USING IN SITU IR SPECTROSCOPY TO UNDERSTAND SELECTIVE ALKYLATION OF AROMATICS OVER ZEOLITES*

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In situ IR spectroscopy in combination with kinetic measurements was used to clarify the mechanism of the methylation of toluene over zeolitic catalysts. Over basic zeolites (i.e. Rb-X), the main surface species under reaction conditions is toluene strongly bound with the aromatic ring to the cation and with the methyl group to the lattice oxygens of the zeolite. The activated carbon atom of the methyl group reacts with the positively activated C-atom of methanol (formaldehyde) to yield styrene as the main product. Over acidic zeolites (i.e. HZSM-5), methanol is preferentially adsorbed over toluene, the rate of methylation is directly proportional to the surface concentration of the activated methanol species (methoxonium ions at low and methoxy groups at high reaction temperatures). The aromatic ring of toluene is attacked by the reactive alcohol methyl group, giving the xylene isomers as reaction products.

In situ investigations of heterogeneously catalyzed reactions are among the most important experimental techniques to test proposed reaction mechanisms. As catalyzed reactions consist of a series of elementary steps, each of them may control or influence the overall reaction rate. In order to formulate a microkinetic model of the catalyzed reaction, it is necessary to characterize each of these steps including transport, adsorption, surface reaction and desorption. For these investigations it is mandatory that the measurement does not interfere with the processes occurring at the surface and does not alter the catalyst itself. In this respect, spectroscopic methods like FTIR and MAS-NMR spectroscopy provide suitable tools to obtain quantitative and qualitative information on the surface concentrations of reactants, intermediates and products at the catalyst. By combining the in situ analysis of the catalyst with the kinetic analysis of the gas phase, it is possible to link the adsorption complexes at the catalyst surface quantitatively and qualitatively with the selectivity and activity of the catalyst during reaction. The methylation of toluene was taken as example to demonstrate how this experimental approach can be used to clarify the reaction mechanisms of zeolite cata-

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lyzed reactions. The requirements of catalysts for selectively catalyzing the alkylation of the ring or the side chain of aromatic molecules were investigated.

EXPERIMENTAL

Materials

Two different types of zeolites varying in chemical composition and structure were used: the protonic form of zeolite ZSM-5 ($H_{2.6}Al_{2.6}Si_{95.4}O_{196}$, Si/Al = 35) and a cationic form of X faujasite ($Rb_{46}Na_{24}Al_{70}Si_{122}O_{384}$, Si/Al = 1.75).

FTIR Spectroscopy

For the IR measurements, the zeolite powders were pressed into self supporting wafers and placed in a sample holder in the centre of the furnace of an IR cell. The samples were then analyzed in situ during all treatments (e.g. activation, sorption, reaction) by means of transmission absorption IR spectroscopy using a Bruker IFS 88 FTIR spectrometer (resolution 4 cm^{-1}). Two types of experiments were designed to investigate adsorption/desorption as well as reactions under static and flow conditions:

a) For the sorption experiments, a sample compartment with IR transparent windows which could be evacuated to pressures below 10^{-6} mbar* was used[1]. The activated zeolite wafer was contacted with a constant partial pressure (0.001 mbar) of the adsorptive at constant temperature (T = 308 K) until adsorption–desorption equilibrium was achieved (which was monitored by time resolved IR spectroscopy). For the coadsorption experiments, the catalyst was equilibrated with the first reactant. Subsequently (while keeping the partial pressure, 0.001 mbar, of the first reactant constant) the loaded zeolite was exposed to 0.001 mbar of the second reactant. The spectra were normalized for the sample thickness by comparing the intensities of the absorption bands of the adsorbate with the intensities of the lattice vibrational bands of the zeolite between 2 090 and 1 740 cm^{-1}. Quantification of the surface coverage was possible by performing an external calibration with a gravimetric setup (under otherwise identical experimental conditions).

b) For characterizing catalyzed reactions an IR cell, which approximates a continuously stirred tank reactor (volume 1.5 cm^3), equipped with 1/16″ gas in- and outlet tubing and CaF_2 windows, was used[2]. For the characterization of the surface species in the zeolite pores during the reaction, time resolved IR spectra of the catalyst were recorded as the activated zeolite was contacted with a reactant containing He stream. Simultaneously, samples of the effluent gas stream were collected in the sample loops of the multi port valve and which were subsequently analyzed by gas chromatography.

RESULTS AND DISCUSSION

In order to determine the nature and concentration of adsorption complexes at the catalyst surface and to correlate them with the selectivity and activity of the catalyst, sorption as well as coadsorption experiments of methanol and toluene were performed on two types of molecular sieves showing different product selectivities in the methylation

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* 1 bar = 10^5 Pa.

of toluene. The acidic zeolite HZSM-5 catalyzes the alkylation of the aromatic ring, while the basic zeolite Rb-X catalyzes the alkylation of the side chain of toluene. In the experiments described here, the coverage of the active sites (Rb^+, –OH) with probe molecules was lower or equal to 1 molecule/site.

