

# Interactions of a vinyl ether with acid-modified silica-based catalyst studied by ATR-IR spectroscopy

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## Abstract

The interaction of 2-methoxypropene, a vinyl ether, with heterogeneous acid catalysts containing sulfonic acid groups covalently bound to SiO<sub>2</sub> (Deloxan ASP, Degussa) and sulfuric acid adsorbed on TiO<sub>2</sub>-modified amorphous SiO<sub>2</sub> (Degussa), respectively, was investigated by in situ attenuated total reflection infrared spectroscopy. Rapid hydrolysis is observed, which does not, however, require the acid sites. The resulting acetone is adsorbed predominantly on SiOH groups. Promoted by the acid sites a further transformation is observed on the catalysts. Based on the time behavior of the ATR signals of acetone and the product the further reaction likely involves the condensation of 2-methoxypropene and acetone. During the buildup of the reaction product hydronium ions disappear from the catalyst surface. Upon desorption of the reaction product the hydronium ions become prominent again on the catalyst containing adsorbed sulfuric acid. This behavior is less pronounced on the catalyst, which contains sulfonic acid groups. The two investigated catalysts contain vastly different relative concentrations of Brønsted and Lewis acid sites, which can explain the difference in the relative concentration of intermediate and product at the interface in the observed consecutive reaction.

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## 1. Introduction

In fine chemical industry condensations between unsaturated alcohols and unsaturated ethers yielding unsaturated ketones with higher molecular weight are mainly of interest because they provide an efficient route for the production of long-chain compounds [1–6]. These condensation reactions are used in flavor, fragrance, vitamin, and other fine chemical synthesis and can be categorized as Saucy-Marbet reactions [7].

These liquid-phase condensation reactions are mostly carried out with homogeneous acid catalysts. The latter selectively catalyze the reaction but suffer from problems connected with separation from the product mixture. Since these condensation reactions are one out of a series of steps for the synthesis of complex molecules in industry, they have to be selective and environmentally clean. The use of a solid acid catalyst instead of a homogeneous one would be beneficial

for technical applications and thus represents an interesting challenge.

The main goal of the present work was to shed some light on an important step in these condensation reactions, namely the interactions of the vinyl ether reactant occurring at the solid–liquid interface of the solid acid catalyst. Vinyl ether compounds are, for example, used in the Saucy-Marbet-type condensation reactions. In the first, acid-catalyzed step the vinyl ether reacts with an unsaturated alcohol. A subsequent thermal step leads to an unsaturated ketone [4]. Vinyl ethers can furthermore easily be hydrolyzed in the presence of acids. This reaction has been studied thoroughly in the homogeneous phase. From these studies it emerged that the rate-limiting step is proton transfer [8]. Protonation takes place at the  $\beta$ -carbon of the vinyl ether and not at the oxygen, giving rise to a stable carbocation [9].

We have used attenuated total reflection (ATR) infrared spectroscopy [10] in previous studies to explore solid–liquid interfaces consisting of thin metal films [11,12], supported metals [13,14], and oxide catalysts [15]. Here the technique is applied to investigate the complex transformation of a simple vinyl ether, 2-methoxypropene, with solid acid catalysts based on silica modified with sulfonic and sulfuric acid.

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## 2. Experimental

### 2.1. Chemicals and catalysts

2-Methoxypropene (MP, Teranol AG), 2,2-dimethoxypropane (DMP, Teranol AG), mesityloxide (MSO, Fluka, > 90%), acetone (Merck, > 99.8%), diacetone-alcohol (DAA, Fluka, ~ 99%), pyridine (Fluka, > 99.8%), pentadecane (Fluka, > 98%), 1-propane sulfonic acid (PSA, Fluka, > 99%), *n*-hexane (Merck, for spectroscopy), and 1-butanol (Acros Organics, > 99.5%) were used as received.

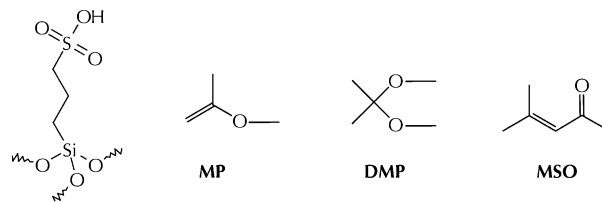
The following catalysts were used: SiO<sub>2</sub> gel 60 (Fluka, puriss. for column chromatography), Deloxan ASP I/9 (Degussa, copolycondensate of propyl(3-sulfonic acid)siloxane, and SiO<sub>2</sub>; alkyl sulfonic acid polysiloxane; particle-size: 0.1–0.4 mm; stable at temperatures < 230 °C) and sulfated and TiO<sub>2</sub>-modified amorphous SiO<sub>2</sub> (Degussa, consists of < 15% sulfuric acid, 80–95% SiO<sub>2</sub> and < 10% TiO<sub>2</sub>).

### 2.2. Attenuated total reflection infrared spectroscopy

SiO<sub>2</sub> gel (Fluka), sulfated and TiO<sub>2</sub>-modified amorphous SiO<sub>2</sub>, and Deloxan ASP I/9 (Degussa) thin films were prepared from a suspension of the corresponding material (500 mg) in water (for chromatography, Merck, 10 ml). The suspension was deposited on a Ge internal reflection element (IRE) and the solvent evaporated in air. After deposition the films were rinsed with *n*-hexane to remove loose deposits and the coated IRE was mounted within the walls of a home-made stainless-steel infrared cell described elsewhere [11,13].

In situ ATR-IR measurements were performed by flowing a *n*-hexane solution of the substrate at the desired concentration saturated with argon over the thin film after stabilization of the IR signal (> 1 h) by flowing Ar-saturated solvent. The adsorption step was followed by a desorption step consisting in the flow of neat solvent saturated with argon. Solutions were pumped through the cell by means of a peristaltic pump at ca. 0.6 ml/min flow rate. All measurements were carried out at 25 °C on a Bruker IFS 66 spectrometer equipped with a liquid nitrogen cooled HgCdTe detector by accumulating 200 scans at 4 cm<sup>-1</sup> resolution. Spectra are reported as absorbance  $A = -\log(I/I_0)$ , where  $I$  and  $I_0$  is the intensity of sample and reference, respectively.

