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Methylation of phenol by methanol on acidic zeolite H–Y investigated by *in situ* CF MAS NMR spectroscopy

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Dedicated to Professor Dr. h.c. Harry Pfeifer, University of Leipzig, on the occasion of his 75th birthday

In situ ^{13}C MAS NMR spectroscopy under continuous-flow (CF) conditions was applied to study the mechanism of the methylation of phenol by methanol on acidic zeolite H–Y. *Ex situ* GC-MS was used as a complementary technique to confirm the nature of the chemical species remaining on the catalyst after the *in situ* MAS NMR investigations. Anisole and cresols were observed as the main reaction products in the initial step of the reaction. By use of the stopped-flow (SF) technique, the consecutive transformation of anisole to cresols was observed at the reaction temperature of 413 K indicating that anisole is an unstable primary product and an important intermediate.

KEY WORDS: methylation of phenol; zeolite H–Y; reaction intermediates; reaction mechanism; *in situ* NMR spectroscopy; stopped-flow technique.

1. Introduction

The progress in heterogeneous catalysis depends, *inter alia*, on our knowledge of the nature of surface sites and of the mechanisms of the reactions occurring on these sites. A variety of *in situ* spectroscopic techniques [1] have recently been developed for directly observing the events taking place in heterogeneous catalysis and for getting "snapshots" of working solid catalysts under real reaction conditions. MAS NMR spectroscopy, which can provide both structural and dynamic information about heterogeneous catalytic systems, is generally considered to be among the most powerful tools for such *in situ* studies. More recently, on the basis of *in situ* MAS NMR spectroscopy under continuous-flow (CF) conditions applying the MAS NMR rotor as a microreactor [2], new stopped-flow (SF) protocols were introduced, which were shown to allow the determination of reaction intermediates and to furnish valuable information on the mechanisms of heterogeneously catalyzed reactions [3–7]. For example, by using the *in situ* SF MAS NMR technique, the mechanisms of aniline methylation on acidic zeolite H–Y [3] and on basic zeolite Cs,Na–Y/CsOH [4] were elucidated. Furthermore, the method was applied to investigate the nature and reactivity of surface methoxy species which contribute, most probably, as intermediates to the methanol-to-olefins (MTO) reaction [5–7].

The heterogeneous reaction systems studied so far by *in situ* MAS NMR spectroscopy under flow conditions involved exclusively volatile reactants. These reactants were either gaseous or liquid at ambient temperature and could be readily transported to the reactor in a carrier gas. Our *in situ* MAS NMR techniques under flow conditions were now extended to reactants and products which are considerably less volatile. As one of the first applications, the methylation of phenol with methanol on acidic zeolite H–Y was studied by *in situ* MAS NMR spectroscopy under flow conditions. While phenol methylation on solid catalysts has previously been studied [8–17], no *in situ* investigation of reaction intermediates has so far been reported. Complementary to *in situ* MAS NMR spectroscopy, *ex situ* GC-MS was used to confirm the nature of the chemical species remaining on the working catalyst after the *in situ* MAS NMR investigations.

2. Experimental

2.1. Materials

Zeolite Na–Y ($n_{Si}/n_{Al} = 2.7$) was purchased from Degussa AG, Hanau, Germany. The ammonium form of zeolite Y was prepared by a fourfold ion exchange of 5 g of zeolite Na–Y at 353 K in a 1.0 M aqueous solution of NH_4NO_3 (80 mL) [18]. After a degree of ammonium exchange of 90% had been attained, the material was washed in deionized water and dried at room temperature. Subsequently, zeolite NH_4–Y was

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heated in a vacuum of $p \leq 10^{-2}$ Pa with a rate of 20 K h^{-1} up to the final temperature of 673 K. The material was calcined at this temperature and a pressure Below 10^{-2} Pa for 12 h leading to zeolite H–Y. Zeolite H–Y was characterized by AES-ICP, XRD, and ^{1}H, ^{27}Al, and ^{29}Si MAS NMR spectroscopy which indicated that the material resulting after cation exchange and calcination was neither damaged nor dealuminated.

