Spectroscopic and kinetic study of the alkylation of phenol with dimethyl carbonate over NaX zeolite

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The interaction of phenol and dimethyl carbonate (DMC) with acid-base sites in zeolite NaX has been studied using FTIR, UV and mass spectroscopy. At room temperature, phenol is predominantly adsorbed by hydrogen bonding to basic oxygen atoms of NaX. At higher temperature, phenol is partially deprotonated over basic sites to form phenolate anions; the latter undergo H-bonding to zeolitic hydroxy groups and Na⁺ ions. DMC forms a chelating complex with Na⁺ ions at room temperature which decomposes at 150 °C into dimethyl ether and CO₂. FTIR experiments of coadsorbed reactants show that, in the presence of phenol, DMC is mainly bonded by its carbonyl oxygen to Lewis acid sites. The formation of anisole sets in at 150 °C and proceeds presumably *via* nucleophilic attack at the methyl carbon of DMC by the oxygen atom of H-bonded phenol or phenolate. Kinetic measurements reveal that the reaction order is negative in phenol but positive in DMC pointing to site blocking by strongly adsorbed phenol.

Aryl alkyl ethers represent an important group of chemicals used as reactants for the production of dyes, agricultural chemicals, antioxidants or stabilizers for polymers.¹ They may also be used as octane boosters and replace currently used non-metallic additives such as methyl tert-butyl ether.² The simplest representative of this class of compounds is phenyl methyl ether, anisole, which is produced commercially by alkylation of phenol with methanol. Alkylation can take place on the aromatic ring or the heteroatom, leading to cresol or anisole, respectively. The selectivity depends, besides experimental factors, on the acid-base properties^{3,4} and pore structure^{5,6} of the catalyst. Namba et al.⁷ studied the selectivity of phenol alkylation with methanol over H/Na/Y catalysts. They found that the yield of anisole increased with the Na: H ratio over zeolite Y. The nature of the alkylating agent seems, likewise, to play a role in the selectivity, although no systematic study exists as yet. The use of DMC yields high selectivities in the N- and O-alkylation of aniline and phenol, respectively, when basic zeolites are used as catalysts.⁸ Recently, Fu and Ono⁹ reported a selectivity of 93% for the Oalkylation of phenol at a conversion of 82% over NaX zeolite using DMC as the alkylating reactant. The environmentally friendly properties of DMC make it preferable to toxic and corrosive alkylating reactants such as dimethyl sulfate or methyl halides.¹⁰ NaX proved to be the most active and stable catalyst for this particular alkylation reaction.⁶

The formation of anisole by alkylation of phenol with DMC proceeds according to:

$$2 \text{ PhOH} + \text{DMC} \Rightarrow 2 \text{ PhOMe} + \text{CO}_2 + \text{H}_2\text{O} \qquad (I)$$

Elementary steps have been proposed for this reaction, based on catalytic test results over alkali-metal exchanged X and Y zeolites, which include the formation of phenolate ions as a reaction intermediate.⁸ IR spectroscopic data on the interaction of phenol with solid catalysts are scarce and pertain to acidic supports¹¹ or oxidation catalysts.^{12,13} No IR spectroscopic data have been reported so far on the adsorption of phenol or DMC on basic zeolites. The incentive of this study is, therefore, to characterize the adsorption states of DMC and phenol on NaX and to discriminate potential reaction intermediates in the alkylation reaction by IR and UV spectroscopy. The study of the adsorbed phase is supplemented by a mass spectroscopic analysis of the gaseous products evolved during decomposition of DMC over NaX. Finally, kinetic measurements on the alkylation of phenol with DMC were carried out with the aim to determine the reaction orders in both reactants. Based on spectroscopic and kinetic data, the structure and reactivity of surface complexes with the individual adsorbates phenol and DMC and a reaction scheme for the formation of anisole are proposed.

Experimental

Sample preparation

The reactants, DMC and phenol, were adsorbed at room temperature (rt) on a commercial NaX catalyst (Union Carbide, Lot No: 12 LBS 1360028) with an Si : Al ratio of 1.2. Prior to adsorption of the organic reactants, the catalyst was calcined in a flow of 50 ml min⁻¹ oxygen (Linde) for 2 h at 500 °C at a heating rate of 0.8 K min⁻¹ and subsequently evacuated at 500 °C for 20 min.

The desorption and decomposition of adsorbed molecules was studied by heating the sample stepwise to increasing temperatures in vacuum. After each heat treatment, an IR or UV spectrum was taken at rt. Both the IR and UV cell allowed *in situ* pretreatments up to 500 °C under gas atmosphere or in vacuum ($p = 10^{-5}$ mbar) and allowed to dose controlled amounts of the organic reactants *via* vapour-phase adsorption. Calibration measurements were made in which DMC was evaporated into a dose volume of 5 ml at 0 °C , while phenol was dosed into a container of 150 ml at rt before being dosed onto an NaX wafer. The quantities of DMC and phenol per dose volume correspond to *ca.* 0.1 and 0.2 molecules, respectively, per supercage. Phenol and DMC were purified before use by sublimation and distillation, respectively, onto activated molecular sieve 4A.