Diffuse reflection infrared spectra (DRIFT) were measured using a Prying Mantis DRIFT accessory together with an environmental chamber (HVC-DRP-2, Harrick). Measurements were performed at ambient conditions.



PSA on Deloxan surface

Scheme 1. Structure of the surface 3-propane sulfonic acid groups of Deloxan as well as of 2-methoxypropene (MP), 2,2-dimethoxypropane (DMP), and mesityloxide (MSO).

## 3. Results

### 3.1. Characterization of the sulfonic acid groups of Deloxan

The surface of Deloxan ASP I/9, which contains 3-propane sulfonic acid groups (Scheme 1), showed signals at 3737, 2979, 2952, 2898, 1725, 1636, 1459, 1415, and 1355 cm<sup>-1</sup> (DRIFT). Signals associated with the SiO<sub>2</sub> matrix were found at 1094, 948, and 802 cm<sup>-1</sup>.

1-Propane sulfonic acid in hexane solvent showed absorptions at 3649, 3438, 2967 (2975 cm<sup>-1</sup> for neat PSA), 2939 (2941), 2880 (2885), 1461, 1370, 1340, 1296, 1170, 1095, 1071, and 1012 cm<sup>-1</sup>. The signals at around 2900 cm<sup>-1</sup> can be assigned in both cases to the C–H stretchings of the methylene and methyl groups of PSA. The signal at 3737 cm<sup>-1</sup> found in Deloxan reveals the presence of free silanol groups. The signal at ca. 1460 cm<sup>-1</sup> is likely due to the deformation mode of CH<sub>2</sub> groups.

Sulfonic acid groups were assigned by following the behavior of the typical signals of PSA upon addition of a base. Titration of PSA with pyridine in hexane solvent indicated that signals at 1370 and 1170 cm<sup>-1</sup> must be assigned to the characteristic stretching vibrations of S=O groups. Consistently, these signals were attenuated at increasing pyridine concentrations and completely disappeared at equivalence, whereas new bands grew in at 1233 and 1140 cm<sup>-1</sup>. Sulfonic acids absorb at 1350–1342 cm<sup>-1</sup> ( $\nu_{AS}$ ) and 1165–1150 cm<sup>-1</sup> ( $\nu_S$ ), whereas sulfonates absorb at 1372–1335 and 1195–1168 cm<sup>-1</sup> [16]. Hence, the signal of Deloxan at 1355 cm<sup>-1</sup> is likely due to SO<sub>3</sub><sup>-</sup> groups.

The broad signal around 1725 cm<sup>-1</sup> observed in the DRIFT spectrum in air can be assigned to the deformation vibration of hydronium ions. In a dehydration study of Nafion membranes (perfluorinated polymeric sulfonic acid, trademark of E.I. du Pont de Nemours Co.) a broad signal has been observed at around 1720 cm<sup>-1</sup> and assigned to a deformation vibration of hydronium ions [17].

### 3.2. Pyridine adsorption on SiO<sub>2</sub> and Deloxan

Pyridine is an excellent probe for investigating the acidity of solid materials since its adsorption on Lewis and Brønsted acid sites affords distinctly different sets of signals in

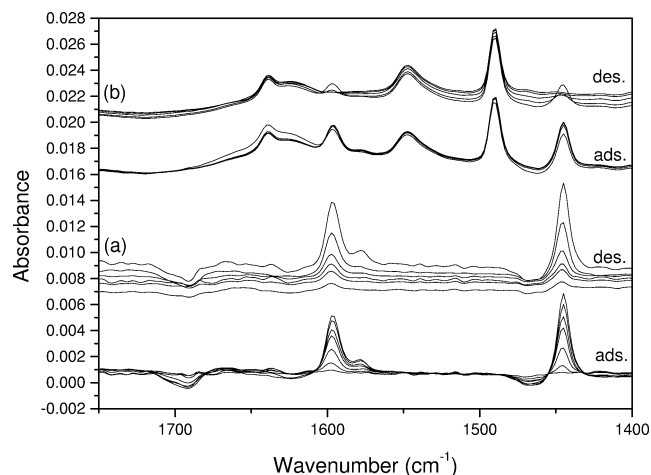


Fig. 1. ATR spectra of pyridine adsorption on (a) SiO<sub>2</sub> and (b) Deloxan from a 10<sup>-2</sup> M solution in hexane as function of time. Adsorption and desorption steps are shown for both materials. During the desorption step neat solvent was flown over the sample.

the two cases. Fig. 1 shows the ATR spectra of pyridine contacted with (a) SiO<sub>2</sub> and (b) Deloxan from a 10<sup>-2</sup> M solution in hexane. The SiO<sub>2</sub> surface displays the typical signals due to pyridine hydrogen-bonded to silanol groups, which is denoted HPy (Table 1). These signals are found at 1595, 1578, and 1445 cm<sup>-1</sup> and are almost completely attenuated due to desorption when flowing neat hexane solvent.

In contrast to SiO<sub>2</sub>, Deloxan exhibits three additional bands at 1638, 1550, and 1490 cm<sup>-1</sup>, which are assigned to pyridinium ions bound to Brønsted acid sites (BPy) [18]. These sites are associated with the sulfonic acid groups present on the Deloxan surface. The very broad negative band around 1725 cm<sup>-1</sup> and the broad positive band at 1620 cm<sup>-1</sup> arising upon pyridine adsorption indicate the transformation of hydronium ions to water. Hence pyridine is protonated by the hydronium ion. On desorption, the signals due to HPy are almost completely attenuated, whereas those corresponding to BPy are only slightly affected showing that pyridine strongly binds to the Brønsted sites of the Deloxan surface. Table 1 summarizes the assignment of the observed signals for pyridine on SiO<sub>2</sub> and Deloxan.