Methanol-^{13}C (^{13}C-enrichment 99%) was purchased from Cambridge Isotopes. Phenol (99.9%) was obtained from Acros Organics and recrystallized from toluene.

2.2. *In situ NMR experiments*

The experimental set-up used for the *in situ* MAS NMR investigations under flow conditions was described elsewhere [2b]. Considering the relatively high melting point (316 K [19]) and low vapor pressure (e.g., 393 Pa at 323 K [20]) of phenol, the *in situ* NMR equipment was modified to allow mechanistic studies of phenol methylation under flow conditions: A heated saturator (for phenol) was positioned very close to the NMR probe, and the lines inside the MAS NMR probe were heated at 393 K, in order to avoid condensation of phenol or reaction products.

Prior to the *in situ* MAS NMR experiments, ca. 200 mg of the dehydrated solid catalysts were filled into a 7 mm MAS NMR rotor under dry nitrogen in a glove box and pressed to a cylindrical catalyst bed. After transferring the rotor into the high-temperature Doty MAS NMR probe, a second *in situ* dehydration was performed at 673 K for 1 h under flowing nitrogen (30 cm^{3}/min). During the *insitu* MAS NMR experiments under CF conditions at temperatures between 298 and 523 K, carrier gas (dry nitrogen) loaded with phenol (^{13}C isotopes of natural abundance) and methanol (^{13}C-enriched, 99%) was injected into the MAS NMR rotor reactor applying the equipment described elsewhere [2b]. In different experiments, modified residence times, W/F, of $^{13}CH_3OH$ between 40 and 100 g h/mol were used, and the molar $^{13}CH_3OH$ to phenol ratio was adjusted to 2 : 1 and 3 : 1. The SF protocol applied was described in Ref. [4].

2.3. *Solid-state NMR spectroscopy*

^{13}C MAS NMR investigations were performed on a Bruker MSL-400 spectrometer at a resonance frequency of 100.6 MHz. The *in situ* ^{13}C MAS NMR experiments under flow conditions were carried out at the respective reaction temperature with a sample spinning rate of ca. 2.0 kHz inside a modified DSI-740 7 mm STD MAS NB NMR probe of Doty Scientific Instruments, Texas, USA (see Ref. [2b]). The spectra were recorded after a $\pi/2$ pulse excitation, applying high-power proton decoupling, and using a repetition time of 5 s. To record ^{13}C MAS NMR spectra obtained under CF and SF conditions, 256 and 96 scans were added, respectively. The ^{13}C MAS NMR spectra were referenced to tetramethylsilane (TMS).

2.4. *Ex situ GC-MS analysis of species formed on the catalysts*

After the *in situ* MAS NMR measurements, the catalysts were subjected to acid digestion, extraction and GC-MS analysis to confirm the nature of the species remaining inside the pores. The used catalyst was first dissolved in 4.0 cm^{3} of 2.0 M HCl to destroy the inorganic framework. Subsequently, the organic species were extracted with 1 cm^{3} of $CHCl_3$. A 2.0 mm^{3} sample of the extracted organics was injected into a Hewlett-Packard 5890 gas chromatograph with a Hewlett-Packard 5972 mass-selective detector. A split ratio of 1 : 40, a Hewlett-Packard ULTRA 2 column (crosslinked 5% phenylmethyl silicone, length 50 m, inner diameter 0.2 mm, film thickness 0.33 μm) and a helium flow rate of 0.5 cm^{3}/min were applied. The column was heated from 323 to 473 K with a heating rate of 20 K/min.

