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Surface Chemistry of Benzoyl Compounds on Oxides, an FT-IR Study

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Adsorption and surface reactions on various oxides have been monitored by IR spectroscopy, with benzaldehyde, benzoic acid, methylphenylketone, and 2-phenyl-2-propanol. The oxides were chosen to represent typical adsorption properties (SiO_2, γ-Al_2O_3, and α-Mn_3O_4). Surface reactions were observed at various temperatures, starting from room temperature. The results concern three points: (i) identification of adsorbed species, arising on different oxides under increasing temperatures; (ii) the possible sequence of reaction steps in the insertion (oxidation) or removal (reduction) of oxygen, into or from the molecules studied; and (iii) the conclusion that a Cannizzaro reaction is not likely so that the insertion (and removal) is most probably by the Mars and van Krevelen mechanism.

INTRODUCTION

It is attractive to prepare aldehydes from their corresponding carboxylic acids. The standard method used nowadays is the so-called Rosenmund reduction, first converting a carboxylic acid into an acyl chloride; in the second step this chloride is converted into the aldehyde. However, the unavoidable production of diluted HCl and the handling of corrosive gases are drawbacks of this technology. A desirable alternative would be a one-step gas-phase reduction. Some oxides are known to be good catalysts for this reduction (*1*). Surprisingly the fundamental knowledge of the underlaying mechanism is still fragmentary; it is the aim of this paper to contribute to this knowledge by a study of the mechanism of adsorption of benzaldehyde, benzoic acid, methylphenylketone and 2-phenyl-2-propanol on three oxides: SiO_2, γ-Al_2O_3, and α-Mn_3O_4. These oxides differ in their binding properties: SiO_2 exposes weakly acidic OH-groups to the gas phase, γ-Al_2O_3 exposes, besides the OH-groups, also O-atoms and Al-cations, and α-Mn_3O_4 offers next to the OH-groups, the O-atoms and Mn-cations. There is also a possibility to release an oxygen from its lattice or to abstract and accept "O" from the adsorbing molecules. An observation of the surface at different temperatures should reveal how and when the various just mentioned mechanisms set in.

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EXPERIMENTAL

Sample Preparation and Chemicals Used

α-Mn_3O_4 was prepared by thermal decomposition of manganese(II) hydroxide in air at 390 K. The hydroxide was precipitated from a heated (around 360 K) aqueous solution of manganese(II)nitrate ($Mn(NO_3)_2 \cdot 4H_2O$, Fluka/Switzerland) with ammonia (approximately 7 *M*) of the same temperature, at pH = 9. The total amount of ammonia was quickly poured into the glass. This was essential in order to obtain finally an infrared-transparent α-Mn_3O_4 sample. The white suspension obtained was boiled for 30 min while stirring. The pH was kept at 9 by adding ammonia (NH_4OH). Cooling to ambient temperature, filtration, and washing with successively demi-water, ethanol, and ether were the last steps before the ther-

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mal decomposition. The IR spectra and the XRD pattern of the sample obtained by the above described method are consistent with the literature data (*2*, *3*). The total surface area of such a sample is typically in the range 20–30 $m^2 g^{-1}$.

The silica and alumina used in this study were Aerosil 200 and γ-Al_2O_3, both commercially available from Degussa/Germany. The specified surface area of SiO_2 and γ-Al_2O_3 is 200 and 100 $m^2 g^{-1}$, respectively.

The benzoyl compounds used, benzaldehyde (over 99% pure) and methylphenylketone (over 98% pure), were obtained from Merck-Schuchardt Germany. In order to check the possible presence of the supposed adsorption complexes, benzene (over 99.7% pure, Merck Germany) and 2-phenyl-2-propanol (97% pure, Aldrich-Chemie Germany) were used. All those compounds were admitted as gases and were degassed prior to use. Benzoic acid (Merck, over 99.9% pure) was, because of the very low vapor pressure at 298 K, brought onto the catalyst in an aqueous solution and the water was removed thereafter by slow evaporation under pumping.

IR Spectroscopy

The transmission IR experiments were carried out using thin self-supporting pellets of about 50 mg of the sample material. These pellets were pressed at pressures of 10 MPa and subsequently placed in an all-metal transmission cell mounted with CaF_2-windows (see Fig. 1). These windows were transparent in the infrared region down to 1000 cm^{-1}. The cell was connected with a conventional gas manipulation/evacuation system (during evacuation of a sample generally a pressure in the range 10^{-3}–10^{-5} Pa is achieved). The experiments were carried out in a vacuum system, which is schematically presented in Fig. 2. The pellet could be heated to 675 K and cooled to 77 K (by filling the metal Dewar with liquid nitrogen) while being kept in the beam. The oxidation, reduction, and adsorption procedures were also performed *in situ*. Before adsorption of a compound, an infrared spectrum of the oxide was recorded at the temperature of adsorption and one at each of the temperatures at which the other spectra (after adsorption of the adsorbate) were taken. These background spectra, taken in the absorbance mode, were automatically subtracted from the absorbance spectrum obtained after adsorption and heating to the corresponding temperature. The FT-IR spectra were recorded with an evacuable spectrophotometer, Bruker IFS-113v, equipped with a liquid-nitrogen-cooled MCT (mercury cadmium telluride) detector. The data obtained using this spectrophotometer were handled by an Aspect 2000 computer, using the commercial software.

RESULTS AND BAND ASSIGNMENT

Adsorption of Benzaldehyde and Benzoic Acid

Preliminary adsorption experiments showed that after admittance of benzene into the infrared cell at room temperature and subsequent evacuation, no (infrared-active) species remained on the surfaces of the three oxides studied. Therefore, any strong adsorption of an active compound containing a phenyl group is likely caused by the presence of the substituents.

Figure 3 presents the IR spectra in the 2000–1000 cm^{-1} range, obtained upon adsorption of benzaldehyde at 300 K on SiO_2, γ-Al_2O_3, and α-Mn_3O_4. The wavenumbers and corresponding assignments of the main IR absorption bands are given in Table 1. Figure 3 shows also the spectrum of gas-phase benzaldehyde. A comparison of the gas-phase spectrum with the liquid-phase spectrum (*4*) shows clearly a shift of the carbonyl stretching frequency (1709 cm^{-1}) to higher wavenumbers for the gas-phase spectrum (1727 cm^{-1}). This shift is explained by mutually interacting dipoles of molecules in the liquid phase.

Adsorptoin of benzaldehyde on SiO_2 causes a downward shift of ν(C=O) of 15 cm^{-1} with respect to liquid benzaldehyde, although the adsorption is purely physical

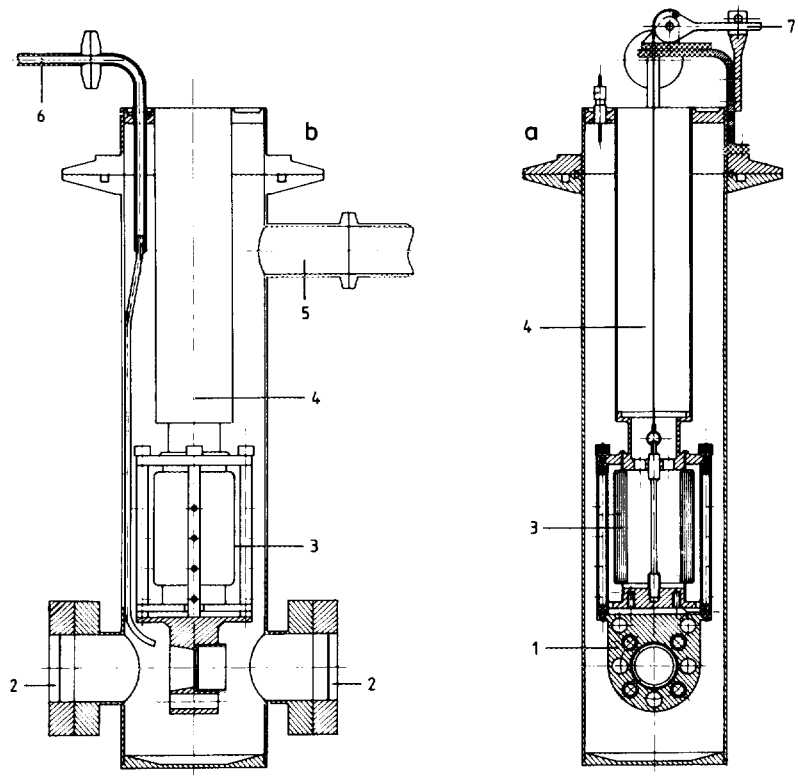

FIG. 1. Front (a) and side (b) view of the infrared transmission cell: (1) copper sample holder, (2) transmission windows (CaF_2), (3) stainless steel bellows, (4) metal Dewar vessel, (5) vacuum system connection, (6) inlet for purge gases, and (7) lever controlling the stainless steel bellows.

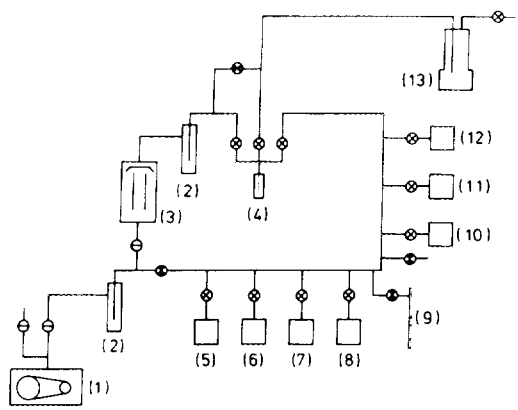

FIG. 2. Schematic representation of the vacuum system for infrared transmission experiments: (1) oil rotary pump, (2) cold trap, (3) oil diffusion pump, (4) Pirani manometer, (5–8) stock vessels for various gases, (9) Hg manometer, (10–12) stock vessels for various gases, and (13) infrared transmission cell.

and reversible upon evacuation. This shift in the carbonyl vibrational frequency is most likely due to the interaction of the oxygen atom of the carbonyl group with the silica surface. This interaction is probably via the hydrogen atom of a surface silanol group. Support for this interaction is supplied by the theoretical work performed by Catalán and Yáñez (5). These authors showed the existence of two electrostatic potential minima located around the oxygen atom of benzaldehyde, corresponding to the two electron lone pairs of this atom. These minima should be the preferred locations for the interaction with protons. Furthermore, the intensity of the ν(C=O) absorption, when compared with the other bands, is remarkably smaller than that observed in the liquid phase. This might imply a decrease of the molar extinction coefficient of the carbonyl

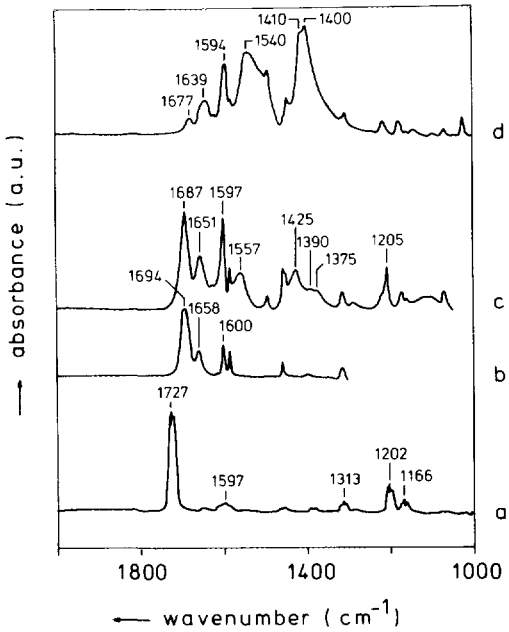

FIG. 3. FT-IR spectra of benzaldehyde in the gas phase (a) and adsorbed on SiO_2 (b), γ-Al_2O_3 (c), and α-Mn_3O_4 (after pumping) (d) at 300 K.

group upon adsorption, which would be another support for the idea of an interaction through the carbonyl group.

The IR spectra of benzaldehyde adsorbed at 300 K on γ-Al_2O_3 and α-Mn_3O_4 consist of a set of absorption bands assignable to ΦCHO species and of a number of bands which have to be assigned to benzoate surface species (*6–8*) (see Table 1). The IR absorption bands around 2825, 2730, 1687, 1651, and 1390 cm^{-1} for γ-Al_2O_3 and around 2815, 2730, 1682, 1650, and 1397 cm^{-1} for α-Mn_3O_4 strongly decrease upon evacuation and can thus be ascribed to weakly, molecularly adsorbed ΦCHO. The position of the ν(C=O) band of the molecularly adsorbed benzaldehyde on both oxides (a shift with respect to the liquid phase is observed of 22 and 27 cm^{-1}, respectively) makes it likely that benzaldehyde is coordinated to the metal ions exposed on the surface. In complexes of benzaldehyde, in which the aldehyde as a ligand is bound to a metal ion through its oxygen atom, the carbonyl stretching vibration is shifted by 50 to 80 cm^{-1} to lower frequencies compared with liquid benzaldehyde (*9*). Although the shifts observed in the experiments presented here are smaller than those observed in complexes of benzaldehyde, an interaction with the metal ion seems to be more reasonable than an interaction with surface hydroxyl groups only. α-Mn_3O_4 has hydroxyl groups which are less acidic than the silanol groups mentioned above. This should result in a smaller ν(C=O) shift than the one found with SiO_2 and not in a larger shift, as observed. The smaller ν(C=O) shift of adsorbed benzaldehyde with respect to benzaldehyde bound as a ligand in a coordination compound, might be explained by shielding of the (coordinatively unsaturated) cations exposed on an oxide surface, by the oxygen atoms in the neighbourhood.

After desorption upon evacuation (at 300 K) of benzaldehyde adsorbed on γ-Al_2O_3, bands around 2930 (w) and 2850 cm^{-1} (m), which are characteristic of C–H stretching vibrations, remain. Also the bands related to the ν(C–H) vibration of the aromatic ring are still observable. These bands and the observed band characteristic of the carbonyl group suggest that the desorption is not complete at 300 K and some benzaldehyde is still present at the surface.

TABLE 1

FT-IR Spectra of Benzaldehyde Adsorbed on Oxides at 300 K

IR bands (cm^{-1}) of ΦCHO adsorbed on			Assignment		
			Vibration	Surface species	Ref.
SiO_2	γ-Al_2O_3	α-Mn_3O_4			
1694	1687	1677	ν(C=O)	Benzaldehyde	(*4*)
1658			2γ(C–H)	Benzaldehyde	(*4*)
	1651	1639		Asymm. covalent benzoate	(*8*)
1600	1597	1594		Benzald. + benzoate	(*7*, *4*)
	1557	1540	ν(C–C)	Benzoate	(*7*)
	1425	1410	$\nu_a(CO_2)$	Benzoate	(*7*)
	1375		$\nu_s(CO_2)$	Benzylalcoholate	(*7*)
	1205			Benzylalcoholate	

Note. For γ-Al_2O_3 and α-Mn_3O_4 the values are given for the spectra after pumping. ν = stretching vibration, γ = bending vibration, a = asymmetric, and s = symmetric.

In the case of α-Mn_3O_4, low transmission of IR radiation above 2500 cm^{-1} (due to strong scattering) makes the identification of bands between 3200 and 2800 cm^{-1} difficult.

At this point we discuss the observed conversion of benzaldehyde to benzoate surface species in more detail. Benzoate species can arise by (i) extraction of lattice oxygen (Mars and van Krevelen mechanism) or by (ii) Cannizzaro-type reaction upon which one of two aldehyde molecules is oxidized by the surface OH group and the other is converted (by hydrogen atoms from the first molecule) into alcoholate.

We turn to the Cannizzaro mechanism (ii) later, so let us start here with the Mars and van Krevelen mechanism. Obviously, adsorption of the aldehyde should be dissociative:

$$\Phi CHO \rightarrow \Phi CO_{ads} + H_{ads}.$$

The species ΦCO_{ads} is subsequently transformed to a benzoate by using oxygen of the lattice. Such an abstraction of H and formation of a benzoate was described by Vohs and Barteau (*10*), in their study on the adsorption of benzaldehyde on the (0001)-Zn(polar) surface of ZnO. Vohs and Barteau report that on the (0001)-O surface of ZnO, on which Zn ions are shielded off by oxygen ions in the top-layer, benzaldehyde is coordinated to the surface through the aromatic ring. This indicates that the presence of metal ions at the oxide surface is essential for the dissociative adsorption of benzaldehyde to occur. This adsorption is than followed by surface benzoate formation.

Sachtler *et al.* (*8*) suggested that the conversion of benzaldehyde into a symmetric benzoate surface species on silica supported SnO_2/V_2O_5 is preceded by a stage in which an asymmetric and covalent benzoate structure is formed (Fig. 4). These authors assigned the IR band at 1632 cm^{-1} found with their catalysts, to this covalent structure. The presence (after evacuation) of a band around 1651 cm^{-1} with γ-Al_2O_3 and one around 1639 cm^{-1} with α-Mn_3O_4 makes it very likely that the same intermediate exists

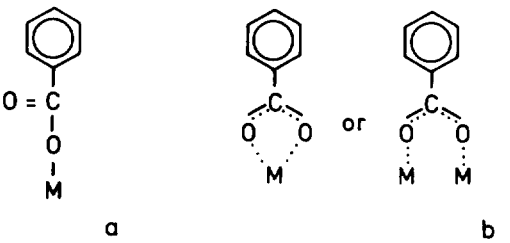

FIG. 4. Schematic representation of the asymmetric (a) and the symmetric (b) benzoate complex.

on all oxides just mentioned. In the subsequent step of the conversion a symmetric benzoate ion should be formed (Fig. 4b). According to the assignments by van Hengstum *et al.* (*6*), the positions of $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ absorption bands of the symmetric benzoate structure on γ-Al_2O_3 (1557 and 1425 cm^{-1}, respectively) and on α-Mn_3O_4 (1540 and 1410 cm^{-1}, respectively) indicate that the benzoate structure is "bridging." In a so-called bridging structure, the carboxylate ion is coordinated to two metal ions. Formation of bridging carboxylate structures upon aldehyde adsorption on oxide surfaces have been suggested also by Vohs and Barteau (*11*).

In Fig. 5 the influence of the temperature (in the range 300–675 K) is shown with the spectrum of benzaldehyde adsorbed on α-Mn_3O_4. All bands that remain at 475 K can be ascribed to the surface benzoate vibrations, while after heating to 575 K and subsequently to 675 K additional formation of surface carbonate species is observed. This can be concluded from the appearance of the bands around 1454, 1360, and 1240 cm^{-1}. At this moment it is not clear whether the carbonate species are formed upon destructive oxidation of the phenyl ring or by abstraction of the carbonyl group from benzaldehyde. Both oxidations are reported in the literature. The adsorption of benzaldehyde on Y_2O_3 (*12*) and ZnO (*10*) is known to lead to decarboxylation, resulting in the formation of benzene. However, the adsorption of benzaldehyde on oxygen-rich transition metal oxides, such as V_2O_5 (*13*)

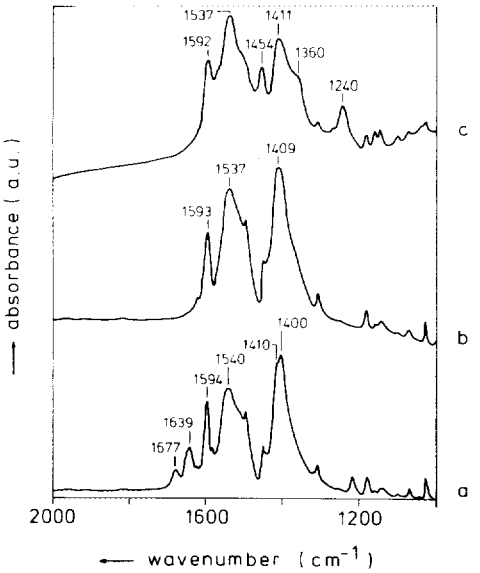

FIG. 5. FT-IR spectra of benzaldehyde adsorbed on α-Mn_3O_4 at 300 K (a) and after heating to 475 K (b) and 675 K (c).

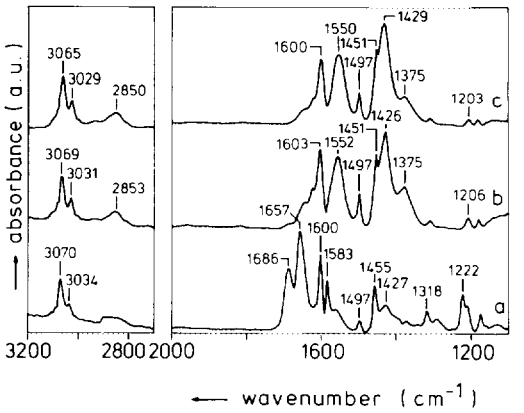

FIG. 6. FT-IR spectra of benzaldehyde adsorbed on γ-Al_2O_3 at 300 K (a) and after heating to 375 K (b) and 675 K (c).

and MnO_2 (*10*), is known to lead to a complete oxidation of the phenyl ring.

Admission of H_2 into the cell at 575 K causes a slow intensity decrease of the benzoate absorption bands. Although the products emerging in the gas-phase during this experiment were not identified, a similar experiment with surface benzoate on a Y_2O_3 catalyst revealed benzaldehyde to be the main desorbing product. King and Strojny (*12*) suggested that interaction of hydrogen with the surface benzoate is necessary to disconnect the benzoate–oxide bond, thereby forming the gaseous benzaldehyde. The hydrogen transfer from the gas-phase molecules to the final product can occur through the surface hydroxyl groups.

In contrast to α-Mn_3O_4, increasing the temperature in the system ΦCHO_{ads} + γ-Al_2O_3 to 575 K did not affect the spectrum obtained after evacuation at 300 K (Fig. 6). This indicates that the benzoate species is more stable on this surface than on the α-Mn_3O_4 surface. The IR absorption bands observed with this system at 2938, 2850, 1375, 1203, and 1105 cm^{-1} disappeared upon oxidation with molecular oxygen at 575 K. The spectrum that remained after prolonged oxidation at this temperature is ascribable to benzoate surface species (main bands: 3065, 1600, 1550, 1497, 1429, and 1180 cm^{-1}). The bands which disappear upon oxidation have been shown by Kuiper *et al.* (*7*) to belong to the surface benzylalcoholate. The authors (*7*) explain the formation of this species by the so-called Cannizzaro reaction and state that upon oxidation these species are converted into surface benzoate species. Since benzylalcoholate can also arise from hydrogenation of benzaldehyde, the presence or absence of a Cannizzaro reaction requires a check.

Adsorption of benzoic acid on γ-Al_2O_3 and α-Mn_3O_4 produces the IR-spectra as presented in Fig. 7. The wavenumbers differ only slightly from those seen with benzaldehyde adsorption and, as can be seen from Fig. 7b, the main spectral features resemble those of the sodium salt very much. However, they differ totally from those of the acid itself (Fig. 7a). For a more detailed analysis of the IR spectra of the benzoic (and salicylic acid), see Ref. (*14*).

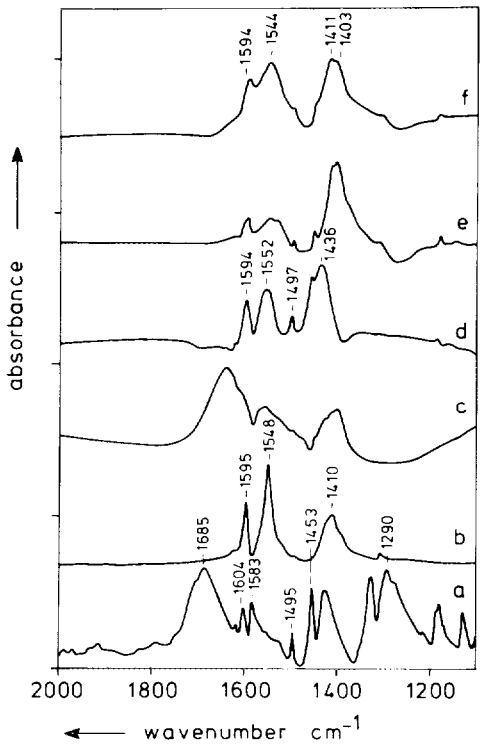

FIG. 7. FT-IR spectra of benzoic acid adsorbed on γ-Al_2O_3 at room temperature (c) and at 575 K (d) and adsorbed on α-Mn_3O_4 at room temperature (e) and at 575 K (f). For reference purposes, the spectra of benzoic acid (a) and sodium benzoate (b) are included.

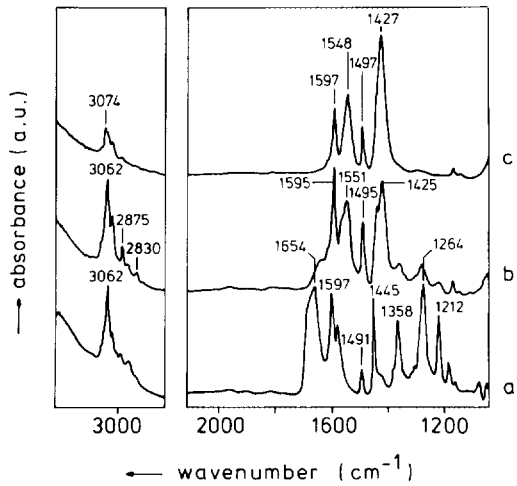

FIG. 8. FT-IR spectra of methylphenylketone adsorbed on γ-Al_2O_3 at 300 K (a) and after heating to 475 K (b) and 575 K (c).

Admittance of molecular H_2 at 575 K to the benzoate bound to γ-Al_2O_3 did not cause any change in the IR spectrum.

Adsorption of Methylphenylketone and 2-Phenyl-2-propanol

In order to gain more information about the mechanism of adsorption and surface reactions of the studied molecules, adsorption of some related molecules has been performed too.

Figure 8 presents the changes with temperature (in the range 300–575 K) of the spectrum obtained upon the adsorption of methylphenylketone on γ-Al_2O_3. The spectrum obtained at 300 K is almost identical with the IR spectrum of liquid methylphenylketone known from the literature (*4*), only the ν(C=O) band is shifted from 1689 cm^{-1} (for the liquid) to 1654 cm^{-1} (adsorbed phase). An additional experiment with gaseous methylphenylketone shows this last band to appear at 1727 cm^{-1}. The frequency shift observed when going from gaseous to liquid methylphenylketone has to be explained by the effect of mutually strongly interacting dipoles of molecules in the liquid phase. The additional frequency shift when going from the liquid to the adsorbed methylphenylketone can be explained by a relatively strong interaction of the adsorbed molecules with the oxide surface. Again, the adsorption site is most likely an exposed metal ion. Heating to 475 K produces a spectrum which consists of the methylphenylketone absorption bands and the bands assignable to benzoate species ($\nu_{as}(CO_2)$ = 1551 cm^{-1} and $\nu_s(CO_2)$ = 1425 cm^{-1}) and bands around 2875 and 2830 cm^{-1}, of which the most likely assignment is to the C–H stretching vibrations of surface methoxy groups (*15*) (the ν(C–O) band of the methoxy is not observable, because γ-Al_2O_3 is not transparent in the range (1100–1000 cm^{-1}) where it should be observed). This

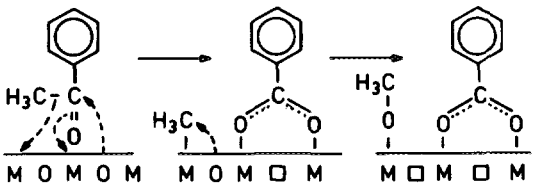

FIG. 9. Schematic representation of a possible reaction of methylphenylketone on oxides.

indicates that the bond between the methyl and carbonyl group is broken by the oxidising surface (Fig. 9).

The behaviour of methylphenylketone on α-Mn_3O_4 in the temperature range 300–575 K is similar to that on γ-Al_2O_3. The differences between γ-Al_2O_3 and α-Mn_3O_4 are that on α-Mn_3O_4 the adsorbed methylphenylketone starts to dissociate already at 300 K and that the bands ascribed to methoxy species (2855 (broad) and 1055 cm^{-1}) disappear already at 475 K. If methylphenylketone underwent a Cannizzaro-type reaction, products as surface benzoate and adsorbed 2-phenyl-2-propanol could have been expected. The potential presence of an adsorbed alcohol could be tested by monitoring the IR spectra of the adsorbed 2-phenyl-2-propanol.

Adsorption of 2-phenyl-2-propanol has been monitored by IR spectroscopy with γ-Al_2O_3 as adsorbent (Fig. 10). The most

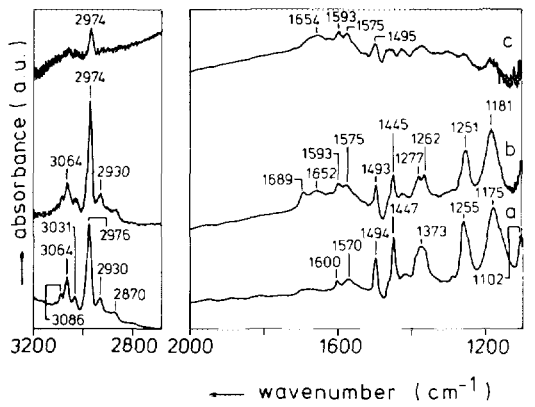

FIG. 10. FT-IR spectra of 2-phenyl-2-propanol adsorbed on γ-Al_2O_3 at 300 K (a) and after heating to 475 K (b) and 575 K (c).

intense band in this spectrum is the one at 2976 cm^{-1}, characteristic of an aliphatic C–H stretching vibration. Comparison of this spectrum with the one recorded upon adsorption of methylphenylketone, in which the mentioned band is not present, shows many differences and it can be concluded that most likely an easy fission (at the indicated temperatures) of two C–CH_3 bonds is not taking place. Vice versa, the absence of the 2976-cm^{-1} band upon adsorption of methylphenylketone indicates the likely absence of a Cannizzaro reaction.

DISCUSSION

The arguments used in the band assignment have already been presented above. Here, we concentrate our attention on the facts which might be useful from the point of view of the mechanism of the selective reduction of acids.

Monitoring by IR spectroscopy of the surfaces of active catalysts directly under the conditions at which reaction occurs supplies us with very complicated information since too many coexisting species can be detected and it is not clear how and in which order they appear on the surface. Therefore, one has to develop a strategy which lets us unravel the information. It appeared to be an advantage (*14*, *16*), when three oxides are compared in their adsorption behaviour: (1) SiO_2 with (mostly) OH groups on its surface. This surface allows us to identify the species bound by physical adsorption and by hydrogen bridges, (2) γ-Al_2O_3 which exposes besides the OH groups also oxygen and aluminium (cationic) centres, (3) α-Mn_3O_4 which exposes to the gas-phase all centres mentioned above and moreover, its oxygen can participate in oxidation–reduction reactions. When adsorption is monitored from low to higher reaction temperatures the IR spectra can reveal the order in which the various species appear on the surface. A subsequent reaction with other (potential) reaction components can help to identify the reactive species.

Two points of the mechanism can be ad-

dressed on the basis of the data presented in this paper: (i) the sequence of reaction steps and (ii) the possible existence of the Cannizzaro reaction in oxidation of aldehydes on oxides. The latter point touches a problem of the general mechanism of the oxidation reactions of organic molecules. Up to now, most of these oxidations (running between about 300 and 700 K) were found to involve the so-called Mars and van Krevelen mechanism (*17*). With this mechanism a single organic molecule extracts oxygen out of the oxide lattice. In contrast to it, a Cannizzaro oxidation could, in principle, take place on the surface as a reaction between two adsorbed molecules of aldehyde.

In contrast to the selective reduction of benzoic acid, the "reversed" process, the selective oxidation of benzaldehyde to benzoic acid, has already been a subject of research. Sachtler *et al.* (*8*) suggested a reaction mechanism for this selective oxidation reaction over a silica supported SnO_2/V_2O_5 catalyst. This mechanism is confirmed by our data. Dissociative chemisorption of benzaldehyde at room temperature produces an asymmetric organometallic benzoate (Fig. 4a) and a surface hydroxyl group. Thereafter, the first mentioned species converts into a symmetrical benzoate complex (Fig. 4b) upon ageing or heating. The symmetrical benzoate complex converts into benzoic acid after water vapour admission. It seems reasonable to expect that the selective reduction of benzoic acid proceeds through essentially the same pathway, but in the reversed direction: dissociative adsorption–symmetric benzoate–asymmetric benzoate–benzaldehyde.

We have mentioned in brief (see Fig. 7) some results obtained with benzoic acid. In a parallel study, the results of which have been published elsewhere (*14*), adsorption of benzoic (and salicylic) acid has been monitored by IR spectroscopy, with the same strategy as outlined above. A detailed analysis of those data revealed, that the adsorption of acids is dissociative leading to very stable (at least up to 573 K on both γ-Al_2O_3 and α-Mn_3O_4) benzoate-like structures. On γ-Al_2O_3 the coordination of the benzoate to the metal ion is bridging. With the α-Mn_3O_4, the catalytically most interesting oxide, the bonding is to a high extent ionic (*14*). This adsorption is very easy, the difficult steps of the reduction are the subsequent ones.

As an alternative to the mentioned mechanism of benzaldehyde oxidation on the silica supported SnO_2/V_2O_5, a Cannizzaro mechanism has been suggested for the formation of benzoate surface species on Al_2O_3 (*7*). In this reaction one benzaldehyde molecule is oxidised to benzoate and another is simultaneously reduced to benzyl alcohol (by a transfer of the hydrogen atom from the other aldehyde group). A possible existence of the Cannizzaro reaction on the oxides is investigated here, by using methylphenylketone. The existence of a Cannizzaro reaction should manifest itself by the formation of 2-phenyl-2-propoxy surface species, by a transfer of the methyl group. A similar bond cleavage occurs also upon adsorption of methylbenzoate on Y_2O_3 (*12*) leading to the formation of methoxy and benzoate surface species. Following the suggestions by Vohs and Barteau (*10*) with respect to the behaviour of aromatic oxygenates on ZnO, we expect that the benzoyl compounds undergo a nucleophilic attack at the (slightly positively charged (*5*)) carbonyl centre by surface (lattice) oxygen or hydroxyl groups followed by elimination of an (rest-group) anion producing the surface benzoate species. Upon adsorption of benzaldehyde, methylphenylketone, or methylbenzoate an elimination of a hydrogen, methyl, or methoxy group, respectively, should thus occur. The next reaction step could be a nucleophilic attack at the rest-group by surface oxygen (or hydroxyl groups). This would explain the formation of methoxy species upon adsorption of methylphenylketone on γ-Al_2O_3 (see Fig. 8). The bands ascribed to methylphenylketone and methoxy species disappear upon a temperature increase to 575 K, leaving only the spectrum of benzo-

ate surface species. The Cannizzaro reaction is thus most likely absent.

CONCLUSIONS

1. The adsorption on oxidic materials of aromatic compounds including an oxygen-containing functional group occurs mainly through this functional group.

2. The adsorption of benzaldehyde on silica occurs through a hydrogen bond of the oxygen atom of the carbonyl group to the surface silanol groups.

3. The reaction of benzoyl compounds on the rather basic metal oxides γ-Al_2O_3 and α-Mn_3O_4 involves a nucleophilic attack at the carbonyl centre by surface oxygen (or hydroxyl), producing surface benzoate species.

4. The existence of a heterogeneous catalyzed Cannizzaro reaction to explain the formation of benzyl alcoholate on oxides is not supported by the surface chemistry of methylphenylketone.

5. Under the applied reaction conditions, the hydrogenation of surface benzoate species, probably to benzaldehyde, occurs possibly on the transition metal oxide α-Mn_3O_4, but not on γ-Al_2O_3.

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