The relative concentration of Brønsted and Lewis acid sites, on which pyridine is adsorbed, can be estimated from the infrared spectra at saturation. The information needed is the absorption coefficient for the corresponding vibrational modes at 1445 (19b mode of pyridine) and at about 1550 cm<sup>-1</sup> (19b mode of pyridinium ion). The relative concentration of Brønsted and Lewis sites  $C_B/C_L$  is

$$\frac{C_B}{C_L} = \frac{A_{1550} \varepsilon_{1445}}{A_{1445} \varepsilon_{1550}}$$

Here  $A_{1550}$  and  $A_{1445}$  are the integrated absorbances of the 19b modes at 1550 and 1445 cm<sup>-1</sup>, associated with Brønsted and Lewis sites, and  $\varepsilon_{1550}$  and  $\varepsilon_{1445}$  are the molar absorption coefficients for the corresponding bands at 1550 and 1445 cm<sup>-1</sup>. Values of 1.24 and 1.56 cm<sup>2</sup> μmol<sup>-1</sup> have been

Table 1  
Observed IR bands and assignment of ring vibrations for neat pyridine and pyridine adsorbed on SiO<sub>2</sub>, Deloxan, and sulfated TiO<sub>2</sub>-modified amorphous SiO<sub>2</sub>

Neat	SiO <sub>2</sub>	Deloxan	Sulfated TiO <sub>2</sub> -modified SiO <sub>2</sub>	Assignment [27]	
				Mode	
		1639	1638	8a	ν(CCN) BPy
1597	1597	1596	1596		ν(CCN) HPy
1580	1578	1578	1578	8a	ν(CCN) HPy
		1547	1544	19b	ν(CCN) + δ(CCN) BPy
		1489	1488	19a	ν(CCN) + δ(CCN) BPy
1481				19a	ν(CCN) + δ(CCN)
1439	1445	1444	1445	19b	ν(CCN) + δ(CCN) HPy

BPy and HPy denote pyridine adsorbed on Brønsted and Lewis sites, respectively.

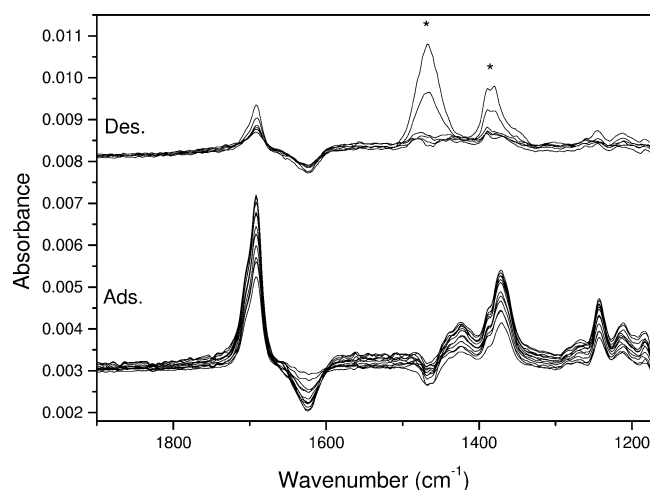


Fig. 2. ATR spectra as a function of time recorded while flowing MP at 10<sup>-3</sup> M in hexane over SiO<sub>2</sub>. Asterisks indicate uncompensated contribution from the solvent.

reported for  $\varepsilon_{1550}$  and  $\varepsilon_{1445}$ , respectively [19]. Using these values a relative concentration  $C_B/C_L$  of 1.3 can be estimated from the spectra. It should, however, be noted that for sulfated silica–zirconia mixed oxides the absorption coefficient  $\varepsilon_{1550}$  of the pyridinium ion was found to decrease significantly at high sulfate density [19].

### 3.3. Interaction of 2-methoxypropene with SiO<sub>2</sub> and Deloxan

The ATR spectra of MP (10<sup>-3</sup> M) on SiO<sub>2</sub> are depicted in Fig. 2. A sharp signal develops at 1692 cm<sup>-1</sup> with a shoulder at ca. 1700 cm<sup>-1</sup>. A number of signals are also found at 1424, 1387, 1371 (s), 1242 (s), and 1211 cm<sup>-1</sup>. The negative band at around 1620 cm<sup>-1</sup> is due to the displacement of water. On desorption these signals are attenuated. No characteristic signals of MP can be detected.

Fig. 3 shows ATR spectra recorded while flowing MP (10<sup>-3</sup> M) over Deloxan. No signals originating from dissolved MP can be detected. A band at ca. 1700 cm<sup>-1</sup> grows in fast accompanied by bands at 1422, 1372, and 1240 cm<sup>-1</sup>.

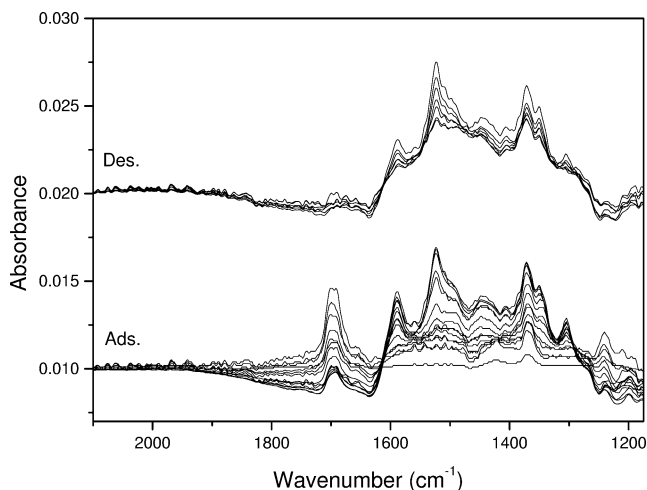


Fig. 3. ATR spectra as a function of time recorded while flowing MP at  $10^{-3}$  M in hexane over Deloxan.