Spectroscopic techniques

For FTIR experiments, the sample was pressed at 100 bar into a self-supporting wafer (8 mg cm⁻²) and mounted in a portable Pyrex cuvette equipped with CaF₂ windows. Spectra were recorded on a Bruker IFS66 vacuum spectrometer in the transmission mode. A DTGS detector was used, accumulating 128 scans at a spectral resolution of 2 cm⁻¹. For UV measurements, 300 mg of sample were pressed at 25 bar and mounted into a quartz cell behind an optical window of Suprasil 300. Spectra were taken in the range between 200 and 500 nm in diffuse reflectance on a Varian Cary 5 spectrometer.

For mass spectroscopic studies, 50 mg of sample were given a standard pretreatment in a reactor attached to a Schlenck line as described above. After exposure to phenol or DMC at rt, the reactor was briefly evacuated before being transferred to a Balzer mass spectrometer. The desorption of gaseous products was continuously monitored while heating the sample to $300 \,^{\circ}$ C at a rate of 5 K min⁻¹.

Catalytic test

Gas-phase alkylation of phenol by DMC has been carried out in a continuous flow reactor at a reaction temperature of 200 °C. The phenol and DMC partial pressures were in the range 1–4 mbar at a GHSV of *ca.* 200 000 h⁻¹. Conversions were kept below 10%.

Results

Adsorption of phenol at room temperature

Fig. 1(a) shows the FTIR spectrum of phenol adsorbed on NaX at rt. Strong absorption bands are detected at 1591, 1492, 1475 and 1238 cm⁻¹. The band at 1591 cm⁻¹ and its shoulder at 1599 cm⁻¹ can be readily assigned to the 8a and 8b deformation vibrations of the aromatic ring.14,15 These bands are slightly displaced to lower wavenumbers as compared with phenol in CCl₄ solution where they occur at 1596 and 1604 cm⁻¹.¹⁵ Bands at 1492 and 1475 cm⁻¹ are ascribed to normal modes 19a and 19b of the ring. While the position of vibration 19b is the same as that of neat phenol at 1474 cm^{-1} , there is a red shift of 8 cm^{-1} for vibration 19a of adsorbed phenol. The intensive absorption band at 1238 $\rm cm^{-1}$ is ascribed to the C-O stretching vibration of self-associated phenol. A broad triplet of bands consisting of a maximum at 1386 cm⁻¹ and two shoulders around 1404 and 1360 cm⁻¹ is mainly attributed to the in-plane C-O-H-bending vibration of phenol. However, coupling of this mode to a C=Cstretching vibration has also been discussed,¹⁶ as well as the occurrence of phenol polymers.¹⁷ The spectrum in the C-Hstretching region is depicted in Fig. 2. A poorly resolved feature with absorption maxima at 3065 and 3047 cm⁻¹ is typical of the C-H-stretching vibrations of the aromatic ring





of phenol. These bands are superimposed on a broad and strong absorption around 3100 cm^{-1} . The broadness, intensity and low frequency shift of this band indicate the presence of perturbed OH groups which belong most likely to phenol H-bonded to zeolite oxygen atoms. The position of this band is considerably red shifted as compared with monomers of phenol¹⁸ which are characterized by a narrow O–H-stretching band at 3657 cm⁻¹. In addition, there is a series of bands at 2955, 2840, 2719 and 2619 and 2506 cm⁻¹ which are equally spaced by *ca*. 120 cm⁻¹.

Fig. 3(a) displays the UV spectrum of phenol after rt adsorption on NaX. Two main absorption bands can be distinguished at 221 and 269 nm, which are attributed to the primary $({}^{1}B_{1u} \leftarrow {}^{1}A_{1g})$ and secondary $({}^{1}B_{2u} \leftarrow {}^{1}A_{1g})$ electronic transitions of the π -electron system of phenol.¹⁹ Note that the primary band at 221 nm is red shifted by 10 nm as compared with the pure substance. It has been shown that both bands undergo shifts to lower energies with increasing electron-donating ability of the substituent.²⁰ The observed shift possibly indicates an H-bonded state of phenol in which the oxygen atom is more negatively polarized and hence a better electron donor than free phenol. A small shoulder can be discerned at *ca*. 296 nm in Fig. 3(a) indicating the presence of small amounts of phenolate ions, in accordance with literature data reporting electronic transitions of phenolate at 235 and 287 nm.²⁰



Fig. 1 FTIR spectra in the region of aromatic ring vibrations after adsorption of phenol on NaX (*ca.* 0.3 molecules per supercage) at 25 °C followed by (a) 1 h evacuation at 25 °C, (b) 200 °C, (c) 250 °C, (d) 300 °C and (e) 350 °C

Fig. 2 FTIR spectra in the region of C—H- and O—H-stretching vibrations after adsorption of phenol on NaX (*ca.* 0.3 molecules per supercage) at 25 °C followed by (a) 1 h evacuation at 25 °C, (b) 200 °C, (c) 250 °C, (d) 300 °C and (e) 350 °C

