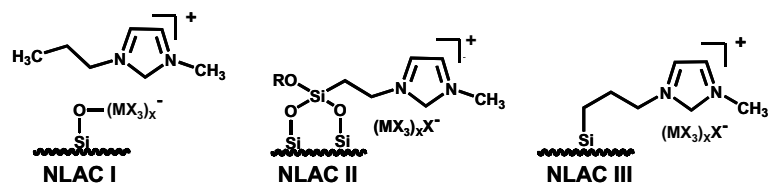
lecular catalysts has been extended by applying ionic liquids [64]. Molecular species dissolved in an ionic liquid or ionic liquids with catalytically active cations or anions are immobilized on porous supports such as silica, alumina or polymers. The negligible vapor pressure of the ionic liquids inhibits the loss of the immobilized catalyst phase.

Besides an adsorption without any chemical change, ionic liquids can be bonded to the surface of solid supports in different ways either via the cation or via the anion. This approach is schematically presented for the example of the so-called novel Lewis acid catalysts (NLACs) in Fig. 8 [65]. For the classical microporous zeolites, two major restrictions have to be considered: firstly, retention of an ionic liquid after extraction of the nonbonded fraction is in some cases considerably less on zeolites than on macroporous supports. For instance, 23 % of chloroaluminate-based ionic liquids is bonded on macroporous  $\text{SiO}_2$ , but only 7 % on zeolite Na-Y [65]. Secondly, a hydrogen halide may be liberated during grafting of the ionic liquid on the support, resulting in an damage or complete destruction of the zeolite crystal structure. Immobilization of ionic complexes without any loss of the support pore structure is, however, possible by covalent bonding via the cation (NLAC II or III, see Fig. 8). This was demonstrated for the preparation of Lewis acid catalysts on ordered mesoporous MCM-41- or HMS-type materials [66]. By using mesoporous supports, mass transfer restrictions could be minimized. Still, the question is whether the high costs of zeolites or ordered mesoporous materials compared to those of macroporous inorganic or polymeric supports for immobilized ionic liquids can be justified.

### 3.3 Potential and Future Challenges

The relatively few examples of zeolite utilization in ionic liquids as solvents only allow a preliminary estimation of the potential for future applications. In summary, the following trends can be outlined:

- High variability for the preparation of ionic liquids with different cation/anion combinations allows interactions with active surface sites of zeolites and other porous materials for adsorptive separations and heterogeneous catalysis to be systematically controlled.
- Cation exchange capacity of zeolites offers the opportunity to directly influence the active sites both in a zeolite and in an ionic liquid. In this context, the formation of Brønsted-acid sites in an ionic liquid phase, possibly with a time-dependent concentration, is a particularly attractive option. However, to fully exploit the application potential, further systematic studies are needed.
- In some zeolite-catalyzed conversions, higher reaction rates were observed than in conventional liquid solvents, in some cases even at lower temperatures. The range of applications where ionic liquids offer similar advantages will certainly be expanded by further investigations.
- While zeolites are less suitable as supports for the immobilization of ionic liquids with intrinsic catalytic activity or with



**Figure 8.** Schematic representation of Lewis acid catalysts obtained by immobilization of ionic liquids on silica surfaces (Novel Lewis Acid Catalysts, NLACs). Linking of ionic liquid (M: metal, X: halide) can be achieved via the anion (NLAC I) or the cation by grafting after synthesis (NLAC II) or by adding the ionic liquid during synthesis of the silica support and subsequent conversion with a Lewis acid (NLAC III).

dissolved metalloorganic complex catalysts, ordered mesoporous materials with large specific surface areas and pore volumes are interesting alternatives with high application potential.

Important challenges for future research and development work on zeolite applications in ionic liquids include:

- Stability of zeolites in ionic liquids under application-relevant conditions is largely unknown.
- As for supercritical fluids, a fundamental understanding of the influence of ionic liquids on mass and heat transfer within the pores and cavities of zeolites is lacking.
- Although the potential for using ionic liquids to facilitate product separation is evident, there are only few examples where ionic liquids have been used as media for conversions with zeolites and related micro- and mesoporous catalysts. Interesting options for continuous processes emerge for multiphase catalysis with ionic liquids as reaction phases and with supercritical fluids as transport phases for reactants and products.

## 4 Outlook

Besides their important and well-established role as catalysts in the refining and petrochemical industries, zeolites continue to open up new fields of application, especially in the synthesis and processing of fine and specialty chemicals. It is for these applications that the demand for alternative, innovative and tailored solvent systems will increase in order to develop environmentally friendly, intrinsically safe and sustainable chemical processes.

Moreover, innovative solvent systems provide interesting opportunities for improving conventional gas-phase processes which are still among the core applications of zeolites. Most importantly, deactivation of zeolite catalysts due to coking can often be ameliorated or even avoided when using supercritical fluids or ionic liquids as processing solvents. This way, the spectrum of conversions exploiting the special shape-selectivity effects of zeolites can be significantly extended.

Still, as yet, there has been very little evidence that processes at active sites for adsorption or heterogeneous catalysis and mass transport occurring within the zeolite pores can be controlled or tuned by the specific properties of supercritical fluids or ionic liquids. A deeper understanding of these processes, gained, e.g., by in-situ spectroscopy or computer simulations

on the molecular level, may lead the way to new applications. The tunable properties of supercritical fluids and ionic liquids can without doubt be used to control the selectivity of conversions occurring predominantly on the outer crystal surface of zeolite catalysts. In this context, the use of innovative solvents might be particularly attractive for applications of modern zeolite materials such as nanocrystalline or delaminated zeolites.

Supercritical fluids and ionic liquids also offer new opportunities for facilitated and process-integrated product separations. For such applications, combining supercritical fluids and ionic liquids seems to be most interesting. It is to be expected that, against this background, attractive and novel process options for the application of zeolites in alternative solvents such as supercritical fluids or ionic liquids will open up in the near future.

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