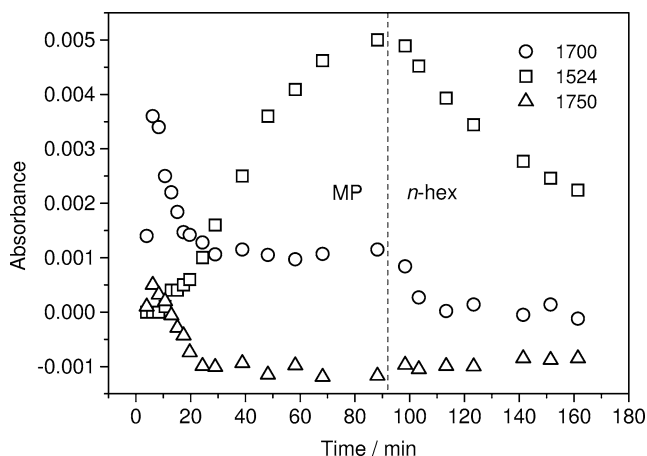


Fig. 4. Time dependence of the signals at 1700, 1524, and 1750  $\text{cm}^{-1}$  for the experiment depicted in Fig. 3.

Other strong signals grow in with time at 1589, 1524, 1447, 1351, and 1304  $\text{cm}^{-1}$ , whereas that at 1700  $\text{cm}^{-1}$  decreases and then levels off. The time behavior of the signals at 1700  $\text{cm}^{-1}$  and of, for example, that at 1524  $\text{cm}^{-1}$  resembles the typical time behavior for a consecutive reaction. In Fig. 4 the absorbance signals at 1700, 1524, and 1750  $\text{cm}^{-1}$  are shown as a function of time. The time behavior indicates that the species associated with the signal at 1700  $\text{cm}^{-1}$  is transformed to the species associated with the signal at 1524  $\text{cm}^{-1}$  or that the latter species displaces the former from the surface. A very broad negative signal centered at around 1700  $\text{cm}^{-1}$  starts to show up when the signals at 1589, 1524, 1447, 1351, and 1304  $\text{cm}^{-1}$  grow. The time behavior of this band is also given in Fig. 4 (absorbance at 1750  $\text{cm}^{-1}$ ). This signal is likely associated with hydronium ions.

The characteristic band at about 1700  $\text{cm}^{-1}$  in Figs. 2 and 3 shows the presence of a carbonyl compound. A possible candidate is acetone. Enol ethers such as MP are readily hydrolyzed by acids [20], resulting in a carbonyl compound

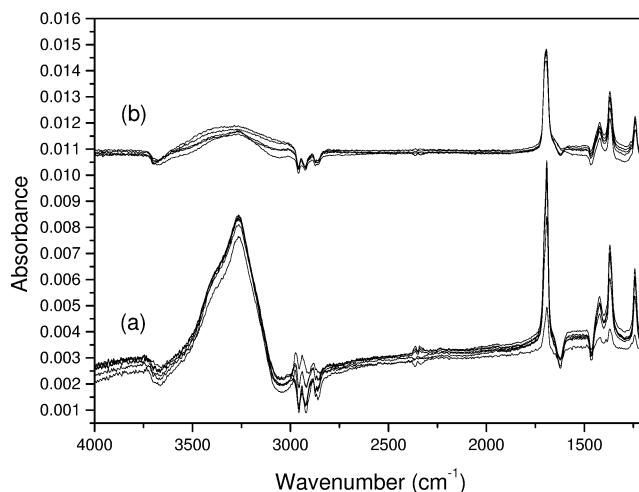


Fig. 5. ATR spectra of acetone adsorption on (a)  $\text{SiO}_2$  and (b) Deloxan from a  $10^{-3}$  M solution in hexane as function of time. The whole spectral range up to 4000  $\text{cm}^{-1}$  is shown, revealing the negative band due to hydrogen bonding to Si–O–H groups. The negative bands slightly below 3000  $\text{cm}^{-1}$  are due to the solvent.

and an alcohol. In the case of MP hydrolysis this results in acetone and methanol. Fig. 5 shows the ATR spectra recorded when contacting a  $10^{-3}$  M solution of acetone on (a)  $\text{SiO}_2$  and (b) Deloxan. On  $\text{SiO}_2$ , signals are observed at 1693, 1423, 1369, and 1242  $\text{cm}^{-1}$  in the spectral region above 1200  $\text{cm}^{-1}$ . The signal at about 1693  $\text{cm}^{-1}$ , representing the stretching vibration of the carbonyl group of acetone, is composed of two overlapping bands. Since dissolved acetone absorbs at 1722  $\text{cm}^{-1}$  in *n*-hexane the signal at 1693  $\text{cm}^{-1}$  is assigned to acetone hydrogen-bonded to the surfaces. This is further corroborated by the negative band above 3600  $\text{cm}^{-1}$  due to hydrogen-bonded Si–O–H groups. It has been reported that acetone shows two signals for the C=O stretching vibration on  $\text{SiO}_2$  [21]. The existence of the two signals has been attributed to the presence of two types of silanol groups, i.e., isolated and grouped. On Deloxan, similar frequencies are found for the characteristic signals of acetone. A slight difference is observed for the shape of the C=O signal: on Deloxan the high- and low-frequency components of the carbonyl stretching band have similar intensity, whereas on  $\text{SiO}_2$  the low-frequency component is stronger. For acetone adsorbed on zeolites it was shown that the carbonyl vibration shifts depending on the adsorption site. A frequency of 1700–1705  $\text{cm}^{-1}$  is expected for acetone bound to SiOH groups, of 1690–1702  $\text{cm}^{-1}$  for acetone on Lewis sites and of 1655–1682  $\text{cm}^{-1}$  for acetone on Brønsted sites [22]. The weak band at around 1650  $\text{cm}^{-1}$  observed for acetone on Deloxan may be attributed to a small fraction of acetone bound to Brønsted sites. The band is partly overlapped by the negative signal due to desorption of water.

Comparison of Figs. 2 and 3 with Fig. 5 confirms that acetone is formed upon contacting MP with  $\text{SiO}_2$  and Deloxan. In Table 2 vibrational frequencies observed when contacting  $\text{SiO}_2$  and Deloxan, respectively, with MP and acetone are

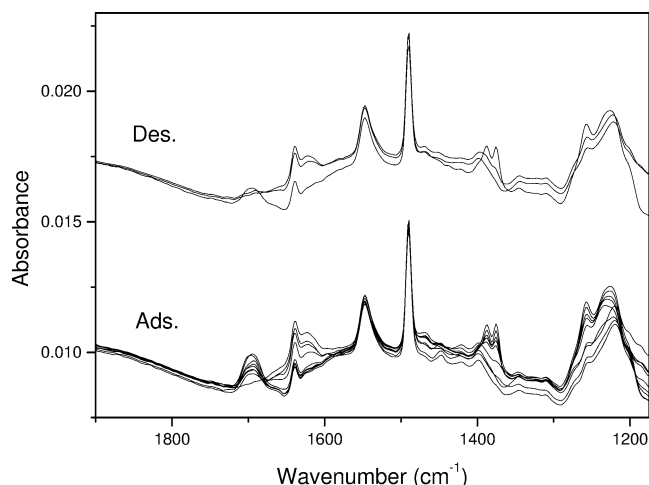


Fig. 6. ATR spectra of MP adsorption on pyridine precovered Deloxan from a  $10^{-3}$  M solution in hexane as function of time. Pyridine adsorption was performed from a  $10^{-2}$  M solution and after desorbing weakly bound pyridine by flowing neat solvent.

compared. Moreover, if acetone is admitted to the  $\text{SiO}_2$  film, on which MP has been previously reacted, similar signals are observed.

On Deloxan acetone formation is possibly acid-catalyzed, whereas the silanol groups may be responsible for the observed reaction on  $\text{SiO}_2$ . Water adsorbed on the surface is affected by the reaction on both materials. The negative bands observed at around  $1650\text{ cm}^{-1}$  in Fig. 3 and at  $1624\text{ cm}^{-1}$  in Fig. 2 show consumption or displacement of water.

The nature of the further reaction of acetone on Deloxan, evident by the weakening of the signal at ca.  $1700\text{ cm}^{-1}$  and the simultaneous increase of the signals at  $1589$ ,  $1524$ ,  $1447$ ,  $1351$ , and  $1304\text{ cm}^{-1}$ , is less clear. Since MP and acetone are present on the surface, a reaction involving these species is likely. Condensation of acetone [23] can be ruled out, since admission of acetone alone does not lead to the bands noted above. Knözinger and co-workers [24] observed signals at  $1585$ ,  $1523$ , and  $1453\text{ cm}^{-1}$  when adsorbing acetone onto a Y/MgO catalyst at  $200^\circ\text{C}$ . These signals grew in at detriment of the signal due to adsorbed acetone (found at  $1711\text{ cm}^{-1}$ ). The authors claimed that this behavior is due to the dimerization of acetone to diacetone-alcohol (DAA) and the following dehydration to mesityloxide (MSO). In order to check whether the signals observed in Fig. 3 ( $1589$ ,  $1524$ ,  $1447$ ,  $1351$ , and  $1304\text{ cm}^{-1}$ ) are associated with MSO and DAA, respectively, the two compounds were also adsorbed on Deloxan. Only hydrogen-bonded species could be observed in the ATR spectra and no signal corresponding to the ones observed when admitting MP could be found.

The sulfonic groups of Deloxan promote the further transformation of acetone and MP. This becomes clear when the sulfonic groups are blocked and MP is subsequently contacted with the modified material. An ideal way of blocking acid sites of a catalyst is pyridine adsorption. Hence, pyridine was first adsorbed on Deloxan from a  $10^{-3}$  M solution in hexane. Signals characteristic of both hydrogen-

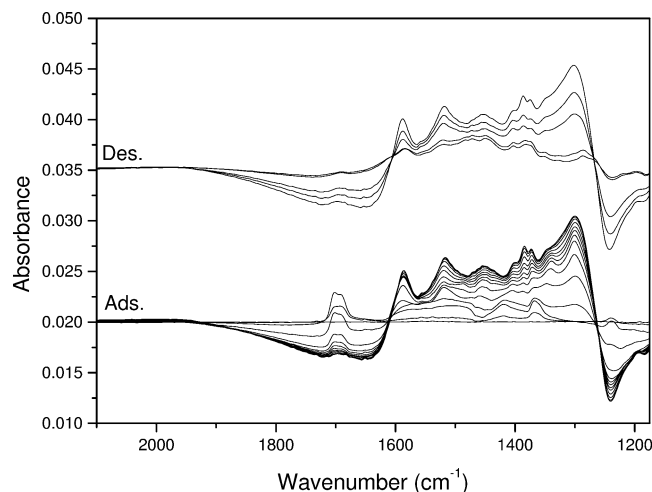


Fig. 7. ATR spectra as a function of time recorded while flowing a  $10^{-3}$  M solution of MP in hexane over sulfated and  $\text{TiO}_2$ -modified  $\text{SiO}_2$ .

bonded pyridine and pyridinium ions were observed. Then hydrogen-bonded species were totally removed with the following solvent flow. At this point MP was admitted to the surface. Fig. 6 shows that the signals associated with acetone appear under these conditions, similarly to MP adsorption on  $\text{SiO}_2$ . The reactions following acetone formation are, however, suppressed when the acid sites are blocked. This shows that the acid sites are responsible for the further transformations observed after acetone formation.