The IR spectra of adsorbed methanol (see Fig. 1) show distinct differences for the two materials. The absorption maxima of the bands attributed to the CH stretching vibrations found for methanol adsorbed[3,4] on HZSM-5 were quite close to those observed for methanol adsorbed on amorphous silica[5] (see Table I). With Rb-X, however, these bands were shifted to lower wavenumbers ($\Delta\nu$ = 20 and 30 cm^{-1} compared to toluene adsorbed on silica) suggesting strong interaction of the methyl group with the framework oxygens. Note, that not only the wavenumbers but also the shape and the

TABLE I
Absorption maxima y (in cm^{-1}) of the bands of the CH stretching vibrations of sorbed methanol and toluene

Sample	Methanol		Toluene		
	y_{asym}	y_{sym}	y(arom)	$y(CH_3)_{asym}$	$y(CH_3)_{sym}$
SiO_2	3 000, 2 956	2 850	3 084, 3 065 3 032	2 929	2 880
HZSM-5	3 012, 2 993 2 958	2 856	3 086, 3 060 3 030	2 925	2 877
Rb-X	2 936	2 820	3 045, 3 020	2 913	2 857

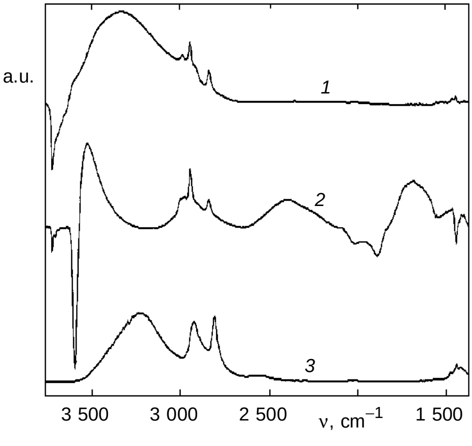

FIG. 1
Difference IR spectra of methanol ($p_{methanol}$ = 0.001 mbar, T = 308 K) adsorbed on SiO_2 (*1*), HZSM-5 (*2*), and Rb-X (*3*). For better comparison, different scaling of the individual spectra was used

relative intensities of these bands were quite different for the various catalysts (see Fig. 1). The hydroxyl group of methanol sorbed on Rb-X gave rise to a broad band centred around 3 236 cm^{-1}. Note, that the absorption maximum of the ν_{stretch} of a free OH group of alcohols is found ≈ 3 600 cm^{-1}. The much lower wavenumber and the broadness of the band indicate, therefore, strong hydrogen bonding of the hydroxyl group to the zeolite lattice. Thus, we propose that methanol is coordinately bonded via the lone electron pair of its oxygen to the cation in zeolite Rb-X. In addition, strong interactions of the hydroxyl group as well as of the methyl group of the alcohol with the basic lattice oxygens of Rb-X exist leading to a strong activation of the molecule not present in HZSM-5.

Methanol adsorbed on zeolite HZSM-5 (Fig. 1) gave rise to bands associated with OH vibrations at 3 545, 2 900, 2 400 (y_{stretch}) and 1 687 cm^{-1} (y_{def}). These absorption features were attributed to a methoxonium ion hydrogen bonded to the lattice of HZSM-5 (see refs[3,4,6]). With increasing temperature, elimination of water from the methoxonium ion proceeds leading to the formation of a methoxy group associated with the negatively charged lattice ($\mathrm{Si{-}OCH_3{-}Al}$) of HZSM-5 (e.g. refs[7–9]). In contrast, hydrogen is abstracted from methanol adsorbed on the basic zeolite Rb-X yielding in the formation of formaldehyde and formates with a strongly positively polarized C-atom[10,11].

The IR spectra of toluene adsorbed on the acidic zeolite HZSM-5 and on the basic Rb-X (see Fig. 2) show clear differences in the bands of the CH stretching vibrations in the aromatic and aliphatic region[12] (see Table I). The significant changes in the relative intensities and the absorption maxima of the aromatic CH stretching vibrations suggests that the molecule is bound via its aromatic ring to the Rb^+ cation. The high loading of large cations in Rb-X generates a high electrostatic field at the aromatic nuclei perturbing the π-electrons and directing in this way the selectivity towards alkylation of the side chain[13]. In addition, the methyl group is strongly interacting with the basic frame-

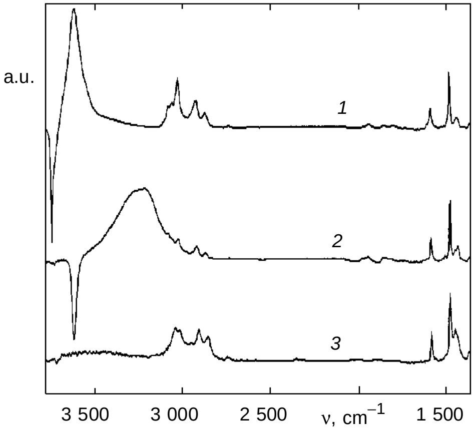

FIG. 2
Difference IR spectra of toluene (p_{toluene} = 0.001 mbar, T = 308 K) adsorbed on $\mathrm{SiO_2}$ (*1*), HZSM-5 (*2*) and Rb-X (*3*). For better comparison, different scaling of the individual spectra was used

work oxygen atoms and is, thus, activated to interact with the positively polarized C-atom of the methylating species.

