JOURNAL OF CATALYSIS **121**, 153–164 (1990)

# Thermal Desorption and Infrared Studies of Amines Adsorbed on $SiO_2$, $Al_2O_3$, $Fe_2O_3$, MgO, and CaO

## I. Diethylamine and Triethylamine

ROLF SOKOLL, HARTMUT HOBERT, AND IRMTRAUT SCHMUCK

*Sektion Chemie der Friedrich-Schiller-Universität, Lessingstrasse 10, 6900 Jena,*
*German Democratic Republic*

Received June 20, 1988; revised April 26, 1989

The adsorption of diethylamine and triethylamine on $SiO_2$, $\gamma$-$Al_2O_3$, $\alpha$-$Fe_2O_3$, MgO, and CaO at the solid/vapour interface has been studied by infrared spectroscopy and temperature-programmed desorption (TPD). At beam temperature hydrogen bonding between surface hydroxy groups and amine molecules (both amines) and dissociative adsorption (diethylamine only) occur on $SiO_2$. Adsorption on the other oxides mainly involves the formation of coordination bonds between amine molecules and Lewis-acidic surface sites (coordinatively unsaturated cations). With increasing temperature during the TPD runs, amine molecules adsorbed on the different surface sites undergo chemical transformations (including C–C-, C–N-, and N–H-bond breakages) which cause the desorption of characteristic reaction products.

## INTRODUCTION

Amines are of considerable industrial importance and find application in almost every field of modern technology, agriculture, and medicine. Thus a variety of N-containing substances, e.g., quaternary ammonium salts (*1, 2*) or aliphatic and aromatic amines (*3–5*), are used as corrosion inhibitors in aqueous and nonaqueous (*6, 7*) metal/liquid systems. In this context not only the fundamental mechanisms of the interaction between active substances and surfaces of the solids are interesting but also other problems such as the relations between structure and efficiency of the organic additives (*8, 9*) or chemical reactions (*8, 10*) and thermal stability (*11, 12*) of the formed surface complexes. The latter questions are also very important in the application of amines as components of lubricating oils (*13, 14*).

Although there has been much work on these problems there is a lack of systematic fundamental investigations. For this reason we deal in our work with the adsorption and reaction behaviour of amines on the surfaces of oxides. The amines were selected in such a way that a diversity of the possible structural conditions could be considered by the use of representative compounds. To realize different properties of the oxides, we used as adsorbents $SiO_2$ (an already well investigated oxide, the mainly active centres of which are surface hydroxy groups), $\gamma$-$Al_2O_3$ and $\alpha$-$Fe_2O_3$ as oxides of important metallic materials with strong Lewis-acidic surface sites, and MgO and CaO with basic properties. In 1986 we published several articles concerning our investigations of the interaction between aliphatic *n*-amines and oxides (*14–18*). Continuing this work we now report on the results obtained with a variety of other amines.

## EXPERIMENTAL

Samples of CaO (MgO) were obtained by vacuum decomposition (1023 K, $1 \times 10^{-3}$ Pa) of pressed disks of $CaCO_3$ ($MgCO_3$) in the infrared cell. The BET surface area of the resulting CaO (MgO) was ca. 50 (200)

0021-9517/90 $3.00

m$^2$/g. X-ray powder diffraction analysis confirmed that the samples were polycrystalline, and the infrared spectra show no or only very small absorptions of isolated surface hydroxy groups (CaO: 3695 cm$^{-1}$; MgO: 3722 cm$^{-1}$).

Samples of $\alpha$-$Fe_2O_3$ were obtained by vacuum decomposition (573 K, $1 \times 10^{-3}$ Pa) of pressed disks of goethite ($\alpha$-FeOOH, prepared from $Fe(NO_3)_3 \cdot 9H_2O$ (*19*)) in the infrared cell. The BET surface area of the resulting hematite was ca. 160 m$^2$/g and is drastically reduced with increasing evacuation temperature by irreversible sintering (*20*)). Evacuation of $Fe_2O_3$ at higher temperatures also leads to a major reduction in overall spectral transmission. This is to be attributed to the increasing nonstoichiometry of the $Fe_2O_3$ sample, as its composition changes toward that of magnetite (*20, 21*). Under the conditions described, freshly prepared $\alpha$-$Fe_2O_3$ shows four infrared bands at 3727, 3658, 3624, and 3478 cm$^{-1}$. The absorptions between 3600 and 3800 cm$^{-1}$ can be ascribed to different types of isolated surface hydroxy groups, whereas the broader maximum at 3478 cm$^{-1}$ is caused by hydroxy groups which are involved in strong hydrogen bonding interactions with adjacent OH-groups (*22*).

The other oxides were Aerosil 300 (Degussa) and Aluminiumoxid C (Degussa; BET surface area ca. 80 m$^2$/g).

Infrared spectra were recorded by a Specord 75 IR spectrometer (VEB Carl Zeiss, Jena) coupled with a KRS 4200 computer (VEB Robotron) in the range 4000–1200 cm$^{-1}$. For monitoring the desorption spectra and for identification of the desorption products a CH8 mass spectrometer (Varian Mat) connected to the TPD apparature was used. All desorption experiments were carried out with oxide samples saturated by amine vapour and reevacuated for 4 h at room temperature. To always obtain identical surface conditions the oxide samples were initially activated under vacuum ($p = 1 \times 10^{-3}$ to $6 \times 10^{-4}$ Pa) for 2 h: $SiO_2$, $Al_2O_3$, 973 K; MgO, CaO, 1023 K; $Fe_2O_3$, 573 K (IR), 738 K (TPD). Infrared spectra were recorded of the oxides activated under vacuum, after contact with the amine (1 h) and evacuation at beam temperature, and finally after evacuation at stepwise increasing temperatures and subsequent cooling to beam temperature.