### 3.4. Adsorption of 2,2-dimethoxypropane on $\text{SiO}_2$ and Deloxan

Hydrolysis of MP to acetone leads to the formation of methanol. The latter can further react with MP to DMP. In order to check whether DMP may be produced when contacting Deloxan with MP, DMP was adsorbed on  $\text{SiO}_2$  and Deloxan. The behavior of DMP on the two materials is similar to that described above for MP. In both cases the signal assigned to acetone is observed at around  $1700\text{ cm}^{-1}$  and on Deloxan it disappears again afterward, whereas the signals at  $1589$ ,  $1524$ ,  $1447$ ,  $1351$ , and  $1304\text{ cm}^{-1}$  appear. Acetals easily hydrolyze to the corresponding ketone [25]. However, acetals can also be converted to enol ethers [26]; i.e., DMP could react back to MP. It is important to note that no adsorbed DMP has been detected when contacting MP with Deloxan. Similarly no adsorbed DMP was observed when admitting dissolved DMP.

### 3.5. Interaction of 2-methoxypropane with sulfated and $\text{TiO}_2$ -modified $\text{SiO}_2$

The reaction of MP was also tested on another sulfated catalyst: sulfated and  $\text{TiO}_2$ -modified amorphous  $\text{SiO}_2$ .

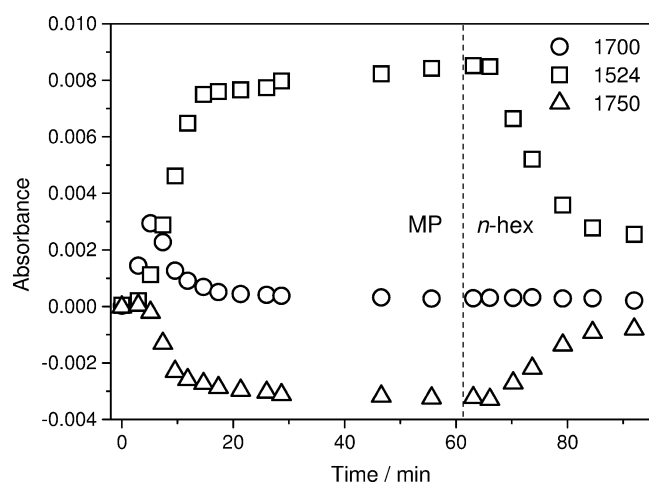
Fig. 7 shows the ATR spectra recorded while contacting this material with MP. Fig. 8 shows the corresponding time behavior of the absorbance at  $1700$ ,  $1524$ , and  $1750\text{ cm}^{-1}$ .

Table 2

Observed bands and proposed assignment for acetone and 2-methoxypropene on SiO<sub>2</sub> and Deloxan

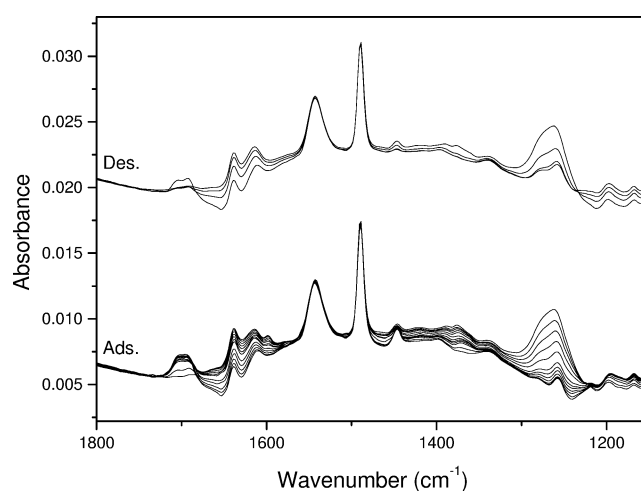
Acetone			2-Methoxypropene			Assignment
Dissolved <sup>a</sup>	SiO <sub>2</sub>	Deloxan	Dissolved <sup>a</sup>	SiO <sub>2</sub>	Deloxan	
1722 + sh.↑	1691 + sh.↑	1693 + sh.↑		1692 + sh.↑	1699 + sh.↓	$\nu(\text{C}=\text{O})$
			1660			$\nu(\text{C}=\text{C})^{\text{b}}$
			1598			Overtone $\omega(\text{CH}_2)^{\text{b}}$
					1589	$\nu(\text{C}=\text{O})^{\text{c}}$
					1524	$\nu(\text{C}=\text{C})^{\text{c}}$
			1451			$\delta_{\text{AS}}(\text{CCH}_3)^{\text{b}}$
					1447	$\nu(\text{C}-\text{O})^{\text{c}}$
1420	1423	1422		1424	1422	$\delta(\text{CH})$
1364	1369	1371		1371	1372	$\delta(\text{CH})$
			1370			$\delta_{\text{S}}(\text{CCH}_3)^{\text{c}}$
					1351	OCH <sub>3</sub>
					1304	OCH <sub>3</sub>
			1285			$\nu(\text{C}-\text{O})^{\text{b}}$
1222	1242	1240		1242	1240	$\nu(\text{C}-\text{C})$

↑ and ↓ refer to high- and low-energy shoulder, respectively.