Thermal treatment of adsorbed phenol

Fig. 1(b)-(e) show the effect of thermal treatment in vacuum on the IR spectrum of phenol adsorbed on NaX. Heating to 200 °C leads to depletion of band intensity at 1475, 1386 and 1238 cm⁻¹, while the band at 1492 cm⁻¹ grows. The band at 1238 cm^{-1} is simultaneously shifted to 1254 cm^{-1} , and a shoulder at 1270 cm⁻¹ appears, together with a band at 1297 cm^{-1} . As the sample is further heated to 300 °C, the band at 1475 cm⁻¹ in Fig. 1(c) disappears and the broad band at 1386 cm⁻¹, characteristic of H-bonded phenol, is eroded. An isosbestic point exists between the bands at 1492 and 1475 cm⁻ indicating a transformation of phenol from state A into state B, C or D in Scheme 1. State A can be assigned to H-bonded phenol. States **B**, **C** and **D** are characterized by the loss of the $\delta_{\rm COH}$ vibration and a blue shift of the $v_{\rm C-O}$ vibration and correspond most likely to the deprotonated form of phenol. The high-frequency shift of the v_{C-O} vibration to 1254 cm⁻¹ after heating to 200 °C is in line with an enhancement of the CO bond strength when phenol undergoes H-bonding to basic oxygen atoms of the zeolite lattice. This is consistent with the assumption that the increased negative charge on the oxygen atom of phenolate should enhance the double bond character of the C-O bond by resonance effects.²¹ The appearance of C-O-stretching bands at 1270 and 1297 cm⁻¹ after heating to 200 °C is indicative of deprotonated phenol, in which the CO bond is further strengthened. A high-frequency shift of the $v_{\rm C-0}$ vibration to 1270 cm⁻¹ has been reported for phenolate in basic aqueous solution.²²

When the sample is further heated to 350 °C, the band at 1254 cm⁻¹, corresponding to state **A**, vanishes, while bands at 1270 and 1297 cm⁻¹ remain. After heat treatment to 350 °C the amount of adsorbed phenol decreased by ca. 50% of the initial amount of adsorbed phenol. This is due to desorption of phenol, but formation and subsequent desorption of reaction products such as diphenyl ether may also contribute to the loss of aromatic compounds after heat treatment to 200 °C and higher temperatures. Fig. 2 demonstrates the effect of thermal treatment on the O-H- and C-H-stretching bands. As evident from Fig. 2(b), the broad feature of perturbed OH groups is significantly depleted on its high-frequency side at ca. 3300 cm⁻¹, while intensity remains on the low-frequency wing when the sample is heated to 200 °C. This seems to indicate the presence of two different H-bonded phenol species with different degree of perturbation of the phenolic hydroxyl group.

As the intensity of the high-frequency component of perturbed O—H-stretching bands is depleted, the cluster of bands between 2955 and 2506 cm⁻¹ seems to be proportionally diminished in intensity. Complete deprotonation of phenol over NaX is achieved at 300 °C, as evident from the disappearance of all spectral features characterizing H-bonded phenol in Fig. 2(d). The deprotonation manifests itself also in a shift of the C—H-stretching vibrations at 3065 and 3047 cm⁻¹ of phenol to 3058 and 3032 cm⁻¹ of phenolate. Remarkably, there are few free zeolitic hydroxyl groups detected after heating to 300 °C, indicating that those groups are either strongly perturbed or further condensation has occurred.

Fig. 3(b)–(f) illustrate the effect of a stepwise heat treatment to 250 °C in vacuum on the UV spectrum of phenol. Significant changes are observed after heating to 100 °C; these are characterized by the appearance of a shoulder at *ca.* 240 nm. Concomitantly, the weak band at 296 nm, which was present as a shoulder in Fig. 3(a) and (b), becomes prominent in Fig. 3(c). Simultaneously, the intensity of the original bands at 221 and 269 nm decrease. Bands at 240 and 296 nm can be ascribed to phenolate ions, in accordance with literature data reporting electronic transitions at 235 and 287 nm.¹⁹ Further heating, to 250 °C, depletes the overall band intensity and leads to an inversion of the intensity ratio of bands at 269 and 296 nm.

DMC adsorption at room temperature

Fig. 4(a) shows the carbonyl and C-H-deformation vibrations of DMC adsorbed on NaX at rt. Three main absorptions can be discerned at 1753, 1461, and 1312 cm⁻¹. The feature with a maximum at 1753 cm^{-1} represents the C=Ostretching vibration of DMC.²³ There are two shoulders at 1769 and 1742 cm⁻¹, which possibly indicate different adsorption states of DMC. The intense absorption band with maximum at 1311 cm⁻¹ corresponds to the antisymmetric stretching vibration of the $\dot{CO_2}$ entity in DMC. It is broadened by a shoulder on the low-frequency side. An exhaustive interpretation of the vibrational spectrum of DMC has been given by Collingwood et al.24 Bands at 1461 and 1433 cm⁻¹ are assigned to deformation vibrations of the methyl groups of DMC. A third band at 1475 cm⁻¹ which is absent in dilute solutions of DMC in CCl₄ appears in Fig. 4(a). Fig. 5 depicts the corresponding C-H-stretching region



Fig. 3 UV diffuse reflectance spectra of phenol adsorbed on NaX at 25 °C followed by (a) 1 h evacuation at 25 °C, (b) 100, (c) 150, (d) 200 and (e) 250 °C



Fig. 4 FTIR spectra in the carbonyl-stretching region of DMC adsorbed on NaX (*ca.* 0.1 molecules per supercage) at 25 °C followed by (a) 15 min evacuation at 25 °C and after subsequent evacuation for 1 h at (b) 50, (c) 80, (d) 100, (e) 150 and (f) 200 °C