3. Results and discussion

3.1. *Phenol methylation under CF conditions*

Figure 1 shows the *in situ* ^{13}C CF MAS NMR spectra recorded during the reaction of phenol and methanol on acidic zeolite H–Y. During these experiments, a mixture of $^{13}CH_3OH$ ($W/.F = 100$ g h/mol) and phenol with a molar ratio of 2 : 1 was injected into the MAS NMR rotor reactor. Up to a temperature of 373 K, the *in situ* ^{13}C CF MAS NMR spectrum consists of a single signal at 50.3 ppm caused by ^{13}C-enriched methanol adsorbed on zeolite H–Y [5], while no signals of reaction products occur (figure 1a). As shown in figure 1b, phenol methylation by methanol on zeolite H–Y starts at 393 K. The signals at 63.6 and 60.2 ppm are due to “side-on” and “end-on” adsorbed dimethyl ether (DME) formed from methanol [5]. The signal at 57.2 ppm is attributed to the methyl group of anisole (C_6H_5–$O^{13}CH_3$). This assignment was confirmed by adsorption of pure anisole on zeolite H–Y. With respect to solution ^{13}C NMR data of anisole (55 ppm [21]), the 2 ppm low-field shift of the methyl signal indicates an interaction of anisole with Brønsted acid sites of the zeolite. The signal at 15.5 ppm is due to *ortho*-cresol (*ortho*-$C_6H_4(OH)^{13}CH_3$), while the signal at 19.0 ppm has to be attributed to *para*- and *meta*-cresol (*para*- and *meta*-$C_6H_4(OH)^{13}CH_3$). These assignments were confirmed by adsorption of authentic cresol samples on dehydrated zeolite H–Y. The stepwise increase of the reaction temperature from 393 to 453 K (figure .1b–e) led to a gradual increase of the cresol content, while the content of anisole decreased with increasing temperature.

Ex situ GC-MS was applied to clarify the nature of the chemical species formed and retained on the working catalyst during the *in situ* MAS NMR investigation. Figure 2a shows the gas chromatogram with MS (GC-MS) operated in the total ion count mode, obtained

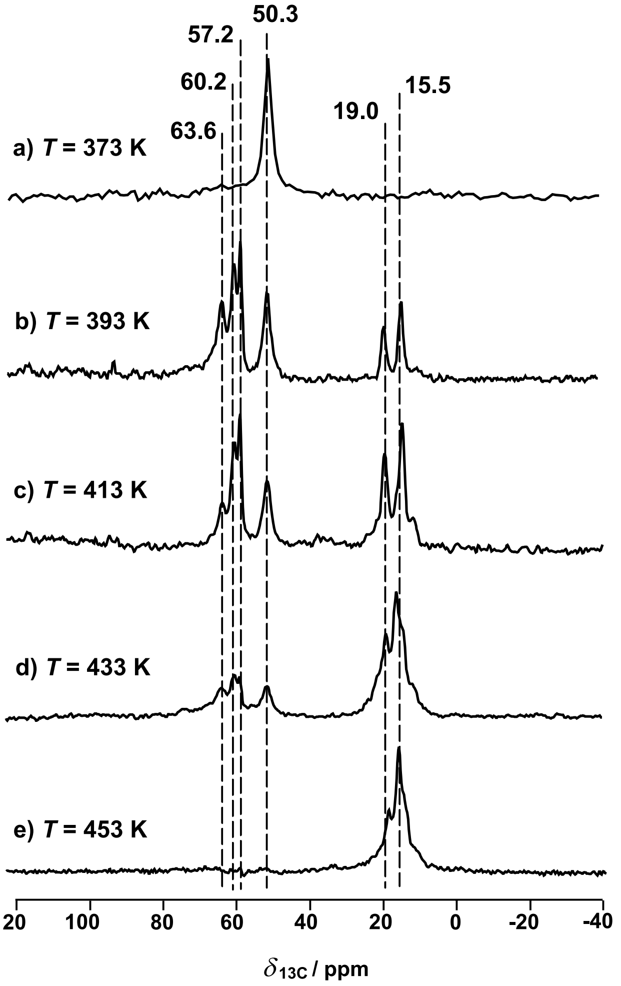

Figure 1. *In situ* ^{13}C MAS NMR spectra recorded during the reaction of phenol (^{13}C-isotopes of natural abundance) and methanol (^{13}C-enriched) on zeolite H–Y under flow conditions at reaction temperatures of 373–453 K. During these experiments, a mixture of ^{13}CH$_3$OH ($W/F = 100$ g h/mol) and phenol with a molar ratio of 2 : 1 was injected into the MAS NMR rotor reactor.