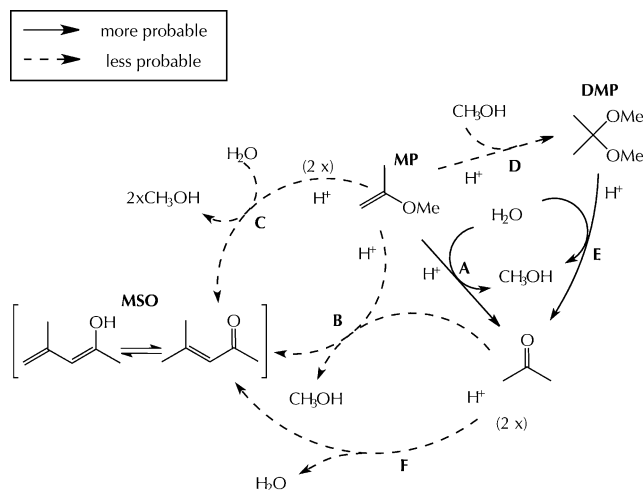
<sup>a</sup> In *n*-hexane.<sup>b</sup> For the assignment of MP vibration refer to [28].<sup>c</sup> For these assignments refer to [24].Fig. 8. Time dependence of the signals at 1700, 1524, and 1750 cm<sup>-1</sup> for the experiment depicted in Fig. 7.

As observed in the case of Deloxan, acetone is formed in the early stages of MP adsorption. Further contact leads to the same bands in the 1400–1600 cm<sup>-1</sup> spectral range that have been described for MP on Deloxan. The time behavior of the signals at 1700 and 1524 cm<sup>-1</sup> again show the behavior of a consecutive reaction.

The acid sites of Deloxan are responsible for reactions following hydrolysis of MP to acetone. This has been verified through blocking of these sites by pyridine adsorption. The same strategy was applied to sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub>. Fig. 9 depicts the ATR spectra of pyridine adsorbed on the sulfated and TiO<sub>2</sub>-modified silica from a 10<sup>-3</sup> M solution in hexane. Signals at 1596, 1578, and 1445 cm<sup>-1</sup> and at 1638, 1544, and 1488 cm<sup>-1</sup> indicate formation of HPy and BPy species, respectively. A negative signal at 3701 cm<sup>-1</sup> suggests that pyridine partly adsorbs on

Fig. 9. ATR spectra of MP adsorption on pyridine pre-covered sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub> from a 10<sup>-3</sup> M solution in hexane as function of time. Pyridine adsorption was performed from a 10<sup>-2</sup> M solution and after desorbing weakly bound pyridine by flowing neat solvent.

silanol groups, as expected. From the relative intensities of the bands of adsorbed pyridine and pyridinium ion at 1445 and 1550 cm<sup>-1</sup> a relative concentration C<sub>B</sub>/C<sub>L</sub> of 8.6 can be estimated. The amount of Brønsted relative to Lewis sites is much higher on the sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub> than on Deloxan. When flowing hexane the HPy species desorb from the sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub>, although very slowly compared to desorption from Deloxan. Acetone is the only product detected when MP is admitted to the thin film, as the doublet at 1702–1692 cm<sup>-1</sup> suggests. This confirms that also on sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub>, Brønsted acid groups are responsible for the reaction of MP.



Scheme 2. Observed products and reaction pathways of 2-methoxypropene (MP).

## 4. Discussion

### 4.1. Identified surface species and reactions

Scheme 2 summarizes the reactions found by ATR spectroscopy. Acetone formation (step A in Scheme 2) is observed when contacting Deloxan and SiO<sub>2</sub>, respectively, with MP (Figs. 1 and 2). Acetone can be formed by hydrolysis of MP, which is corroborated by the negative water bands. The fact that acetone formation is observed on SiO<sub>2</sub> as well as on Deloxan shows that Brønsted acid groups are not a prerequisite for hydrolysis, although hydrolysis of vinyl ethers in the homogeneous phase is found to be acid catalyzed involving a proton transfer as the rate-determining step [9].

The hydrolysis is fast, since adsorbed MP could be found neither on SiO<sub>2</sub> nor on Deloxan. Also the signal of the acetone detected at the interface increases fast after admitting MP, as is seen in Fig. 4. The formed acetone adsorbs on SiOH groups. On Deloxan part of the acetone may furthermore interact with the Brønsted acid groups as the weak band at about 1650 cm<sup>-1</sup> indicates (Fig. 3). On Deloxan a further transformation is observed leading to a species with characteristic bands at 1589, 1524, 1447, 1351, and 1304 cm<sup>-1</sup>. Pyridine adsorption clearly shows that this further transformation requires Brønsted acid sites.

Acetone formation by hydrolysis of MP results in methanol. Likely the further transformation observed in the ATR experiments when admitting MP to Deloxan involves MP, acetone, or methanol. Acetone dimerization (step F in Scheme 2) can be excluded since admittance of acetone alone does not result in the signals observed when admitting MP to Deloxan. The time behavior of acetone at the interface and of the species associated with the signals at 1589, 1524, 1447, 1351, and 1304 cm<sup>-1</sup> strongly indicates that the transformation yielding the new species is not just a dimerization of MP. If this were the case one would expect a fast increase of the signals associated with the reaction prod-

uct from the very beginning of MP admittance. In contrast the signals (e.g., at 1524 cm<sup>-1</sup>) of the newly formed product grow in retarded with respect to MP admittance and acetone formation, as is clearly seen both on Deloxan and on sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub> (Figs. 4 and 8). In fact the time dependence of the signals strongly indicates that acetone is also involved in this transformation. Based on these considerations the most likely transformation in this respect is therefore an acid-catalyzed condensation of acetone and MP, which would yield MSO (step B in Scheme 2). On the other hand admittance of MSO (and DAA) to Deloxan did not yield the signals at 1589, 1524, 1447, 1351, and 1304 cm<sup>-1</sup>, which shows that the species giving rise to the signals at 1589 and 1524 cm<sup>-1</sup> does not correspond to molecular MSO (nor DAA). However, it could be attributed to the enol form of MSO (or DAA). The newly formed species is only slowly desorbing from the interface when flowing neat solvent.