Fig. 5 FTIR spectra in the C—H-stretching region of DMC adsorbed on NaX (*ca.* 0.1 molecules per supercage) at 25 °C followed by (a) 15 min evacuation at 25 °C and after subsequent evacuation for 1 h at (b) 50, (c) 80, (d) 100, (e) 150 and (f) 200 °C

of adsorbed DMC. Bands at 3027 and 2965 cm⁻¹ in Fig. 5(a) have been ascribed to the antisymmetric and symmetric stretching vibrations of methyl groups, whereas the small absorption situated at 2861 cm⁻¹ has been interpreted as a combination band of two C—H-deformation vibrations.²⁴

Thermal treatment of adsorbed DMC

In order to follow the reactivity of DMC, the sample was heated stepwise to 200 °C in vacuum. A spectrum was taken after each thermal treatment. Fig. 4(b) shows the sample after heating at 50 °C for 1 h. It is evident that major losses of absorbance occurred at 1753 and 1296 cm⁻¹. These bands are close to 1756 and 1281 cm⁻¹ of neat DMC²⁵ and can most likely be attributed to physisorbed DMC. At the same time, the band intensity at 1769 cm^{-1} increased. As the sample is further heated, the antisymmetric and symmetric O-C-Ostretching bands diminish continuously and vanish completely at 150 °C. Fig. 4(b) reveals the appearance of additional bands at 1664 and 1345 cm⁻¹ which have been attributed to bidentate carbonate groups ligated to $Na^{\,+}$ ions.^{26,27} At the same time, a shoulder at 1454 cm^{-1} emerges on the low frequency side of the $\delta_{\rm CH}$ vibration of DMC methyl groups. The carbonate bands and the new C-H-deformation band at 1454 cm⁻¹ grow in concert when the sample is further heated to 80 and 100 °C under vacuum. The bidentate carbonate bands and the C-H-deformation band at 1454 cm⁻¹ decrease when the sample is heated above 150 °C, and an additional band pair at 1485 and 1428 cm⁻¹ develops. The latter bands have been assigned by Jacobs et al.²⁸ to Na⁺-bonded symmetric carbonate ions.

Fig. 5 illustrates the changes occurring in the C–Hstretching region upon heat treatment of DMC. The change in the adsorption state of DMC, which is induced by heating to $50 \,^{\circ}$ C, entails a slight blue shift of the symmetric C–Hstretching vibration to 2969 cm⁻¹. After heating to 80 $^{\circ}$ C, the carbonyl vibrations of DMC are strongly depleted. There is, however, no loss in intensity of the band at 2969 cm⁻¹. Fig. 5(c) shows an additional absorption band at 2997 cm⁻¹ and an enhancement of absorbance at 2863 cm⁻¹. It is plausible to assume the formation of a second type of CH₃ group at 80 $^{\circ}$ C which is characterized by bands at 2997, 2969 and 2863 cm⁻¹. Further heating to 100 $^{\circ}$ C generates a shoulder at 2956 cm⁻¹ and a band at 2850 cm⁻¹ which grow in concert with the C—H-deformation band at 1454 cm⁻¹. At the same time another absorption band at 2822 cm⁻¹ appears together with a shoulder at 2945 cm⁻¹ and a weak and broad band around 2900 cm⁻¹. The latter three bands represent, most likely, a third type of methyl group.

The thermal decomposition of DMC adsorbed on NaX at rt (ca. 1.5 molecule per supercage) has been followed by mass spectroscopy. Fig. 6 illustrates the evolution of peaks corresponding to m/z = 45, 44, 29 and 15. The peak at m/z = 44can readily be ascribed to CO_2 . The peaks at 15, 29, and 45 are representative of both DMC and dimethyl ether (DME). Injection of pure DME and DMC into the mass spectrometer yielded ratios of m/z = 15 to m/z = 45 of 1.3 and 5, respectively. It should be mentioned that, under the experimental conditions encountered in this study, the relative abundance of fragments with m/z = 15 and 45 is different from literature data.²⁹ A plot of the ratio m/z = 15 to m/z = 45 [Fig. 6(b)] reveals indeed that, during decomposition of DMC over NaX, the ratio is 5 initially, in accordance with the desorption of DMC. This ratio starts dropping at temperatures above 100 °C and reaches a constant value of 1.4 above 200 °C which corresponds to desorption of DME. The declining part of the curve indicates the onset of DME desorption. Evolution of CO_2 sets in at around 60 °C. The appearance of CO_2 in the gas phase is evidence of the decomposition of DMC. Interestingly, the onset of detection of peak 15 occurs at ca. 100 °C. This means that DMC decomposes between 60 and 100 °C while its methyl groups are retained on the surface. The peak ratio m/z = 15 to m/z = 45 is high at temperatures below 100 °C, corresponding to desorption of DMC. The peak ratio decreases above 100 °C, indicating the release of DME.



Fig. 6 Evolution of CO₂ (m/z = 44), DME and DMC (m/z = 15, 29, 45) as a function of time under vacuum as followed by mass spectrometry from DMC-loaded NaX (*ca.* 0.8 molecules per supercage)

Fig. 7 shows the effect of phenol adsorption on the state of preadsorbed DMC at rt. Fig. 7(a) was taken after adsorption of DMC and Fig. 7(b) after subsequent adsorption of phenol. The band at 1238 cm⁻¹ indicates the presence of H-bonded phenol. The difference spectrum (b) – (a) reveals the disappearance of band intensity at 1769 cm⁻¹ and an increase in band intensity at 1742 cm⁻¹ of DMC. The same result (not shown) was also obtained when the order of adsorption was reversed.

Reactivity of phenol and DMC

Fig. 8 demonstrates the effect of heating coadsorbed phenol and DMC. Fig. 8(a) was obtained after adsorption of phenol and DMC at rt and subsequent heating to 100 °C. Remarkably, the intensity of the DMC carbonyl band at 1742 cm⁻¹ is significantly higher than when DMC was heated in the absence of phenol [*cf.* Fig. 4(c)]. Apparently, the decomposi-



Fig. 7 FTIR spectra in the carbonyl-stretching region of NaX after (a) adsorption of DMC at 25 °C, (b) followed by adsorption of phenol at 25 °C and after subtraction (b) – (a). Equal amounts of DMC and phenol, corresponding to *ca.* 0.2 molecules, respectively, per unit cell have been dosed.



Fig. 8 FTIR spectra in the carbonyl-stretching region of NaX after (a) coadsorption of DMC and phenol at $25 \,^{\circ}$ C and followed by brief evacuation and 1 h heating to (b) 100 and (c) $150 \,^{\circ}$ C in the closed cell. Quantities of adsorbed reactants correspond to those of Fig. 7.

tion of DMC is retarded in the presence of phenol. Further heating to 150 °C causes a decrease in band intensity of adsorbed DMC. The aromatic ring vibration at 1591 cm⁻ shifted to 1597 cm⁻¹ and exhibits a shoulder at 1585 cm⁻¹. Concomitantly, the C-H-deformation band of DMC methyl groups at 1461 cm⁻¹ becomes broader and a band at 1238 cm^{-1} arises. In addition, a broad band around 1685 cm^{-1} and a shoulder around 1330 cm^{-1} grow in. These bands can be assigned to HCO_3^- ions. Further heating to 200 °C erodes all carbonyl bands ascribed to DMC but leaves bands at 1597, 1238 cm^{-1} and a doublet at 1454 and 1446 cm^{-1} . Those bands are indicative of anisole which is formed by Oalkylation of phenol. The band assignment for anisole has been checked by adsorption of anisole on NaX in a separate experiment. Note that for Fig. 8(b) and (c) the IR cell was closed during heat treatment in order to trap the reaction products. The v_{O-H} and v_{C-H} stretching vibrational regions presented in Fig. 9 reveal the typical features of H-bonded phenol together with DMC. Upon heating to 150 °C, new bands at 3320, 2958, 2841 and 2818 cm^{-1} appear. The intense and broad band around 3320 cm⁻¹ is characteristic of perturbed hydroxyl groups. Since the typical feature of H₂O hydrogen bonded to $Na \cdots O_z$ acid-base pair sites is missing in Fig. 9, the band at 3320 cm^{-1} is likely to be attributed to H-bonded methanol. Bands at 2958 and 2841 cm⁻¹ can accordingly be ascribed to the antisymmetric and symmetric stretching vibrations of methyl groups in anisole and methanol.

It is important to note that bands at 1685 and 1330 cm⁻¹ are also formed when monomethyl carbonate (MMC), as generated from DMC under dry conditions, is exposed to water and stepwise heated to 80, 100 and 150 °C in the closed IR cell. The heat treatment of MMC with water leads to the depletion of bands at 1664 and 1345 cm⁻¹ while bands at 1685 and 1330 cm⁻¹ build up, together with a band at 3320 cm⁻¹. This result can be rationalized assuming hydrolysis of MMC into hydrogen carbonate and methanol and confirms the band assignment given above.

The reaction of phenol with DMC was also followed by UV spectroscopy. However, reference experiments showed that DMC does not absorb in the wavelength range between 200 and 500 nm while anisole, presenting bands at 224 and 266 nm, appears to be indistinguishable from phenol. Coadsorption experiments revealed that the formation of phenolate is suppressed at $150 \,^{\circ}$ C in the presence of excess DMC,



Fig. 9 FTIR spectra in the C–H- and O–H-stretching region of NaX after coadsorption of DMC and phenol at 25 °C followed by brief evacuation and 1 h heating to (a) 100, (b) 150 and (c) 200 °C in the closed cell. Quantities of adsorbed reactants correspond to those of Fig. 7.



Fig. 10 Reaction orders in DMC (A) and phenol (B) as determined from the dependence of the rate of anisole formation on the partial pressure of the reactants measured at $200 \,^{\circ}\text{C}$

indicating that phenol and/or phenolate reacted with DMC at that temperature.

Kinetic measurements have been carried out in a flow reactor in order to determine the reaction orders of both reactants. Fig. 10 shows the dependence of the reaction rate on the partial pressure of each reactant. Evaluation of the slopes of the bilogarithmic plot yields a positive reaction order in the range +1 for DMC and a negative reaction order of *ca.* -1 for phenol. The negative reaction order in phenol signifies that phenol is strongly adsorbed on the surface and blocks sites for the adsorption of DMC. This in turn means that DMC does not react from the gas phase in an Eley-Rideal type mechanism but from an adsorbed state.

Discussion

Reactivity of phenol

IR data reveal that phenol adsorbed on NaX is predominantly H-bonded at rt. This is evident from the broad O-Hstretching vibration at *ca.* 3100 cm^{-1} of phenol undergoing a hydrogen bond to basic oxygen atoms of the zeolite lattice. The red shift of 10 nm of the primary band in the UV spectrum of phenol adsorbed on NaX as compared to that of neat phenol, is in agreement with the assumption of H-bonded phenol. The primary and secondary electronic transitions of the π -electron system of phenol are sensitive to the electron density of the aromatic ring. Substituents with electron lone pairs can transfer electron density to the ring by resonance effects. Electron donors raise the energy of the HOMO, but affect the energy level of the LUMO to only a small extent, thus resulting in a low-frequency shift of the electronic transitions of the π system.²⁰ A bathochromic shift with respect to free phenol is, therefore, anticipated as a result of H-bonding as it enhances the electron density of the hydroxyl oxygen and hence the donating power of the substituent. An additional interaction of phenol with adjacent Na⁺ ions by either its hydroxyl oxygen atom or the π electrons of the aromatic ring

seems likely, but cannot be inferred from the present spectroscopic data. Quantum chemical calculations by Matsamura *et* $al.^{30}$ show that phenol interacts with Na⁺ ions preferentially by the oxygen atom. Based on this result, structure **A** is proposed in Scheme 1.

The presence of a second broad contribution at 3300 cm^{-1} in the OH-stretching region of phenol adsorbed at rt is ascribed mainly to self-associated phenol or phenol adsorbed on the external surface of the zeolite. Adsorption of phenol on silica yielded a perturbed OH band at 3357 cm⁻¹. Relatively narrow bands at 3530 and 3654 cm⁻¹ for phenol dimers and at 3441 and 3449 cm⁻¹ for trimers in the gas phase have been measured in ionization-detected IR experiments by Ebata et al.³¹ These bands may be present in Fig. 2(a) but masked by the broad feature around 3300 cm⁻¹. The depletion of absorbance around 3300 cm⁻¹ becomes evident in Fig. 2 and corresponds to three processes: (i) Desorption of phenol, (ii) migration of phenol to basic zeolite oxygen atoms and (iii) reaction of phenol to phenolate and/or diphenyl ether. The band at 3300 cm⁻¹ may contain contributions of small amounts of phenolate ions interacting with zeolitic hydroxyl groups via the aromatic ring, as depicted in structure B of Scheme 1. It is known that acidic hydroxyl groups in H-ZSM-5 are shifted by ca. 300 cm⁻¹ upon interaction with adsorbed benzene.³² It is difficult to predict the displacement of an OH band in HNaX when interacting with the π system of phenolate ions. The acid strength of hydroxyl groups in HNaX is weaker than in H-ZSM-5 but the phenolate ion is a stronger π electron donor than benzene. In addition, the adsorption geometry changes from C_{6v} in the benzene proton adduct to a lower symmetry in the phenolate proton adduct.

It is interesting to note that, after rt adsorption of phenol, a series of bands at 2955, 2840, 2719, 2619 and 2605 cm⁻¹ is observed on the low-frequency wing of the band corresponding to perturbed hydroxyl groups in H-bonded phenol. A similar phenomenon has been observed recently by Binet et al.³³ for pyrrole adsorbed on NaX and was attributed to the formation of pyrrolate anions interacting with OH groups of the support. In this study, UV experiments suggest that only small amounts of phenolate should be present at rt. The intensity of the progression of these bands seems to follow the decrease in perturbed OH intensity at 3100 cm^{-1} as the sample is heated to higher temperatures, suggesting that they are related to the presence of H-bonded phenol. Separate experiments using ¹³C₆H₅OH and C₆D₅OH showed that the spacing of these bands is sensitive to isotopic substitution of the ring carbon atoms by ¹³C as well as deuteration of the ring. This suggests that vibrations which include the motion of ring atoms and the hydroxy group are involved in this phenomenon. The origin of this phenomenon is not understood at present and needs further investigation.

Fig. 3(b) shows that phenol is partially deprotonated after heating to 200 °C, as evident from the enhancement of the secondary electronic transition of phenolate at 296 nm relative to that of phenol at 269 nm. The broad and strong absorption at 3100 cm⁻¹ and the δ_{C-O-H} vibration in Fig. 1(b) and Fig. 2(b), respectively, have substantially decreased, indicating that H-bonded phenol has been deprotonated. This is further confirmed by the hypsochromic shift of the C-O-stretching vibration from 1238 cm⁻¹ in self-associated phenol to 1254 cm⁻¹ in zeolite-bonded phenol. After 300 °C, all spectral features in the O-H-stretching region characteristic of Hbonded phenol have vanished [see Fig. 2(d)], but there remains about half of the original intensity in the range of the aromatic ring vibrations [see Fig. 1(d)]. Obviously, part of the phenol has desorbed. Another part of the phenol was deprotonated and formed phenolate ions which are most likely bonded to Na⁺ ions. The further blue shift of the C-Ostretching vibration to 1297 cm⁻¹ may be taken as evidence for Na⁺-bonded phenolate ions. As neither free nor perturbed

OH groups are observed after heating to $300 \,^{\circ}$ C, it is reasonable to suggest their further reaction with phenol to form surface phenyl ethers. The band at 1270 cm⁻¹ is tentatively assigned to the CO-stretching vibration of O_zPh groups. Bands at 1241 and 1260 cm⁻¹ have been measured for (EtO)₃Si(OPh).³⁴ The reaction of NaOPh with O_zPh groups may yield diphenyl ether. Neat diphenyl ether presents a band at 1237 cm⁻¹ which is not observed after vacuum treatments at 300 and 350 °C. It is, therefore, concluded that diphenyl ether, if formed, desorbs at those temperatures. The reactivity of phenol is depicted in Scheme 1.

Reactivity of DMC

A priori, two adsorption modes of DMC inside the supercages of NaX can be envisaged and are illustrated in Scheme 2. Complex E is characterized by an interaction of the carbonyl oxygen with a Na^+ ion. In this structure the C=O double bond is weakened as compared to liquid-phase DMC. IR bands at 1742 and 1281 cm⁻¹ seen in Fig. 4(a) after rt adsorption can be attributed to complex E. Another interaction consists in the formation of a bidentate complex in which the ester oxygen atoms of DMC chelate one Na⁺ ion, as depicted in structure F. For this complex, a strengthening accompanied by a blue shift of the C=O bond is expected with respect to neat DMC. Bands at 1769 and 1312 cm⁻¹ may, accordingly, be ascribed to complex \mathbf{F} in Scheme 2. In both structures, DMC acts as a Lewis base to form an acid-base complex with Lewis acid sites of the zeolite. IR and MS data also revealed the potential of DMC to react with Lewis acid-base pairs of the zeolite. Heating to 80 °C leads to formation of two new types of CH₃ groups which are characterized by bands at 2997, 2969 and 2863 cm⁻¹ for one type and by bands at 2954 and 2850 cm^{-1} for the other type. The latter band pair can be attributed to either adsorbed methanol or silicon-bonded methoxy groups. The band at 1454 cm⁻¹ has to be assigned to the corresponding C-H deformation band. The close proximity of the position of the former three bands to those of DMC suggests a great structural similarity. The triplet of bands at 2997, 2969 and 2863 cm⁻¹ may tentatively be ascribed to monomethyl carbonate (MMC). The formation of two new types of CH₃ groups can be interpreted in terms of an alkyl cleavage of DMC yielding methyl groups and MMC according to reaction (1) of Scheme 3. The generation of methoxy groups is also accompanied by the evolution of a characteristic band pair at 1664 and 1345 cm⁻¹ which is attributed to MMC groups ligated in a bidentate fashion to



 Na^+ ions. Unland observed bands at 1662 and 1344 cm⁻¹ after thermal decomposition of methanol over NaX and ascribed them to bidentate carbonate groups.²⁷ While MMC forms a complex with Na⁺ ions, the CH₃ groups are bonded to surface oxygen atoms of the zeolite. Partial hydrolysis of DMC by traces of water, resulting in the formation of methanol, can, however, not be excluded. In fact, bands at 2954, 2850 and 1450 cm^{-1} are typical of methanol as well as Si-OCH₃ groups. At 100 °C, the band intensity of MMC methyl groups is diminished and a new band pair consisting of a shoulder at 2950 cm^{-1} and a band at 2822 cm^{-1} arise. MS analysis of the gas phase shows that CO₂ is released. This can be rationalized assuming a decomposition of MMC to form Na⁺-bonded methoxy groups, as depicted in reaction (2) of Scheme 3. The low-frequency position of the symmetric C-H-stretching band at 2822 cm^{-1} points to an ionic methoxy group. Bands in the 2820 cm^{-1} region can sometimes be due to overtones or combination bands of the fundamental C-H deformation vibrations of CH₃ or CH₂ groups. There is, however, no fundamental vibration in the appropriate range of Fig. 4(c) and (d) as to account for an overtone at 2822 cm^{-1} . The absence of this band in the spectra of DMC adsorbed on HY is further support for Na⁺ ions as the responsible adsorption sites. The formation of Na+-bound methoxy groups from MMC occurs without participation of adjacent sites. This reaction, as it is not base assisted, may be anticipated to require a higher activation energy. Bensitel et $al.^{35}$ studied the generation of MMC by reaction of CO₂ with methoxy groups adsorbed on ZrO₂. They ascribed bands at 1583 and 1372 cm⁻¹ to monomethyl carbonate ligated in a bidentate fashion to Zr⁴⁺ cations. The zirconia-bound MMC complex decomposed completely into Zr-OCH₃ and CO₂ on heating to 170 °C. At temperatures above 150 °C, band intensity at 2850 and 2822 cm⁻¹ decreases and formation of DME is observed by mass spectrometry. Apparently, Na⁺-bonded methoxy groups react with lattice oxygen bound methyl groups to generate dimethyl ether as illustrated in reaction 3 of Scheme 3. This reaction is similar to the formation of ethers from alcohols over alumina, which has been discussed by Knözinger³⁶ in terms of a nucleophilic attack by the oxygen atom of an O- and H-bonded alcohol to an adjacent alkoxy group. A separate experiment of DME adsorbed at rt yielded also a band at 2820 cm⁻¹ which, however, disappeared after vacuum treatment at 100 °C, because of desorption of DME. This result is in agreement with the detection of DME by mass spectroscopy in the course of DMC decomposition at 150 °C. On the contrary, the absorption band at 2822 cm^{-1} resulting from DMC decomposition is still observed after heating in vacuum to 200 °C. When the sample is heated to 150 °C, two new absorption bands are observed at 1488 and 1430 cm⁻¹ which have been assigned to symmetric carbonate groups. These bands have been shown to be generated from CO₂ and NaX in the dry state.²⁶

Reactivity of coadsorbed phenol and DMC

The coadsorption experiments show that phenol is able to force DMC into one preferential adsorption state corresponding to complex **F** in Scheme 2 while physisorbed and chelating DMC are suppressed. This situation is realized regardless of the order of adsorption of the reactants DMC and phenol. After heating to 100 °C, much more DMC is retained on the surface when phenol is present. This provides evidence that thermal decomposition of DMC into CO₂ and dimethyl ether proceeds *via* chelating DMC as a precursor. It is likely that the alkyl bond cleavage of DMC is favored when DMC is adsorbed in a chelating fashion. The formation of the chelating DMC complex with Na⁺ ions is sterically hindered when phenol is adsorbed on a neighbouring basic oxygen site. However, no firm conclusion can be drawn as to whether an



additional interaction of phenol with the cation takes place. Heating to $150 \,^{\circ}$ C causes the formation of anisole together with methanol and hydrogen carbonate ions. In view of these results, a reaction mechanism is proposed in Scheme 4.

From the negative reaction order in phenol it is inferred that phenol inhibits the reaction by site blocking. The kinetic data further suggest that both reactants are adsorbed on the catalyst surface during the alkylation reaction. If DMC impinging from the gas phase reacted with adsorbed phenol, a positive reaction order in phenol would be anticipated. The reactants are presumably adsorbed on a Na···O_z acid-base pair site. IR data reveal that phenol is activated by H-bonding to a basic oxygen atom, while DMC is adsorbed on the cation via its carbonyl oxygen. A six-membered ring may tentatively be envisaged in the transition state, in which the phenol oxygen atom undergoes a nucleophilic attack on the carbon atom of one DMC methyl group. A concerted electron rearrangement leads to the formation of anisole and methyl hydrogen carbonate. The latter may decompose into hydrogen carbonate and methyl groups. Subsequent elimination of CO₂ would yield H-bonded methanol. Both hydrogen carbonate and H-bonded methanol are detected by IR spectroscopy. The data cannot prove unambiguously whether H-bonded phenol is directly alkylated or first converted into phenolate. While O- and H-bonded phenol appears to be stable up to 250 °C it is conceivable that, in the presence of DMC, a competition for Lewis acid sites occurs, leading to a coadsorption of both reactants in a 1:1 stoichiometry at one acid-base pair site.

An alternative reaction path in which the phenolate oxygen attacks the carbonyl group of DMC to form dimethyl phenyl ortho-ester as an intermediate is also possible. The noncatalytic pyrolysis of acetic acid ortho-ester yields an ether and an ester.37 This reaction proceeds via a ketene acetal, $H_2C=C(OR)_2$. Interestingly, the ketene acetal which can be considered the carbon analogue to $O=C(OR)_2$, dialkyl carbonate, reacts selectively with phenol to form the respective phenyl alkyl ether, PhOR. The assumption of an ortho-ester as an intermediate in the reaction of phenol with DMC would explain the high O-alkylation selectivity observed in this reaction. However, dimethyl ether would be a side product, with a statistical weight of 33%. In order to explain, why much less dimethyl ether is formed, additional assumptions would have to be made with respect to the relative activation energies for the generation of DME and phenyl methyl ether (PME), respectively, from dimethyl phenyl ortho-carboxylic ester.

Conclusions

(1) At room temperature, phenol is preferentially adsorbed by hydrogen bonding to basic oxygen atoms of NaX. Moreover, phenol is partially deprotonated over basic sites to form zeolitic hydroxyl groups and phenolate ions ligated to Na⁺ ions, NaOPh. The zeolitic hydroxyl groups formed are likely to interact with the π -electron system of phenolate ions and are able to form a surface ether, O_zPh, with phenol.

(2) DMC forms two types of surface complexes with Na⁺ ions at room temperature: A chelating complex *via* the ester oxygen atoms and a monodentate complex *via* the carbonyl oxygen atom. The chelating complex reacts with Na···O_z acid-base sites to form dimethyl ether and CO₂. The decomposition of DMC proceeds stepwise *via* formation of monomethyl carbonate, Na-bonded methoxy groups, NaOCH₃, and lattice oxygen-bonded methyl groups, O_zCH₃.

(3) Phenol inhibits the formation of chelating DMC, thus retarding the decomposition of DMC. The formation of anisole proceeds presumably *via* nucleophilic attack at the methyl carbon of DMC by the phenol oxygen. This reaction supposedly takes place on a Na···O_z acid-base site, where DMC is activated on the Lewis acid site by its carbonyl oxygen and phenol on an adjacent Lewis base site by H-bonding. This reaction sets in at *ca*. 150 °C and yields anisole, H-bonded methanol and CO₂.

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