In silica and protonic zeolites such as HZSM-5, the aromatic ring of toluene is interacting via hydrogen bonds with the Si–OH and Si–OH–Al groups of the catalysts. These are shifted by 130 and 390 cm^{-1} to lower wavenumbers, respectively, due to this interaction. The aromatic ring constitutes the preferred site for an attack of the methylating species leading to the formation of xylenes[14].

Coadsorption of both reactants resulted in the formation of a bimolecular complex between methanol and toluene at the acid sites of zeolite HZSM-5. In this complex, methanol is directly sorbed at the Si–OH–Al group of the zeolite, interacting with the protonated hydroxyl group of the methoxonium ion with the aromatic ring of a toluene molecule[12]. It should be mentioned that all active sites were covered with methanol molecules, but only about half of these molecules interacted with a toluene molecule to form the coadsorption complex under our experimental conditions (T = 308 K, p = 0.001 mbar of each reactant). Upon heating the catalyst in a gas stream containing both reactants, this coadsorption complex was observed up to temperatures of 450 K. The decrease in its surface concentration was paralleled with the appearance of the first reaction products (xylenes) in the gas phase. Thus, it was concluded that it forms a possible precursor to the transition state in the methylation reaction. Under reaction conditions, however, the rate of methylation of toluene was found to be directly proportional to the surface concentration of the activated methanol species[15].

Toluene and methanol coadsorbed on Rb-X do not form a bimolecular precursor complex, both reactants seem to be independently adsorbed at the surface. It should be noted, however, that after equilibration with equal partial pressures of both reactants (see Fig. 3, curve *3*), toluene was the main species adsorbed in the pores. Coadsorption

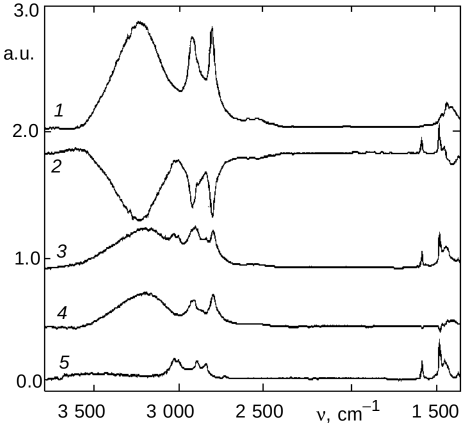

FIG. 3
IR spectra of methanol and toluene ($p_{methanol}$ = 0.001 mbar, $p_{toluene}$ = 0.001 mbar, T = 308 K) coadsorbed on Rb-X. *1* Methanol on Rb-X, *2* changes induced by coadsorption of toluene on Rb-X preequilibrated with methanol (*3*) – (*1*), *3* toluene and methanol coadsorbed on RbX, *4* changes induced by coadsorption of methanol on Rb-X preequilibrated with toluene (*3*) – (*5*), *5* toluene on Rb-X

of toluene onto a surface preequilibrated with methanol (Fig. 3, curve *1*) resulted in a displacement of the main fraction (≈ 80%) of the methanol molecules from the sorption sites[16] (Fig. 3, curve *2*). The same coadsorbed state was reached irrespective of the order of adsorption of the two reactants. It should be noted, that if toluene was adsorbed first (Fig. 3, curve *5*), coadsorption of methanol did not change the coverage of toluene (see Fig. 3, curve *4*). During the reaction, again toluene was preferentially adsorbed over methanol. However, a direct correlation between the rate of methylation and the surface concentration of both reactants was observed.

CONCLUSIONS

It could be shown that in situ IR spectroscopy in combination with kinetic measurements can be used to understand the reaction mechanisms of heterogeneousely catalyzed reactions. The nature and concentrations of surface complexes can be correlated with the selectivity and activity of the catalyst and, thus, a model explaining how zeolites can be used to direct selectivity in a given reaction, can be derived.

Over basic zeolites (i.e. Rb-X), the main surface species under reaction conditions is toluene strongly bound with the aromatic ring to the cation and with the methyl group to the lattice oxygens of the zeolite. The activated and partially negatively charged carbon atom of the methyl group reacts with the positively activated C-atom of methanol (formaldehyde) to yield styrene as the main product. The product selectivity can be completely changed by varying the chemical environment and using an acidic zeolite (i.e. HZSM-5). In this case, methanol is preferentially adsorbed over toluene, the rate of methylation being directly proportional to the surface concentration of the activated methanol species (methoxonium ions at low and methoxy groups at high reaction temperatures). The aromatic ring of toluene is attacked by the reactive alcoholic methyl group giving the xylene isomers as reaction products.

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