All other experimental conditions and the procedure of measuring the TPD spectra were the same as those given in Ref. (*17*).

## RESULTS

Because of the nearly complete identity of the adsorption and reaction behaviour of the amines on MgO and CaO surfaces only the results for MgO as adsorbent are presented.

Figure 1 shows the TPD spectra of all investigated diethylamine/oxide systems,

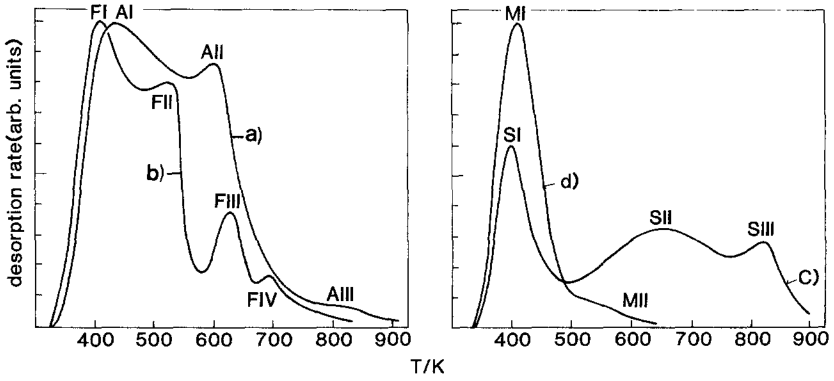


FIG. 1. Thermal desorption spectra of diethylamine adsorbed on oxides: (a) $Al_2O_3$; (b) $Fe_2O_3$; (c) $SiO_2$; (d) MgO.

TABLE 1

Adsorption of Diethylamine on Oxides: Distribution of the Desorption Products

| Desorption product | Temperature of the desorption maximum (K) | | | | |
|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO |
| Diethylamine | 403<br>658 | 433 | 413 | 413 | 413 |
| Acetonitrile | 803 | 598 | 523 | 533 | (533)[a] |
| Ethylene | 803 | 598 | 523 | 533 | (533)[a] |
| Hydrogen | (803)[a] | 598 | 523 | 533 | (533)[a] |
| Carbon dioxide | — | (823)[a] | 628<br>703 | — | — |
| Water | — | (823)[a] | 628<br>(703)[a] | — | — |
| Hydrogen cyanide | 843 | — | — | — | — |
| Methane | 843 | — | — | — | — |

[a] Small amounts.

whereas the main desorption products are given in Table 1.

The TPD results of the triethylamine/oxide systems are represented by Fig. 2 and Table 2. Because of essentially analogous distributions of the desorption products, most of the reactions occurring at elevated temperatures seem to be the same as those in the case of the corresponding diethylamine/oxide systems. The only noticeable differences can be summarized as follows:

(a) Using $SiO_2$ as adsorbent only one nearly symmetrical TPD maximum appears (SI).

(b) Compared to the diethylamine/$Al_2O_3$ system the ratio of desorbing amounts of ethylene and acetonitrile is greater.

(c) Maximum FIII of the TPD spectrum shows a higher relative intensity than that in the case of the diethylamine/$Fe_2O_3$ system.

## INFRARED ABSORPTION SPECTRA

### *Diethylamine*

The most characteristic feature of the infrared spectra of gaseous and adsorbed diethylamine is the band of the NH-stretch-

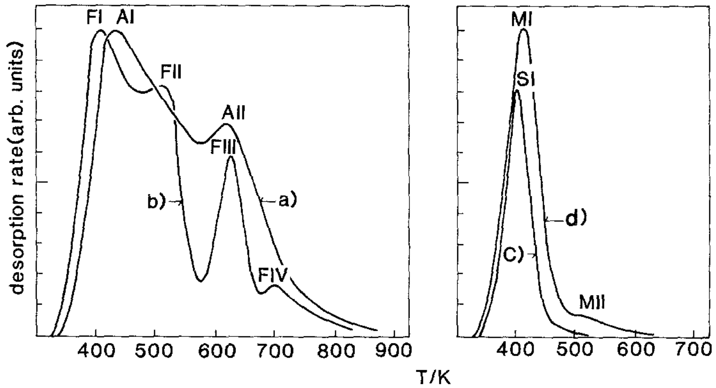


FIG. 2. Thermal desorption spectra of triethylamine adsorbed on oxides: (a) $Al_2O_3$; (b) $Fe_2O_3$; (c) $SiO_2$; (d) MgO.

TABLE 2

Adsorption of Triethylamine on Oxides: Distribution of the Desorption Products

| Desorption product | Temperature of the desorption maximum (K) | | | | |
|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO |
| Triethylamine | 403 | 433 | 413 | 413<br>533 | 413 |
| Acetonitrile | — | 618 | 513 | (533)[a] | — |
| Ethylene | — | 618 | 513 | (533)[a] | — |
| Hydrogen | — | 618 | 513 | (533)[a] | — |
| Carbon dioxide | — | — | 628<br>698 | — | — |
| Water | — | — | 628<br>(698)[a] | — | — |

[a] Small amounts.

ing vibration which appears besides the CH-absorptions.

Figure 3 shows the spectra of freshly activated $Al_2O_3$ and of $Al_2O_3$ evacuated at various temperatures after the adsorption of diethylamine ($\nu$(NH) = 3182 cm$^{-1}$). Similar to the TPD spectrum three characteristic temperature ranges can be distinguished, as detailed below:

(a) Between beam temperature and ca. 533 K the intensity of all bands of adsorbed diethylamine decrease. At ca. 553 K a new band appears at 1654 cm$^{-1}$ which can be ascribed to a C=N-stretching vibration of imine species (*23*). In addition, two weak absorptions become visible at 1570 and ca. 1470 cm$^{-1}$ (shoulder).

(b) In the temperature range of TPD maximum AII the band at 1654 cm$^{-1}$ is reduced in intensity, the absorption at 1570 cm$^{-1}$ is shifted to 1557 cm$^{-1}$, and the shoulder clearly comes out as a weak band at 1475 cm$^{-1}$.

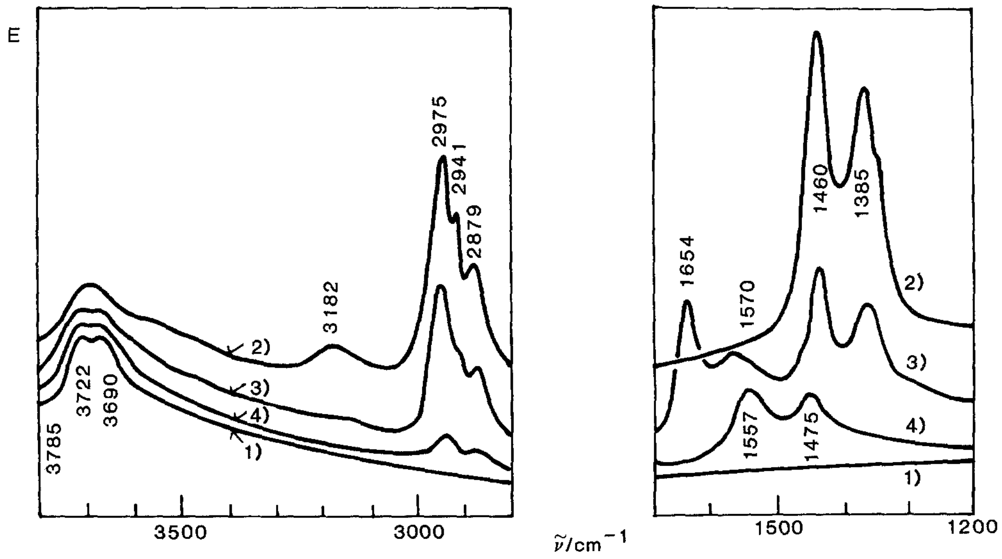


FIG. 3. Infrared spectra of $Al_2O_3$: (1) in vacuum; (2)–(4) after adsorption of diethylamine and subsequent evacuation at (2) beam temperature, (3) 553 K, (4) 773 K.

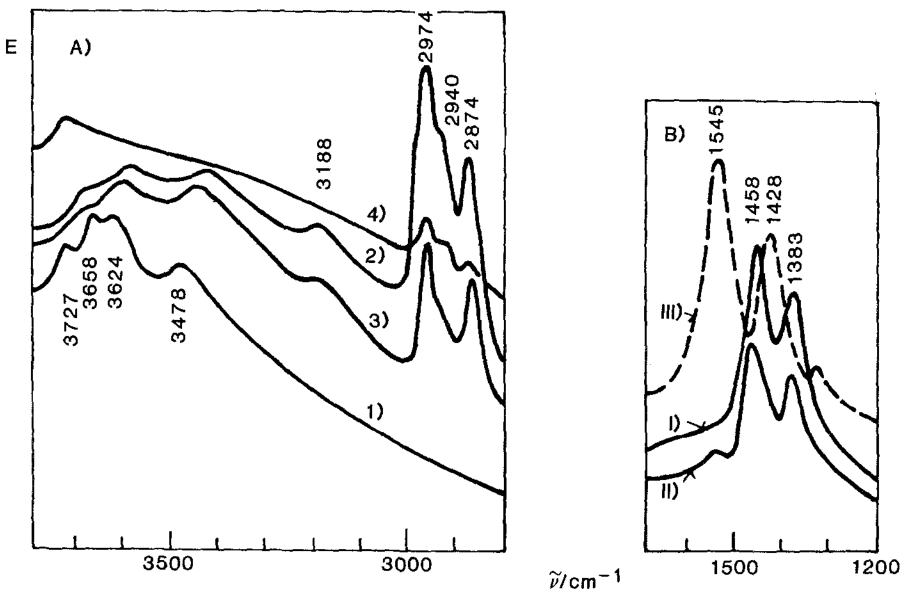


FIG. 4. (A) Infrared spectra of $Fe_2O_3$: (1) in vacuum; (2)–(4) after adsorption of diethylamine and subsequent evacuation at (2) beam temperature, (3) 473 K, (4) 523 K. (B) Difference spectra: (I) = (2)–(1); (II) = (3)–(1); (III) = (4)–(1).

(c) Heating at still higher temperatures leads to a loss of intensity of the latter two absorptions.

Figure 4 shows the infrared spectra of diethylamine adsorbed on $\alpha$-$Fe_2O_3$ ($\nu$(NH) = 3188 $cm^{-1}$). Evacuation at stepwise growing temperatures leads to a loss of intensity of all bands. After heating above 473 K a fundamental change occurs. Simultaneously with a strong overall loss of spectral transmission two new absorptions become visible at 1545 and 1428 $cm^{-1}$ which can be attributed to the antisymmetric and symmetric stretching vibrations of adsorbed acetate species (*24*). By heating at temperatures higher than ca. 573 K the sample completely loses transmission.

No special features are detectable in the case of the diethylamine/MgO system (Fig. 5; $\nu$(NH) = 3215 $cm^{-1}$), because there is only a continuous decrease of all infrared bands with increasing temperature. Using $SiO_2$ as adsorbent after evacuation at ca. 513 K only CH-bands remain, whereas the NH-stretching mode (3292 $cm^{-1}$) is no longer visible (Fig. 6).

*Triethylamine*

Because of the absence of NH-absorptions in this case the influence of the amine adsorption on the OH-bands of, e.g., $SiO_2$, can be clearly demonstrated (Fig. 7). During contact between $SiO_2$ and triethylamine vapour a broad absorption maximum appears (3400–2400 $cm^{-1}$: OH-band, shifted to lower wavenumbers by the formation of hydrogen bonds between isolated silanol groups and amino N atoms) (*26*), whereas the band of the unperturbed isolated silanol groups completely disappears. A weak absorption remains at 3673 $cm^{-1}$ which can be ascribed to laterally interacting adjacent surface hydroxy groups not involved in the adsorption process. Evacuation at beam temperature results in a decrease of the intensity of the broad absorption maximum, whereas the band of the unperturbed isolated silanol groups becomes visible again and reaches the initial intensity after

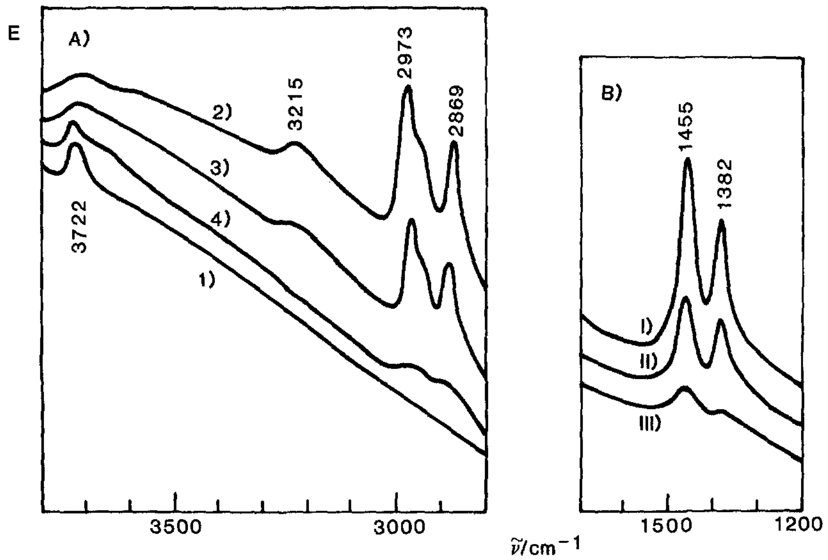


FIG. 5. (A) Infrared spectra of MgO: (1) in vacuum; (2)–(4) after adsorption of diethylamine and subsequent evacuation at (2) beam temperature, (3) 473 K, (4) 573 K. (B) Difference spectra: (I) = (2)–(1); (II) = (3)–(1); (III) = (4)–(1).

heating to 533 K (no remarkable amounts of adsorbed species remain on the $SiO_2$ surface at this temperature). The latter coincides with the already mentioned fact that the TPD spectrum of this system exhibits only one maximum.

The resemblance of the high-temperature reactions of triethylamine/oxide systems to

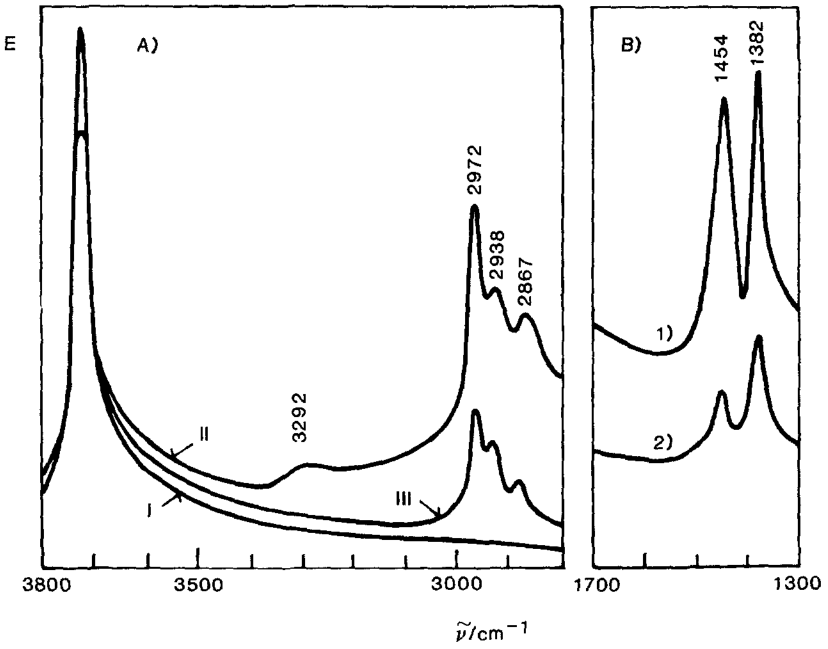


FIG. 6. (A) Infrared spectra of $SiO_2$: (I) in vacuum; after adsorption of diethylamine and subsequent evacuation at (II) beam temperature, (III) 513 K. (B) Difference spectra: (1) = (II)–(I); (2) = (III)–(I).

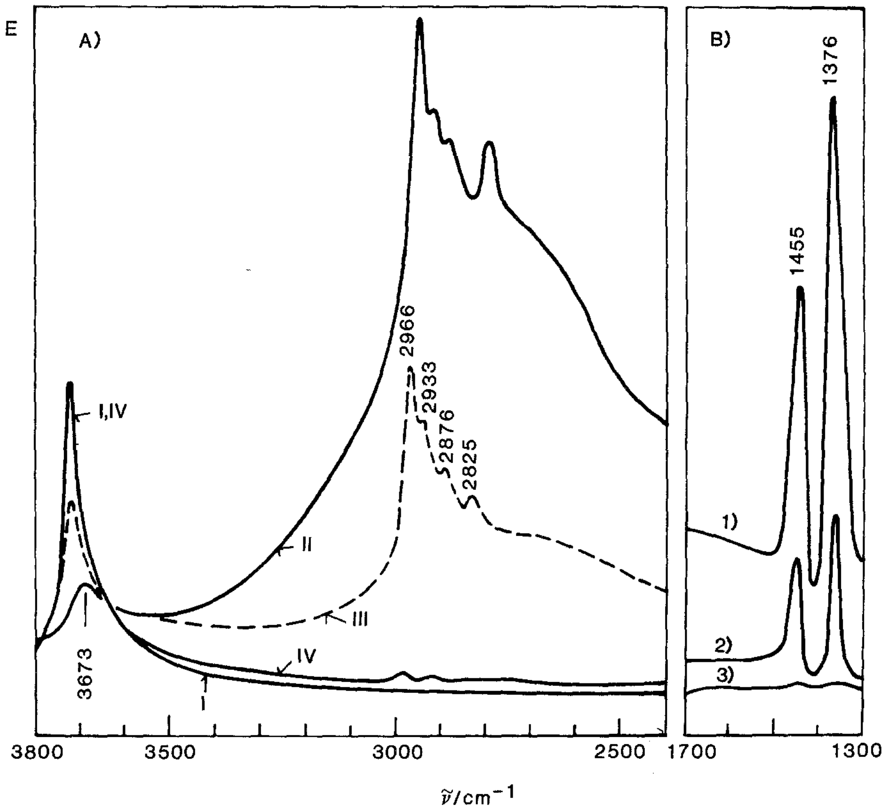


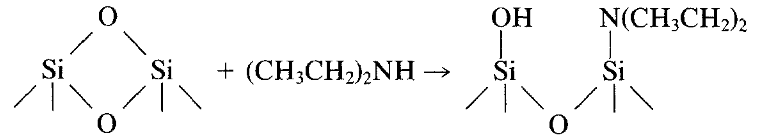
FIG. 7. (A) Infrared spectra of $SiO_2$: (I) in vacuum; (II) in contact with triethylamine vapour; after adsorption and subsequent evacuation at (III) beam temperature, (IV) 533 K. (B) Difference spectra: (1) = (II)–(I); (2) = (III)–(I); (3) = (IV)–(I).

those of diethylamine/oxide systems can also be deduced from the infrared spectra. In the case of $Al_2O_3$ at ca. 523 K a band of adsorbed imine intermediates appears (1654 cm$^{-1}$), and also two weak absorptions of adsorbed carboxylate species are detectable (1571 and 1473 cm$^{-1}$; Fig. 8). On the surface of $Fe_2O_3$ oxidation reactions occur to a great extent which cause the appearance of two strong carboxylate absorptions at 1545 and 1428 cm$^{-1}$ simultaneously with the beginning of the desorption of ethylene and acetonitrile.

## DISCUSSION

### *Diethylamine*

The infrared band of the NH-stretching vibration of diethylamine adsorbed on all the oxides studied is shifted to lower wavenumbers compared to that of the pure gaseous amine ($\nu$(NH) = 3332 cm$^{-1}$). However, this frequency shift is different in the various cases, thus testifying to the existence of different types of amine-adsorbent interactions. With $SiO_2$ the formation of hydrogen bonds between amine molecules and surface hydroxy groups is the main interaction, as can be concluded from the smallest frequency shift of the NH-band together with the simultaneity of diethylamine desorption and restoration of the unperturbed silanol band between beam temperature and ca. 513 K. This result agrees with those of already known investigations (*25*, *26*). As in the case of all other NH-containing amines (*27*) there also occurs a dissociative adsorption according to the following scheme:



(A)

(1)

In this process the active centres of $SiO_2$ are the so-called strained siloxane bridges formed by activation of the oxide in vacuum at temperatures above 673 K (*28, 29*), on which dissociative adsorption of other molecules also takes place (*30–32*). Surface complex (A) cannot be identified with certainty by infrared spectroscopy, because the only bands it shows are noncharacteristic CH-absorptions (Fig. 6, curves (3) and (II)). However, the existence of (A) can be deduced from the decomposition behaviour which is analogous to that of primary amine/$SiO_2$ systems, where a better infrared spectroscopic characterization is possible (*27*). Thus thermal decomposition of (A) begins at ca. 513 K (TPD maximum SII: reversion of the process of dissociative adsorption). At higher temperatures the remaining surface complexes are decomposed along reaction routes which include breakage of C–N and C–C bonds, and thus desorption of the already mentioned products occurs in the temperature range of TPD maximum SIII. Adsorption of diethylamine on $Al_2O_3$ causes a greater frequency shift of the NH-stretching vibration band. This means diethylamine interacts with active sites on the $Al_2O_3$ surface which are more acidic than the surface hydroxy groups of $SiO_2$. Much work has been done to characterize the nature of the surface sites of $Al_2O_3$. From this it is known that Lewis-acidic centres play an important role in adsorption processes. These centres are coordinatively unsaturated $Al^{3+}$ cations exposed on the oxide surface by dehydration of $Al_2O_3$ in vacuum at elevated temperatures. Particularly, adsorption experiments with pyridine have shown the existence of at least two types of such Lewis sites which exhibit different acidity and which are identified with coordinatively unsaturated octahedral ($\mathrm{Al}^{\mathrm{VI}}_{\mathrm{cus}}$) and tetrahedral ($\mathrm{Al}^{\mathrm{IV}}_{\mathrm{cus}}$) $Al^{3+}$ cations (*33*). $\mathrm{Al}^{\mathrm{IV}}_{\mathrm{cus}}$ act as stronger Lewis sites than $\mathrm{Al}^{\mathrm{VI}}_{\mathrm{cus}}$. This is shown by quantum-chemical investigations concerning the

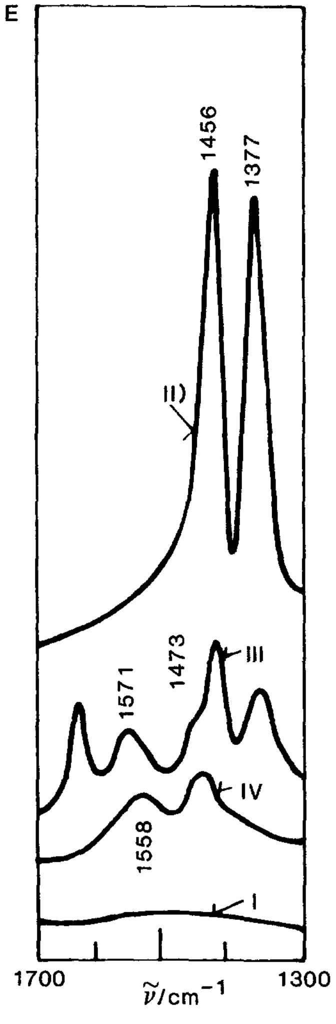


FIG. 8. Infrared spectra of $Al_2O_3$: (I) in vacuum; (II)–(IV) after adsorption of triethylamine and subsequent evacuation at (II) beam temperature, (III) 553 K, (IV) 773 K.

acid–base properties of $Al_2O_3$ (*34*), and, e.g., in the case of $NH_3$ adsorption on $Al_2O_3$ for $Al^{IV}_{cus}$ there was found a higher complex stabilization energy, a lower equilibrium value of the distance N–Al, and a higher molecule-to-surface site electron density transfer than for $Al^{VI}_{cus}$ (*35*). In principle the same conclusions can be drawn from the results gained by investigation of amine/$Al_2O_3$ interactions. Thus from weak Lewis-acidic centres desorption of unchanged diethylamine occurs causing TPD maximum AI, whereas diethylamine molecules coordinated to stronger Lewis-acid sites undergo chemical transformations leading to the desorption of reaction products (TPD maximum AII). Obviously the latter are formed by a surface reaction which is analogous to the previously found dehydrogenation of aliphatic *n*-amines (*18*) according to the following scheme:

---

$$\underset{\text{amine (a)}}{(CH_3CH_2)_2NH} \xrightarrow[-H_2]{} \underset{\text{imine (a)}}{CH_3CH_2N{=}CHCH_3} \xrightarrow[-H_2]{} \underset{\text{nitrile (g)}}{CH_3CN} + \underset{\text{olefine (g)}}{CH_2{=}CH_2} \qquad (2)$$

---

where (a) indicates adsorbed, and (g) indicates gaseous.

This proposal is strengthened by the already mentioned appearance of an infrared band at 1654 $cm^{-1}$ showing the intermediate formation of imine species. A comparison of our results with other literature data shows that the reaction products which we found in our TPD experiments disagree with those reported by Hogan and Pasek (*36*). These workers investigated the adsorption of amines on $Al_2O_3$ by TPD under a flow of helium with a chromatographic column. With diethylamine they found products of deammination (ethylene and ethylamine) and disproportionation (ethylamine and triethylamine). As in the case of *n*-butylamine (*18*) we assume that the differences are due to different experimental conditions. On the other hand, it is known that secondary amines undergo dehydrogenation reactions (formation of imines and nitriles) in contact with metal catalysts at elevated temperatures. In these systems an effective charge transfer upon chemisorption also occurs from amino N atoms to the solid (*37, 38*). Finally the weak infrared bands at 1570 and 1475 $cm^{-1}$ can be attributed to stretching vibrations of adsorbed acetate species. This assumption is supported not only by literature data (*39, 40*) but also by our own results concerning the adsorption of acetic acid on $Al_2O_3$. Moreover, the disappearance of these two bands and desorption of $CO_2$ and $H_2O$ occur simultaneously in the temperature range of TPD maximum AIII, thus showing the capability of $Al_2O_3$ to oxidize adsorbed species to a small extent.

Diethylamine adsorbed on $\alpha$-$Fe_2O_3$ shows the NH-infrared band at only slightly higher wavenumber than in the case of $Al_2O_3$, thus also indicating strong amine/oxide interactions which include electron transfer from the nitrogen atom to Lewis-acidic surface sites of $Fe_2O_3$. Most workers dealing with adsorption processes on $Fe_2O_3$ conclude that there is an interaction between the ad-molecules and one kind of Lewis-acidic surface sites of the solid (*24, 41*). Certain other authors point out that their experimental results refer to the existence of Lewis-acidic centres with different acidity (*20, 42–44*). In the corundum structure of $\alpha$-$Fe_2O_3$ all $Fe^{3+}$ ions are coordinated by six oxygen ions. Therefore on the ideally ordered (0001) face which dominates both external and micropore surfaces of the hematite samples only coordinatively unsaturated octahedral $Fe^{3+}$ ions are expected to act as Lewis-acid sites (*20*). However, taking into account more realistic circumstances, Lorenzelli and Busca (*20*) came to the conclusion that the surface may be successfully modelled by a disordered (0001) face. In such a model two types of Lewis-acidic sites may be identified. Our results also refer to the existence of Lewis centres with varying acidity on the surface of $\alpha$-$Fe_2O_3$. Thus desorption of unchanged diethylamine occurs in the temperature range of maximum FI (amine molecules were coordinated to weak Lewis acid sites), whereas molecules adsorbed on strong Lewis-acid sites undergo the same chemical transformations as in the case of $Al_2O_3$ (Eq. (2)), thus causing TPD maximum FII. Simultaneously with that desorption of reaction products two new infrared bands of adsorbed acetate species develop, indicating an extensive oxidation process. Although detailed information about the mechanism of this oxidation are not available the following general remark can be made (confirmed by the results of all other investigated amine/$Fe_2O_3$ systems): oxidation sets in at that temperature at which chemical transformations of the adsorbed amine begin and reaction products become detectable in the gas phase. This means that unstable intermediate reaction products (ions/radicals) or formed substances which can be easily oxidized are preferably included in the oxidation processes. Therefore it is not necessary to suppose the existence of an additional kind of surface centre on which oxidation proceeds, as was done by Kung *et al.* (*45*) (so-called combustion sites). Thus in the case of diethylamine the formed ethylene or its precursors (ethyl radical or ethyl ion) probably represent the main reaction partner of oxygen in forming the adsorbed carboxylate species. This can be concluded from the reduced ratio of the desorbing amounts of ethylene and acetonitrile compared to $Al_2O_3$. Since only very small amounts of gaseous oxygen are present the solid serves as a source of oxygen, and thus this process must be accompanied by reduction of the $Fe_2O_3$ sample. This is clearly seen by the loss of transmission which does not allow the measuring of infrared spectra up to those temperatures at which desorption of $CO_2$ and $H_2O$ occur. Hence it is only possible to state that a complete oxidation of adsorbed carboxylate species takes place, but intermediate stages of this process are not traceable. Finally, the higher relative intensity of TPD maximum FIII (i.e., the greater extent of oxidation reactions) compared to $Fe_2O_3$/aliphatic *n*-amine systems can be attributed to the well known fact that olefinic hydrocarbons are more easily oxidized than saturated ones (*46*).

As with the other Group II oxides, MgO has the rocksalt structure, and the morphology of its powders may be described as due to cubelets exposing the (100) face. On thoroughly outgassed samples (1073 K or higher) these faces also exhibit coordinatively unsaturated cations and anions. Literature data show the importance of both kinds of active centres on the surfaces of the alkaline earth oxides in adsorption processes: e.g., catalytic isomerization of olefins (*47*) or formation of negatively charged radicals (*49*) on basic surface centres, and bonding of interaction partners to Lewis-acidic sites (*49, 50*). Compared to $Al_2O_3$ and $Fe_2O_3$ there has been generally stated a reduced acidity (*51*) and a more pronounced basic character (*52*) of the corresponding surface centres. To define more closely the nature of the active sites diffuse reflectance and photoluminescence spectroscopies have been used (*53*), and the results were related to three families of surface cation–anion pairs. These sites exhibit different degrees of acidity and basic character, respectively. Because of the basic nature of amines the interaction of diethylamine preferentially takes place with Lewis-acidic centres on the MgO surface. These coordination bonds are weaker than those in the case of $Al_2O_3$ and $Fe_2O_3$ (NH-stretching vibration band of adsorbed diethylamine appears at a higher wavenumber). According to the above mentioned literature data the TPD spectrum shows the existence of different adsorption centres, although a more detailed identification of these surface sites is impossible on the basis of our experimental results. It can only be stated that mainly weak Lewis-acid centres exist from which desorption of unchanged diethylamine occurs (TPD maximum MI), whereas minor amounts of amine molecules coordinatively bonded to more acidic surface sites undergo the same chemical transformations (TPD maximum MII) as in the case of adsorption on strong Lewis-acid centres of $Al_2O_3$ and $Fe_2O_3$ (Eq. (2)).

*Triethylamine*

The reactions which are initiated at elevated temperatures during the TPD runs show that also with triethylamine coordination bonds are formed between N-atoms of the amine molecules and Lewis-acidic centres on the oxide surfaces (with the exception of $SiO_2$). Thus considering the distribution of the desorption products and the appearance of a (C=N)-infrared band it is possible to conclude that triethylamine bonded to strong Lewis-acid sites on $Al_2O_3$ undergo the same chemical transformations as those in the case of diethylamine:

$$\begin{array}{l} \underset{\text{amine (a)}}{(CH_3CH_2)_3N} \xrightarrow[-H_2]{} \underset{\text{olefine (g)}}{CH_2{=}CH_2} + \underset{\text{imine (a)}}{CH_3CH_2N{=}CHCH_3} \\ \qquad \underset{\text{imine (a)}}{CH_3CH_2N{=}CHCH_3} \xrightarrow[-H_2]{} \underset{\text{olefine (g)}}{CH_2{=}CH_2} + \underset{\text{nitrile (g)}}{CH_3CN} \end{array} \tag{3}$$

Temperature-programmed desorption maximum MII of the triethylamine/MgO system is not only formed by the desorption of reaction products but also by unchanged triethylamine. This means that not all of the amine molecules adsorbed on the stronger Lewis acid sites of MgO are decomposed with formation of ethylene and acetonitrile. This phenomenon refers to a possible influence of steric effects on the adsorption and reaction behaviour. Such steric effects are held responsible for the hindrance of dissociative adsorption of tertiary amines on strained siloxane bridges of $SiO_2$, too (*28*). Our results also show that dissociative adsorption of triethylamine did not occur on $SiO_2$, because the two high-temperature TPD maxima are absent (SII and SIII in the case of diethylamine). However, we believe that this is at least partially due to a higher activation energy required for the CN bond breakage than that required for the NH bond breakage (*54*, *55*).

As the presented results show, adsorption and reaction behaviour of triethylamine on $Fe_2O_3$ is similar to that of diethylamine. The higher relative intensity of TPD maximum FIII (compared to diethylamine) confirms the above mentioned assumption that ethylene represents the main reaction partner of oxygen in forming adsorbed carboxylate species, because two ethylene molecules are evolved per each molecule of triethylamine in the nitrile forming reaction (Eq. (3)).

## REFERENCES

1. Meakins, R. J., *J. Appl. Chem.* **13,** 339 (1963).
2. Schlerkmann, H., and Schmitt, G., *Werkst. Korr.* **36,** 216 (1985).
3. Hackermann, N., and Macrides, A. C., *Ind. Eng. Chem.* **46,** 523 (1954).
4. Tezuka, M., Tomoe, Y., and Fujii, S., *in* "Proceedings of the 5th European Symposium on Corrosion Inhibitors, Ferrara, 1980," p. 501.
5. Raicheva, S., Sokolova, E., and Goulamali, M., *Dokl. Bolg. Akad. Nauk* **39,** 85 (1986).
6. Foroulis, Z. A., *Werkst. Korr.* **33,** 121 (1982).
7. Bali, J., Viniczai, L., Mueller, V., Bececzki, V., Nagypataki, G., Isaak, G., Olar, P., Gemes, I., Simov, L., and Kocsis, Z., *Hung. Teljes HU* **34,** 558 (1985).
8. Horner, L., and Pliefke, E., *Werkst. Korr.* **33,** 98 (1982).

9. Fouda, A. S., Madkour, L. H., and Soliman, L. S., *Bull. Soc. Chim. Fr.*, 358 (1986).
10. Gütlich, P., Meysel, W., and Mohs, E., *Werkst. Korr.* **33,** 35 (1982).
11. Frignani, A., Trabanelli, G., Zucchi, F., and Zucchini, M., *in* "Proceedings of the 5th European Symposium on Corrosion Inhibitors, Ferrara, 1980."
12. Treybig, D. S., and Glass, T. W., *Eur. Pat. Appl. EP* **156,** 631 (1985).
13. Yoshida, E., and Sekimoto, M., *Japan Kokai Tokkyo Koho JP* **60,** 250,091 (1985).
14. Sokoll, R., and Hobert, H., *Z. Phys. Chem. (Leipzig)* **267,** 241 (1986).
15. Sokoll, R., and Hobert, H., *Z. Phys. Chem. (Leipzig)* **267,** 321 (1986).
16. Sokoll, R., and Hobert, H., *J. Chem. Soc. Faraday Trans. 1* **82,** 1527 (1986).
17. Marx, U., Sokoll, R., and Hobert, H., *J. Chem. Soc. Faraday Trans. 1* **82,** 2505 (1986).
18. Sokoll, R., Hobert, H., and Schmuck, I., *J. Chem. Soc. Faraday Trans. 1* **82,** 3391 (1986).
19. Rochester, C. H., and Topham, S. A., *J. Chem. Soc. Faraday Trans. 1* **75,** 59 (1979).
20. Lorenzelli, V., and Busca, G., *Mater. Chem. Phys.* **13,** 261 (1985).
21. Wimmers, O. J., Arnoldy, P., and Moulijn, J. A., *J. Phys. Chem.* **90,** 1331 (1986).
22. Rochester, C. H., and Topham, S. A., *J. Chem. Soc. Faraday Trans. 1* **75,** 1073 (1979).
23. Bellamy, L. J., "The Infrared Spectra of Complex Molecules." Methuen, London, 1958.
24. Rochester, C. H., and Topham, S. A., *J. Chem. Soc. Faraday Trans. 1* **75,** 1259 (1979).
25. Child, M. J., Heywood, M. J., Yong, G. H., and Rochester, C. H., *J. Chem. Soc. Faraday Trans. 1* **78,** 2005 (1982).
26. Basila, M. R., *J. Chem. Phys.* **35,** 1151 (1961).
27. Rudakoff, G., Sokoll, R., Hobert, H., and Schmuck, I., *Z. Chem.* **27,** 150 (1987).
28. Morrow, B. A., and Cody, I. A., *J. Phys. Chem.* **80,** 1995 (1976).
29. Boccuzzi, F., Coluccia, S., Ghiotti, G., Morterra, C., and Zecchina, A., *J. Phys. Chem.* **82,** 1298 (1978).
30. Morrow, B. A., and Devi, A., *J. Chem. Soc. Faraday Trans. 1* **68,** 403 (1972).
31. Morrow, B. A., and Cody, I. A., *J. Phys. