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On the Adsorption and Surface Reactions of Nitro- and Nitrosobenzene on Oxides: An IR Study

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Selective catalytic reduction of nitrobenzene to nitrosobenzene is a useful way to prepare the latter compound by a waste-free (lean) process. Since very little is known about the selective removal of oxygen from oxygen-containing compounds, surface reactions of nitro- and nitrosobenzene have been studied, here on SiO_2, γ-Al_2O_3, and α-Mn_3O_4 by Fourier transform infrared spectroscopy and by mass spectrometry. α-Mn_3O_4 is the most active catalyst for the selective reduction of nitrobenzene. However, the study has been extended to SiO_2 and γ-Al_2O_3, which are not active in a steady-state reaction, and the results obtained with the latter two oxides are used to better understand the adsorption and reactions on α-Mn_3O_4. On SiO_2 only weak adsorption of nitro- and nitrosocompounds is observed. On γ-Al_2O_3 complex surface reactions are observed, with products not very different from those on α-Mn_3O_4. However, it is argued that the redox mechanism (i.e., a mechanism involving the lattice oxygen) operates on α-Mn_3O_4, since this is the only oxide from the three mentioned before which produces nitrosobenzene. The IR spectra of adsorbed species on surfaces heated to 573 K indicate that the steady-state reaction runs on a surface covered by a complex mixture of adsorbed species.

INTRODUCTION

The fundamental knowledge on how to insert an oxygen atom into an organic molecule is rather deep and broad, while the knowledge on the selective removal of an oxygen atom is rather meager. To some extent insertion and removal are each other's mirror images, but the analogy is not complete (*1*, *2*), most likely due to the differences in the catalyst's reoxidation step in the generally operating Mars and van Krevelen ("Redox") mechanism (*3*). The differences in the catalyst's reoxidation step should thus be studied in more detail, and this is what a study on selective reduction of organics does.

The practical aspects of a study on reduction can be illustrated by the following example. Nitrosobenzene (ΦNO) can be prepared from nitrobenzene (ΦNO_2) by a stoichiometric batchwise two-step process, with almost zero investment. A reduction by, for example, HCl/Zn to phenyl hydroxylamine, followed by oxidation, for which a perchromate can be used. As easy as the reaction itself is, as difficult it is to dispose of the waste. An alternative is a gas-phase reduction, with CH_4, CO, H_2, or an autoreduction, where about 15% ΦNO_2 is sacrificed for the reduction, which can be very selective and virtually without any waste. Of course, the investment is higher and the need to know more about the reaction in order to control it is higher too.

Here an attempt is made to gain information through IR spectroscopy on the adsorption of nitro- and nitrosobenzene, the two main components in a selective reduction of nitrobenzene. Three oxides have been chosen for this study SiO_2, γ-Al_2O_3, and α-Mn_3O_4. The first oxide exposes to the gas phase predominantly surface OH groups, while on the surface of γ-Al_2O_3 cations, OH groups and oxygen atoms are all present. The reducibility of γ-Al_2O_3 (oxygen removal) is very limited. The Mn-oxide used is the stable form of the oxide upon the se-

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lective reduction of nitrobenzene, irrespective of whether the initial form is MnO or MnO_2 (*4*), and this oxide, unlike SiO_2 and γ-Al_2O_3, can be reduced or oxidized at moderate temperatures. To get some idea of the sequence of transformations upon the reaction, the IR spectra are recorded after heating the samples with the adsorbate to selected representative temperatures. Thermal-programmed surface reactions (*5, 6*) supply information about the products which desorb.

EXPERIMENTAL

Sample Preparation, 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 thermal decomposition. The IR spectrum and the XRD pattern of the sample obtained by the above described method are consistent with the literature data (*7, 8*). The total surface area of such a sample is typically in the range 20–30 m^2g^{-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^2g^{-1}, respectively.

In some experiments KOH-promoted α-Mn_3O_4 was used. To prepare promoted catalysts, an aqueous solution of KOH, with different concentrations depending on the desired final K-concentration, was added to the α-Mn_3O_4 sample, and the solvent was subsequently evaporated from the slurry under stirring at 373 K. The amount of KOH added corresponded with 0.05–2.5 mol% K with respect to Mn. Afterwards, the standard pretreatment *in situ* followed.

The nitrobenzene used in this study was 99.5% pure and obtained from J. T. Baker Chemicals BV/the Netherlands. In order to check the possible presence of the supposed adsorption complexes, benzene (over 99.7% pure, Merck/Germany), nitrosobenzene (97% pure, EGA/Germany), aniline (99%, Merck/Germany), azoxybenzene (British Drug Houses Ltd./England), and acetic acid (over 99% pure, J. T. Baker Chemicals BV/the Netherlands) were used in the adsorption study. The experiments with azoxybenzene as an adsorbate were complicated by the low vapor pressure of this compound. This required the removal of the pretreated oxide sample from the vacuum system and spraying azoxybenzene on the sample. Afterwards the sprayed sample was brought back into the vacuum cell. All compounds used were degassed prior to the use.

IR Spectrometry

The transmission IR experiments were carried out using thin self-supporting pellets of about 50 mg of the sample material. These pellets were pressed using a pressure of 10 MPa. The pellets were subsequently placed in an all-metal transmission cell mounted with CaF_2-windows. 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 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*. Adsorption on the oxide sample was achieved by expansion of the adsorbate gas or liquid vapors from the vacuum system into the cell. Before adsorption of one of the compounds, 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 measured. 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 infrared spectra were recorded with two different spectrophotometers. For the conventional dispersive mode experiments, a dual beam Perkin–Elmer 580B was used. The data handling (acquisition, storage and evaluation) was performed using an Apple II$^+$ computer. 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.

Isothermal or Temperature-Programmed Surface Reaction

Surface reactions were monitored with the oxide powder in a closed vessel, which was part of a high vacuum system. In order to analyze the gas phase above the oxide sample, the system was connected through a metal vacuum valve to a mass spectrometer (Vacuum Generators, MM8-80S) equipped with a computer. The aim of this part of the study was just to relate the behavior of the species (identified by IR spectra) at the oxide surface to the products appearing in the gas phase. Blank experiments have shown that the stainless steel parts of the vacuum apparatus have no influence on the formation of the products monitored.

RESULTS

Adsorption and Surface Reaction of Nitrobenzene

Adsorption experiments showed that upon admittance of benzene into the infrared cell at room temperature and subsequent evacuation, no (infrared active) species remained on the surfaces of any of the three oxides studied.

Figure 1 shows the IR spectra in the range 2000–1100 cm^{-1}, obtained upon the adsorption of nitrobenzene at 300 K, on SiO_2, γ-Al_2O_3, and α-Mn_3O_4. The wavenumbers and the corresponding assignments of the main IR absorption bands are given in Table 1. The spectra can be fully ascribed to nitrobenzene, which indicates that no detectable surface reactions take place at this temperature. Figure 1 also shows the spectrum of nitrobenzene in the gas phase. A comparison of the gas-phase spectrum with the liquid-phase spectrum (9) shows that the absorption bands are at higher wavenumbers in the case of the gas-phase spectrum. The spectra of the adsorbed phase, however, are very similar to the liquid-phase spectrum. Indeed, it is already known that physically adsorbed gases show an IR behavior of the corresponding liquid. This can be explained by the presence of interacting dipoles, both in the liquid and in the adsorbed phase.

It has to be noted that the shift in wavenumber maxima in the nitrobenzene IR spectrum to lower wavenumbers is in the order $SiO_2 < \gamma$-$Al_2O_3 < \alpha$-Mn_3O_4. This implies an increasing strength of interaction in the sequence indicated. Results obtained at higher temperatures will be presented for the individual systems separately.

Adsorption on SiO_2. The adsorption of nitrobenzene on SiO_2 results in a strong intensity decrease of the OH stretching band (around 3740 cm^{-1}) of isolated silanol groups, whereas a broad band arises with a maximum around 3600 cm^{-1}, which indicates that the OH groups are now involved in a hydrogen-bond formation. Thus, the adsorption is likely mediated by H-bonds between nitrobenzene and the isolated surface hydroxyl groups. Evacuation of the system at 300 K results in a total desorption of nitrobenzene from the silica surface, as shown by the complete restoring of the original

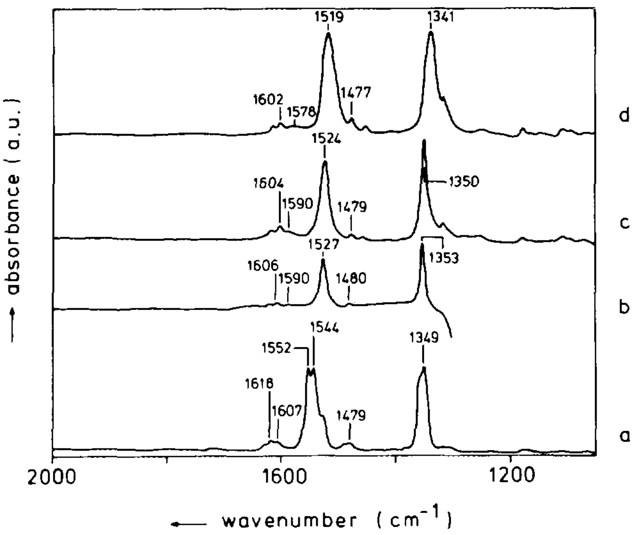

FIG. 1. FT-IR spectra of gas-phase nitrobenzene (a) and nitrobenzene adsorbed at 300 K on SiO_2 (b), γ-Al_2O_3 (c), and α-Mn_3O_4 (d).

background (SiO_2) spectrum. No IR bands appear upon adsorption at higher temperatures.

Adsorption on γ-Al_2O_3. The adsorption of nitrobenzene on γ-Al_2O_3 is obviously stronger than the adsorption on SiO_2. The IR bands characteristic of nitrobenzene change only slightly upon heating to 375 K under continuous evacuation. When the temperature is increased further, the low-temperature bands disappear and broad and weak absorption bands appear around 1600 and 1255 cm^{-1} (the resulting spectrum is not shown in Fig. 1). Similar bands have also been found upon adsorption of CO_2 on several pure metal oxides and they (*10*) can be assigned to bidentate carbonate surface species.

TABLE I

FT-IR Spectra of Nitrobenzene Adsorbed on Oxides at 300 K, Compared to the Liquid-Phase Spectrum

IR bands (cm^{-1}) of ϕNO_2				
SiO_2	γ-Al_2O_3	α-Mn_3O_4	Liquid (9)	Assignment (9)
1606	1604	1602	1608	Ring vibration
1590	1590	1578	1588	Ring vibration
1527	1524	1519	1525	$\nu_a(NO_2)$
1480	1479	1477	1478	Ring vibration
1353	1350	1341	1348	$\nu_s(NO_2)$

Note. ν = stretching vibration, a = asymmetric, and s = symmetric.

A temperature-programmed surface reaction (TPSR) followed by mass spectrometric analysis showed molecular desorption of nitrobenzene up to 450 K, while above this temperature carbon monoxide and carbon dioxide were the only detectable products in the gas phase. The appearance of the carbon oxides in the gas phase is an indirect support for the assignment given above of the bands in the IR spectrum to the carbonate surface species. It is important to note that no indications for the transformation of nitrobenzene into nitrosobenzene have been observed.

The spectra obtained after interaction of ΦNO_2 with γ-Al_2O_3 at 575 K are different from those observed after adsorption at 300 K and heating up to 575 K. The latter procedure lead to the appearance of carbonate IR absorption bands, whereas a complex IR spectrum was the result of the former procedure. The most obvious explanation

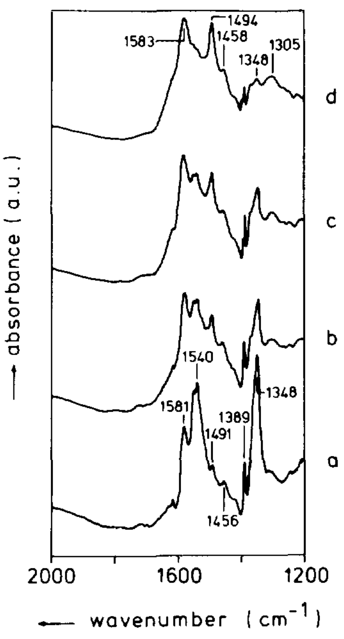

FIG. 2. The development in time of the FT-IR spectrum of nitrobenzene (20 Pa) in contact with γ-Al_2O_3 at 575 K: after 2 (a), 15 (b), 30 (c), and 75 (d) min, respectively.

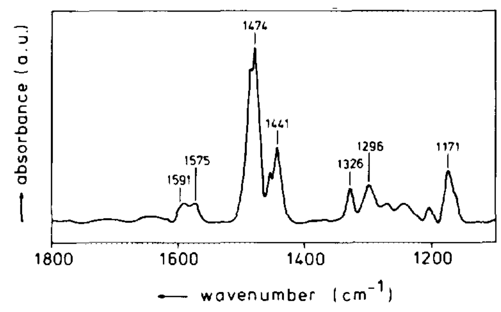

FIG. 3. FT-IR spectrum of azoxybenzene adsorbed on γ-Al_2O_3.

for this difference is that nitrobenzene is mainly desorbed and evacuated upon raising the temperature. Figure 2 shows the spectra obtained as a function of time, after nitrobenzene had been contacted with alumina directly at 575 K. The spectrum changed obviously during the experiment. The IR bands due to the symmetric and asymmetric NO_2 stretching vibrations (around 1348 and 1540 cm^{-1}, respectively) diminished, while new bands appeared. The main bands of the final spectrum are located around 1583, 1494, 1458, and 1305 cm^{-1}. Several attempts have been made to assign this spectrum. The most likely explanation has been found by assuming that some of the nitrobenzene molecules are reduced and others are oxidized on the alumina surface. The bands around 1494, 1458, and the broad band around 1305 cm^{-1} are similar to the main bands obtained after adsorption of azoxybenzene on the same oxide (see Fig. 3). A band observed around 1580 cm^{-1} can be ascribed to a product formed by the oxidation of the aromatic ring of nitrobenzene, of which a carboxylate species is the most likely one.

Adsorption on α-Mn_3O_4. Figure 4 presents the FT-IR spectra observed upon surface reactions of nitrobenzene on α-Mn_3O_4 in the range 300–575 K. It was already mentioned above that the IR band maxima of adsorbed nitrobenzene are shifted upon adsorption to slightly lower wavenumbers

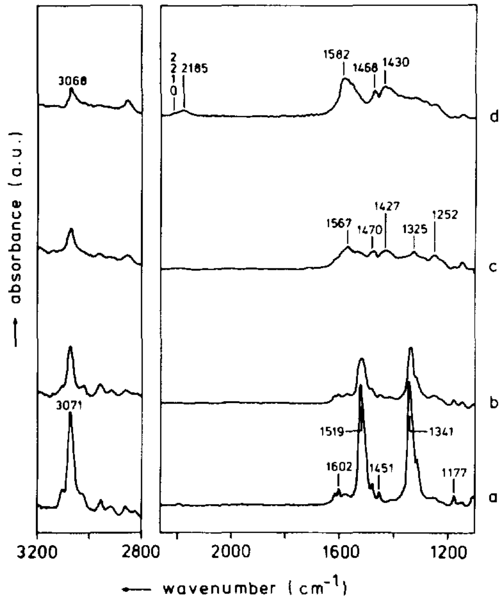

FIG. 4. FT-IR spectra observed upon TPSR of nitrobenzene on α-Mn_3O_4: 300 K (a), 375 K (b), 475 K (c), and 575 K (d).

with respect to liquid nitrobenzene. However, more detailed information about the mode of adsorption has not been obtained and, therefore, no conclusion can be drawn on whether nitrobenzene is adsorbed perpendicular or parallel to the surface. It can be derived from the frequency shifts with respect to the liquid phase that the interaction with the oxide surface is stronger than the mutual interaction of nitrobenzene dipoles in the liquid phase.

A temperature increase during evacuation leads to the appearance of IR bands, which have to be ascribed to the products of surface reactions. This situation is rather different from that with γ-Al_2O_3, where adsorbed nitrobenzene mainly desorbs during the temperature increase. The band around 2185 cm^{-1}, of which the intensity increases with increasing temperature, is also observed after adsorption of nitroalkanes on α-Mn_3O_4 (*11*, *12*). It has been concluded that (iso)cyanate surface species are responsible for this band. The presence of a shoulder around 2210 cm^{-1} implies various adsorption sites or different modes of (iso)cyanate adsorption.

In the range 1800–1000 cm^{-1}, many absorption bands are observed and an unambiguous assignment of all individual bands is difficult. However, the IR band visible around 3070 cm^{-1} (the aromatic C–H stretching vibration) indicates that at least in some adsorbed species the aromatic ring is still preserved.

Several compounds have been adsorbed in order to get information about the species, which could cause the absorptions between 1800 and 1000 cm^{-1}. Nitrosobenzene, aniline, phenol, maleic anhydride, azoxybenzene, acetic acid, ^{15}N-nitrobenzene, and D_5-nitrobenzene were among them. It can be concluded from Fig. 5 that a superposition of the spectra of the acetate (carboxylate) and azoxybenzene surface species agrees very well with the spectrum observed upon nitrobenzene adsorption followed by heating up to 575 K. However, the IR bands which we assign to acetate surface species are not specific, they are common to various carboxylate species.

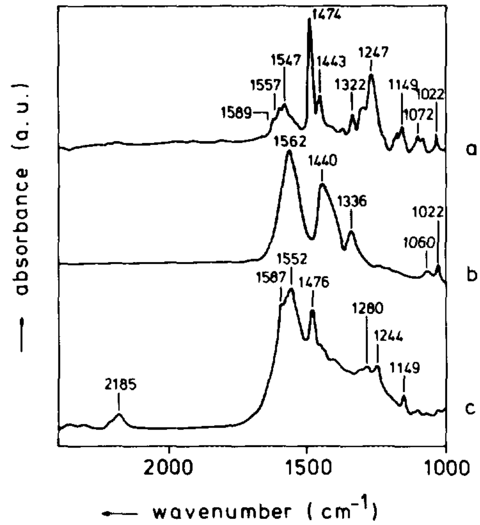

FIG. 5. FT-IR spectra observed upon adsorption of azoxybenzene (a), acetic acid (b), and nitrobenzene (c) on α-Mn_3O_4 at 575 K.

There are some additional arguments in favor of the assignment of the spectra (as in Figs. 4 and 5) to a superposition of spectra of at least two independent species. The spectra obtained after admitting ΦNO_2 to α-Mn_3O_4 at increasing temperatures (in the range 475–575 K) show a variable contribution of bands ascribed either to azoxybenzene or to carboxylates; the first mentioned bands grow faster at higher temperature. On the other hand, only the bands ascribed to azoxybenzene can be suppressed when CH_3I is admitted into the cell.

Various samples of KOH promoted α-Mn_3O_4 (0.0 to 2.5%K) have also been studied in relation to the adsorption and surface reaction of ΦNO_2. By XRD or IR, no K-incorporation into α-Mn_3O_4 was detected (actually substitutional dissolution should not be expected, according to the ionic radii, only formation of new phases is possible), so that effects when observed are mainly from the KOH (or potassium carbonates) on the surface of α-Mn_3O_4. With increasing K-content, the 3620 cm^{-1} band,

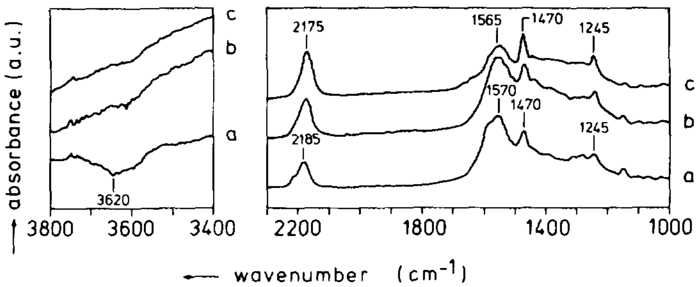

FIG. 6. FT-IR spectra observed upon interaction of nitrobenzene with the "potassium-promoted" samples at 575 K: sample with 0.0 (a), 0.05 (b), and 0.7 mol% K (c) with respect to Mn.

ascribed to isolated Mn–O–H, decreases gradually. Simultaneously, a broad band (OH) at 3450 cm^{-1} somewhat increases. Figure 6 shows what happens when ΦNO_2 is admitted to KOH-promoted (0.05 to 0.7 mol% K) α-Mn_3O_4 at 575 K. We know that, at this temperature, first CO and CO_2 are produced and appear in the gas phase. When the reaction is continued these gases are first followed by aniline and later by nitrosobenzene. Correspondingly, in the adsorbed phase the incipient reaction results in the IR spectra shown by Fig. 6. Analyzing Fig. 6 one observes that the peak at 1570 cm^{-1} (which is ascribed to carboxylate species) is lower, while the band at 1470 cm^{-1} increases, with increasing KOH content. The negative peak at 3620 cm^{-1} means that the Mn–O–H groups, if present, interact readily with ΦNO_2. The band observed around 2185 cm^{-1} is tentatively ascribed to (iso)cyanates (*13*).

A preliminary suggestion can be made here relating the just mentioned IR data to the catalytic ones. It is known (*4*) that promotion by "K" leads to a slight enhancement of the nitrosobenzene formation and to appreciably enhanced formation of easily condensing products (only a few percent of nitrobenzene is spent by this side reaction) like azoxybenzene. Possibly this can be related to the effect of KOH on the intensity of the 1470-cm^{-1} band. It is of interest that no IR active species have been seen showing a strong interaction of ΦNO_2 with the promoting compounds.

Adsorption and Surface Reaction of Nitrosobenzene

Figure 7 shows the spectra of surface species arising upon nitrosobenzene adsorption at 300 K on SiO_2, γ-Al_2O_3, and α-Mn_3O_4. A comparison with the spectra of nitrosobenzene in the gas phase (see Fig. 7a) and in the liquid phase (not presented) shows that significant changes in the spectrum can occur upon adsorption. As in the case of nitrobenzene (see above), the IR bands of nitrosobenzene adsorbed on silica, are only

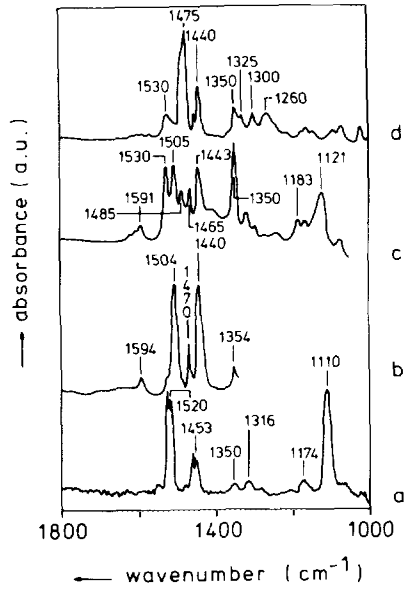

FIG. 7. FT-IR spectra of gas-phase nitrosobenzene (a) and nitrosobenzene adsorbed at 300 K on SiO_2 (b), γ-Al_2O_3 (c), and α-Mn_3O_4 (d).

slightly shifted with respect to the bands in the liquid phase. The ν(N=O) band, observed at 1504 cm^{-1}, is shifted downward by 19 cm^{-1} with respect to the gas phase (*14*). It has been found that upon adsorption of acetaldehyde the ν(C=O) band shows a similar 15 cm^{-1} shift downward, and moreover, its relative intensity (when compared with other bands) is remarkably lower than that observed in the liquid phase. The same feature is also observed for the ν(N=O) band (a lower intensity with respect to the other nitrosobenzene IR bands). The phenyl ring vibrations around 1470 and 1440 cm^{-1} (vibrations 19a and 19b according to the Wilson notation (*15*) are obviously more pronounced in the adsorbate spectrum (Fig. 7).

The final conclusion is that the spectrum revealed upon adsorption on SiO_2 is totally assignable to nitrosobenzene. The adsorption of nitrosobenzene on silica can be described well as a hydrogen bond between the (nitroso group) oxygen atom and surface silanol groups. Indeed, the complete desorption of nitrosobenzene upon evacuation at 300 K indicates a weak interaction of nitrosobenzene with the silica surface.

In contrast to the molecular adsorption on silica, the appearance of several additional IR absorption bands upon the nitrosobenzene adsorption on γ-Al_2O_3 and on α-Mn_3O_4 at 300 K shows that here various reactions take place. In the spectrum of the system nitrosobenzene on γ-Al_2O_3, the same bands as observed upon the nitrosobenzene adsorption on SiO_2 are still clearly visible. Furthermore, the 1530- and 1350-cm^{-1} bands, which bands are characteristic of the nitrobenzene asymmetric and symmetric NO_2 stretching vibrations (see above), are observed on both γ-Al_2O_3 and α-Mn_3O_4. However, at the moment not all bands can definitively be assigned to one or another surface species. The main bands in the spectrum obtained with α-Mn_3O_4 as adsorbent are those found at 1475 (vs), 1440 (s), 1325 (m), and 1260 (m) cm^{-1}. These bands are characteristic of adsorbed azoxybenzene. This indicates that not only nitrobenzene but also nitrosobenzene can be converted into azoxybenzene on the surface of α-Mn_3O_4. In this respect, it has to be remarked that the azoxybenzene IR bands were the only bands, which remained after evacuation and heating. The azoxybenzene species have been found to be stable up to 500 K. Above this temperature additional IR bands arise in the ranges characteristic of carboxylate vibrations.

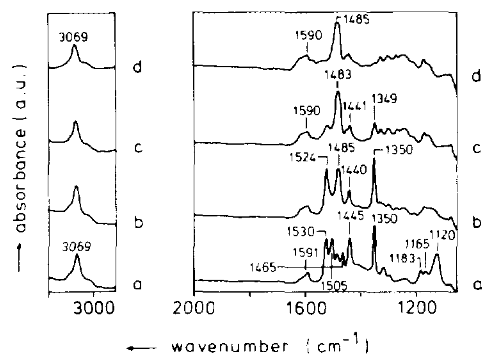

FIG. 8. FT-IR spectra obtained after adsorption of nitrosobenzene on γ-Al_2O_3 at 300 K: p_{eq} = 13 Pa (a) and p_{eq} = 10^{-2} Pa (b); after a successive heating at 375 K (c) and 475 K (d).

The IR spectra which developed upon adsorption of ΦNO on γ-Al_2O_3 and successive heat treatment are presented in Fig. 8. First of all one can see that the IR bands around 1505, 1465, 1445, and 1120 cm^{-1} considerably decrease in intensity, merely as a result of evacuation at 300 K. These bands have to be assigned to the ν(N=O) vibrations and the ring vibrations (19a, 19b, and 13, respectively) of molecularly adsorbed nitrosobenzene. Remarkable is the simultaneous growth of the azoxybenzene absorption bands (1485 and 1440 cm^{-1}) upon heating. These bands grow in the temperature range 300–475 K, whereas the IR bands assigned to adsorbed nitrobenzene diminish in intensity in the same range. Above 475 K the intensity of the azoxybenzene IR bands also decreases, while a weak and broad band appears around 1590 cm^{-1}. This band indicates formation of carboxylate or carbonate surface species, likely by oxidation of the

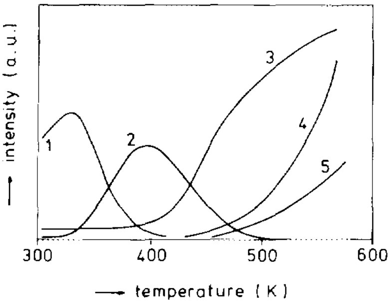

FIG. 9. Temperature-programmed surface reaction of nitrosobenzene on γ-Al_2O_3 as followed by MS: signals corresponding to nitrosobenzene (1), nitrobenzene (2), carbon monoxide [+ dinitrogen?] (3), carbon dioxide (4), and water (5).

phenyl rings of azoxybenzene and/or nitrobenzene.

The "TPSR" of nitrosobenzene on γ-Al_2O_3 as well as on α-Mn_3O_4 was also followed by mass spectrometric analysis. The results of these experiments are shown in Figs. 9 and 10, respectively. The following trends have been observed. On γ-Al_2O_3, the main surface process at lower temperatures (300–375 K) is desorption of nitrosobenzene. Simultaneously with the decrease of the nitrobenzene IR bands, between 300–500 K (see above), detection of gas-phase nitrobenzene takes place. Above 450 K, the main products observed in the gas phase are carbon oxides (CO, m/e = 28; CO_2, m/e = 44; and water, m/e = 18).

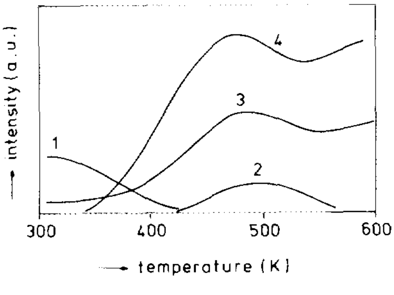

FIG. 10. TPSR of nitrosobenzene on α-Mn_3O_4 as followed by MS: signals corresponding to nitrobenzene (1), benzene (2), carbon monoxide + dinitrogen (3), and carbon dioxide (4).

On α-Mn_3O_4, nitrobenzene has been observed below 425 K, whereas no desorbing nitrosobenzene has been detected in the gas phase at all. The appearance of benzene in the gas phase above α-Mn_3O_4 (between 440 and 540 K) is quite remarkable and implies some dissociation of the C–N bond of adsorbed nitrosobenzene.

The information obtained about the nitrosobenzene/oxide systems leads to the suggestion that under the common reaction conditions ($T > 500$ K) and perhaps at even lower temperatures, nitrosobenzene is not a stable species on those oxide surfaces, which expose metal ions and oxygen ions. On the totally hydroxylated silica surface the adsorption of nitrosobenzene is weak, unreactive, and is based on hydrogen-bond formation. On the surfaces of γ-Al_2O_3 and α-Mn_3O_4 nitrosobenzene reacts immediately at 300 K by the nitroso group. This results in the formation of the oxidation, as well as reduction, products: nitrobenzene and azoxybenzene, respectively. The formation of nitrobenzene on γ-Al_2O_3 is remarkable since nitrobenzene could not be reduced to nitrosobenzene on this oxide. Obviously, the redistribution of oxygen atoms of the adsorbed ΦNO molecules should be considered as the most likely pathway to the products observed.

DISCUSSION

This investigation had been motivated by catalytic problems (*1*, *2*). However, the experiments performed produced results which are interesting from the point of view of surface reactions in general, including the noncatalytic ones.

Infrared spectroscopy is a very useful tool in obtaining information on adsorbed layers and surface reactions, but very often this method is not straightforward. For example, in some cases one has to study also the spectra of simple related molecules (to obtain fingerprints of various groups) or, as appeared to be necessary in our study, to investigate the adsorption of the compounds of interest on adsorbents with a varying reactivity. The latter has been done in the hope that the results obtained with the simpler systems help to interpret the results obtained with the most reactive and complicated system (α-Mn_3O_4). Results obtained confirm the expectation.

The three oxides used as adsorbents differ in a characteristic way: SiO_2 does not expose cations to the surface and the adsorbed molecules interact with weakly acidic OH groups. γ-Al_2O_3 exposes a surface with O, OH, and Al on it, but an extraction of O or OH out of the lattice, although possible (*16*) is not easy. With α-Mn_3O_4 the latter step is much easier. The IR spectra shown above reflect this situation. With SiO_2 the interaction is weak and already upon a moderate temperature increase, nitro- and nitrosobenzene desorb. With alumina both nitro- and nitrosobenzene desorb upon heating, but a part of these molecules loses oxygen (the presence of azoxybenzene indicates that), while other molecules are oxidized to CO, CO_2, and H_2O. This is displayed for nitrosobenzene in Fig. 9. α-Mn_3O_4 is much more reactive: nitrosobenzene does not desorb but reacts immediately further (Fig. 10) and also nitrobenzene reacts at a lower temperature on α-Mn_3O_4 than on γ-Al_2O_3. With γ-Al_2O_3 we do not know yet if the lattice oxygen participates in the reactions observed upon heating. However, we know this is certainly the case for transition metal oxides (*4, 17*).

Nitro- and nitroso-aromatic compounds can obviously be adsorbed physically at room temperature and they can also form H-bridges (see Results). They can form weak bonds to various cations in a mono- or bidentate form. Nitrosobenzene can be head-on or side-on bonded (*18, 19*). Both the nitro- and the nitroso-groups are weakly bound ligands which get easily loosened when the temperature is increased. However, they can serve very well as a precursor state on the way toward dissociation, according to the usual Lennard-Jones scheme (*20*). The presence of O or OH vacancies is expected to be beneficial for dissociation. This is shown schematically in Fig. 11.

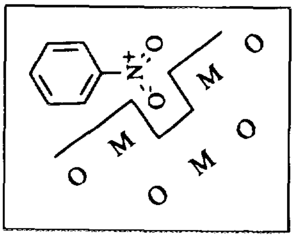

FIG. 11. Schematic representation of the oxide surface vacancies, which are beneficial for dissociation.

Quantum chemical calculations have already supplied us with a rather detailed description of nitro- and nitrosobenzene molecules. While in benzene a negative charge is accumulated under and above the ring, the NO_2- and NO-groups withdraw negative charge from its position in benzene. In nitrobenzene the negative charge is mainly accumulated around the oxygen atoms (as chemical intuition would tell us) and two centers of positive charges appear: one above and under the ring (this is the smaller one) and the other, the larger one, on the C–N bond, approximately in the middle of this bond (*21*). These are the places toward which a potential nucleophilic attack by "O" or "OH" would be directed. Such an attack leads to an oxidative destruction of the ring and the production of CO, CO_2, and H_2O. As already mentioned with transition metal oxides, the lattice oxygen participates in the formation of the just mentioned products (*3, 4, 17*). Extraction of lattice oxygen creates vacancies which can react with other adsorbed or incoming molecules. Once a molecule of nitrosobenzene is formed, the situation in the charge distribution changes. Now a negative charge appears near the "N" and on the ring (*22*). There is much less attraction between the C–N and ring bonds on one side and OH or O on the other side. The slightly negatively charged sites in the nitrosobenzene and the negatively charged surface sites will repel each other and thus help the desorption of

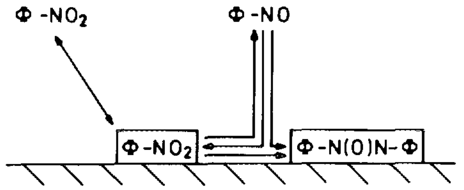

FIG. 12. Surface chemistry of nitro- and nitrosobenzene on α-Mn_3O_4.

nitrosobenzene from the surface. This would explain why under reaction conditions one can observe in the IR the products, which in homogeneous reactions are formed via nitrosobenzene (*23*), but not nitrosobenzene itself.

There are two pathways from nitrobenzene to either nitrosobenzene (in the gas phase) or azoxybenzene (in the adsorbed state), and aniline (in the adsorbed state and gas phase). The first pathway is via "addition (of hydrogen)–dissociation (of the N–O)", the second via "dissociation–addition (or desorption)." The first pathway is most likely operating upon, for example, hydrogen-transfer reactions on MgO (*24*), an oxide which does not tolerate a sufficient number of oxygen vacancies. The second pathway is likely operating on transition metal oxides. The position of alumina in this respect has not been identified yet, although the expectation is that the contribution by the first pathway should be considerable. In any case, with both γ-Al_2O_3 and α-Mn_3O_4 one observes first the formation of carboxylates (products of the oxidation of surface species) on the surface and only in later stages of the reaction azoxybenzene (products of oxygen removal). With a surface reaction on α-Mn_3O_4 the various fragments are first observed and later aniline and nitrosobenzene appear when starting from nitrobenzene, and aniline and nitrobenzene when starting from nitrosobenzene. Nitrosobenzene is never observed in any strongly chemisorbed form. Various reaction steps are schematically summarized in Fig. 12.

We know that nitrobenzene can oxidize MnO and reduce MnO_2 (*1*, *2*, *4*) and reacts to nitrosobenzene on α-Mn_3O_4. With this oxide it is thus very likely that the selective reduction of nitrobenzene is a reaction of the Mars and van Krevelen type (*3*). However, operation of such a mechanism on γ-Al_2O_3 (in rather fast redox reactions) is not very likely, although the redox properties of γ-Al_2O_3 are not negligible either (*16*). Nevertheless, we have not observed formation of nitrobenzene on γ-Al_2O_3, similarly as formation of this molecule has never been observed on MgO. Alumina is obviously able to redistribute "O" in the adsorbed layer, since CO, CO_2, carboxylates, and azoxybenzene are observed on this oxide, and similarly MgO can enable a transfer of H-atoms from hydrogen releasing molecules (e.g., isopropanol). A selective formation of nitroso- from nitrobenzene is most likely confined to oxides which are good redox catalysts.

CONCLUSIONS

Information has been obtained on the adsorption and surface chemistry of nitro- and nitrosobenzene on three oxides: SiO_2, γ-Al_2O_3, and α-Mn_3O_4. The results teach us that:

(1) the interaction of nitro- and nitrosobenzene with surface OH-groups is weak, and molecules adsorbed by this mechanism only desorb at lower temperatures than the usual reaction temperature (573 K).

(2) Only with α-Mn_3O_4, the most active oxide of the three oxides investigated, is formation of gaseoues nitrosobenzene observed. We relate this observation to the redox properties of α-Mn_3O_4, which allow the participation of the lattice oxygen in the surface reactions and continuous catalytic nitrosobenzene formation.

(3) Also γ-Al_2O_3, an oxide exposing cations to the gas phase (like α-Mn_3O_4, but unlike SiO_2), binds nitrobenzene rather strongly and initiates fast reactions of nitrosobenzene to nitrobenzene, as well as some other oxidation reactions (with both com-

pounds); these reactions are tentatively ascribed to the oxygen redistribution reactions in the adsorbed phase.

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