The ATR spectra recorded while admitting MP reveal the behavior of another species at the interface: The negative broad band at around 1700 and 1240 cm<sup>-1</sup> can be assigned to hydronium ions removed from the interface [16,17]. When admitting MP to Deloxan or sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub>, acetone appears before the hydronium ions disappear from the interface, as is seen in Figs. 4 and 8. In the case of sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub>, the disappearance of hydronium ions sets in at the same time as the newly formed species appears. This furthermore indicates that acetone formation is not associated with the acid sites whereas the second transformation is. One possible explanation for the observed behavior is that the acid sites do not only catalyze the second transformation but also serve as adsorption sites for the product. Interestingly, when desorbing the reaction product of the second transformation, the hydronium ion concentration at the interface is largely restored on sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub>, whereas it is only to a minor extent on Deloxan, as can be seen from Figs. 3, 4, 7, and 8.

Methanol can react with MP to form DMP (step D in Scheme 2). We do not have direct evidence for the formation of DMP from the spectra. If DMP is formed, it is either fast hydrolyzed to acetone (step E in Scheme 2) or reacts back to MP and methanol (reverse step D in Scheme 2) or both. This becomes clear from the experiments where DMP was admitted to SiO<sub>2</sub> or Deloxan. In these experiments acetone is formed. On Deloxan the acetone vanishes again and the same bands appear as are observed when admitting MP on Deloxan. Hence, admission of MP and DMP leads to the same observations in the ATR experiment. The proposal made above based on the time behavior of the ATR signals that the second observed transformation is a condensation of acetone and MP would indicate that DMP also reacts back to MP and methanol. It is worth noting that GC analysis of catalytic experiments in a continuous fixed-bed reactor under similar conditions as used in the ATR studies revealed the formation of acetone, methanol, and DMP upon contacting Deloxan with MP, thus supporting Scheme 2.

The transformations observed with Deloxan are not restricted to this particular material, since they were also observed on sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub>. Note that one difference between the two materials is the nature of the Brønsted sites. On Deloxan the Brønsted sites are sulfonic acid groups covalently attached to SiO<sub>2</sub> (Scheme 1) whereas on sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub> the Brønsted sites are sulfuric acid groups adsorbed on TiO<sub>2</sub>-modified SiO<sub>2</sub>. The two materials have a rather different relative concentration of Lewis and Brønsted acid sites as pyridine adsorption shows. Also the very different kinetics of pyridine desorption from Lewis sites (O–H groups) indicates different Lewis acid strengths on the two materials. Note that the observed reactions of MP, acetone formation, and the transformation resulting in the signals at 1589, 1524, 1447, 1351, and 1304 cm<sup>-1</sup>, are observed on both materials, although the Brønsted to Lewis acid site ratio and the nature of the Brønsted site is different. However, the time behavior of the acetone signal and the signal associated with the newly formed species (Figs. 4 and 8) is distinctly different on the two materials. First of all the relative ratio between the maximum acetone signal at 1700 cm<sup>-1</sup> and the signal of the second species at 1524 cm<sup>-1</sup> is larger on Deloxan than on sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub> (compare Figs. 4 and 8). This is consistent with the observation that on Deloxan the C<sub>B</sub>/C<sub>L</sub> ratio (ratio of Brønsted to Lewis sites) is smaller and acetone adsorbs primarily on Lewis sites. Also on sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub> the second transformation is faster than on Deloxan as can be seen from the faster decrease of the acetone signal and the faster increase of the signals corresponding to the product of the second transformation. On Deloxan the latter signals do not reach a stable value before 100 min, whereas on sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub> the signal levels off after 15 min. On the other hand, the steady-state signal of acetone is almost negligible on sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub>, whereas it is significant on Deloxan (compare Figs. 4 and 8). A feasible explanation for these observations is the vastly different C<sub>B</sub>/C<sub>L</sub> ratio (ratio of Brønsted to Lewis sites) on the two materials. Whereas the Lewis sites may be responsible for acetone formation the Brønsted sites promote the subsequent transformation. Due to the smaller C<sub>B</sub>/C<sub>L</sub> ratio on Deloxan the intermediate acetone is found at higher concentrations than on sulfated and TiO<sub>2</sub>-modified SiO<sub>2</sub>.

From the present study a difference between homogeneous and heterogeneous catalysis involving MP emerges. In the latter case self-reactions of MP on the surface represent a difficulty (e.g., in Saucy-Marbet type condensations) not encountered in corresponding homogeneous catalysis. It seems that the presence of Si–OH groups and possibly water on the heterogeneous catalyst and the relatively high surface concentration of MP are promoting fast MP hydrolysis. Such high local concentrations of MP do not occur in a well-mixed homogeneous reaction system and consequently this unwanted hydrolysis step is suppressed. Furthermore, slow dissipation of reaction heat in the heterogeneous case may

lead to local overheating at the active site and thus further promote side reactions.

## 5. Conclusions

When the simple vinyl ether 2-methoxypropene is admitted to heterogeneous acid catalysts, complex transformations are observed at the catalytic solid–liquid interface by attenuated total reflection infrared spectroscopy. MP hydrolyzes fast to acetone. The latter is observed at the interface immediately after admitting MP. The reaction is so fast that MP itself is not observed. This hydrolysis does not require Brønsted acid sites and occurs even on pure silica, although vinyl ether hydrolysis is well known to be acid catalyzed in the homogeneous phase. However, further transformation requires Brønsted sites. The time dependence of the signals of the intermediate acetone and the ones of the product of this transformation indicates that acetone reacts with MP. The product of this reaction, possibly the enol form of mesityloxide, adsorbs on the catalyst surface. The relative abundance of Brønsted and Lewis sites determines the concentration of the intermediate acetone on the surface, since its formation is likely due to the Lewis sites whereas its further transformation is due to Brønsted sites on the catalyst. 2,2-Dimethoxypropane shows the same behavior on the catalysts as MP, acetone formation, and its further transformation, indicating that DMP and MP are easily transformed one into the other on the acid catalysts. ATR infrared spectroscopy turns out to be a viable tool for investigating the transformations at the solid–liquid interface of acid catalysts.

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