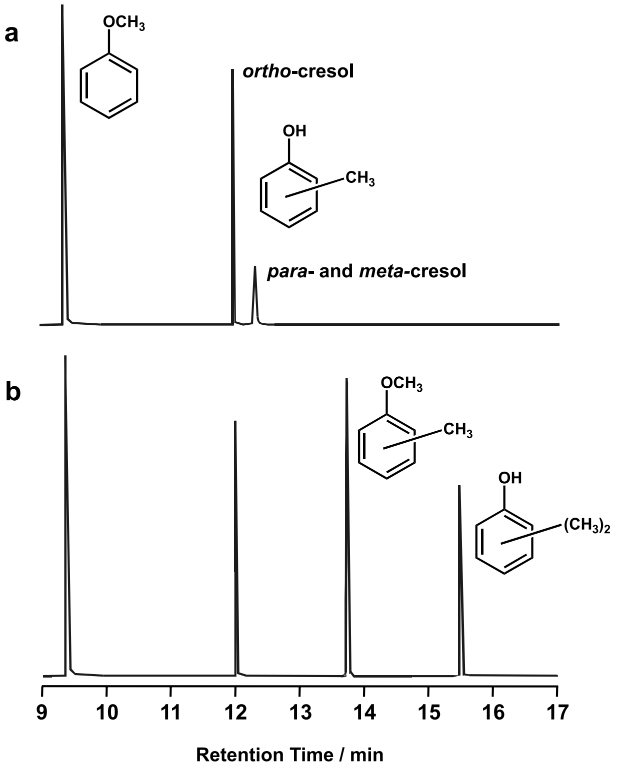

Figure 2. Gas chromatogram (GC-MS total ion count signal) of the extract of zeolite H–Y obtained after phenol methylation under flow conditions at 413 K (a). The catalyst was prepared by flowing a mixture of ^{13}CH$_3$OH ($W/F = 100$ g h/mol) and phenol with a molar ratio of 2 : 1 into the MAS NMR rotor reactor for 18 min. The *in situ* ^{13}C MAS NMR spectrum obtained was similar to that shown in figure 1b. Gas chromatogram (GC-MS total ion count signal) of the extract of zeolite H–Y obtained after phenol methylation under flow conditions at 433 K (b). The catalyst was prepared by flowing a mixture of ^{13}CH$_3$OH ($W/F = 75$ g h/mol) and phenol with a molar ratio of 3 : 1 into the MAS NMR rotor reactor.

from an *ex situ* analysis of the extract from the catalyst after phenol methylation at 413 K under flow conditions. In agreement with the *in situ* MAS NMR results, anisole and cresols were found to be the sole reaction products remaining on the catalyst. Figure 2b shows the GC-MS results obtained after phenol methylation at 433 K. The catalyst under study was prepared by flowing a mixture of ^{13}CH$_3$OH ($W/F = 75$ g h/mol) and phenol in a molar ratio of 3:1 into the MAS NMR rotor reactor. As indicated in fig. 2b, methylated anisoles and doubly methylated phenols are formed besides anisole and cresols.

3.2. *Transformation of anisole to cresols evidenced by SF experiments*

Anisole has been suggested to be an intermediate in the formation of cresols during phenol methylation [8]. In our *in situ* MAS NMR investigation under flow conditions, the signal intensity of anisole decreased at temperatures above 413 K implying a possible intermediary role of this compound. To study the consecutive transformation of the species adsorbed on the working catalyst, a SF protocol [4] was used. Figure 3 shows the *in situ* ^{13}C MAS NMR spectra recorded at 413 K after the flow of reactants was stopped. According to these spectra, the intensity of the anisole signal at 57.2 ppm decreases, while the intensities of the signals of cresols at 15.5 and 19.0 ppm increase. Simultaneously, the total integral of the ^{13}C signals remains almost constant. This finding implies a consecutive transformation of anisole to cresols at the reaction temperature of 413 K. Again, methylated anisoles and doubly methylated phenols may be formed as well.

3.3. *Mechanism of phenol methylation on acidic zeolite H–Y*

The mechanism of phenol methylation on acidic solid catalysts has been thoroughly discussed in the literature [8–17]. Alkylation of phenol with methanol on zeolites

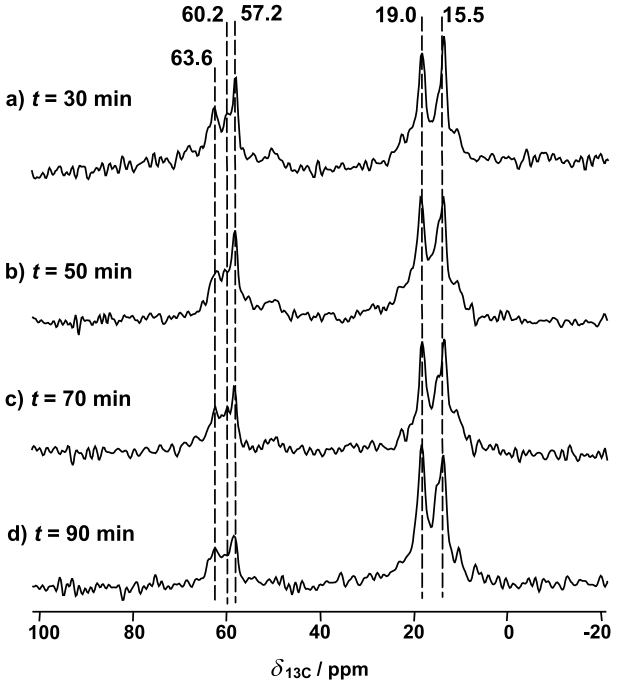

Figure 3. *In situ* ^{13}C MAS NMR spectra of zeolite H–Y recorded at 413 K after the flow of reactants was stopped for t = 30 min (a), 50 min (b), 70 min (c) and 90 min (d). This protocol was utilized to investigate the consecutive transformation of intermediates adsorbed on the working catalyst.

produces both anisole (O-alkylation) and cresols (C-alkylation). It is generally accepted that the acid–base properties of the catalysts employed have a significant influence on the product distribution. For example, O-alkylation can easily occur on weak acid sites, while C-alkylation requires the presence of stronger acid sites [12]. The formation of polyalkylated products requires more severe reaction conditions, i.e., higher reaction temperatures, longer contact times, an excess of methanol in the feed, and/or a sufficiently high acid strength of the catalyst. To prove that the secondary products stem to a large extent from anisole, Marczewski *et al.* [14] studied the reactions of anisole and of a mixture of anisole and methanol on H-USY (ultrastable zeolite Y). They proposed that the direct isomerization of anisole to cresols does not occur and that the alkylation of phenol by anisole leads to cresols and methylanisoles as primary products. Studying the methylation of phenol with methanol on zeolite H-Beta by conventional GC analysis, Xu *et al.* [9] came to the conclusion that anisole is an unstable primary product and an important reaction intermediate. This is strongly supported by the present *in situ* MAS NMR investigations which furnish direct evidence for a transformation of anisole to cresols on the surface of the working H-Y catalyst. On the basis of the experimental material collected so far, no distinction can be made as to whether this consecutive transformation of anisole occurs via a direct, i.e., monomolecular route or via a bimolecular pathway involving the ring methylation of phenol molecules by anisole. Work is underway in our laboratory to shed light on this important mechanistic aspect of acid-catalyzed phenol alkylation.

4. Conclusions

In situ MAS NMR spectroscopy under flow conditions was used in connection with *ex situ* GC-MS analysis for studying the methylation of phenol by methanol on acidic zeolite H–Y. Anisole was found to be an unstable primary product and an important reaction intermediate. At reaction temperatures of $T > 433$ K and with an excess of methanol in the feed, polymethylated cresols were formed as secondary products.

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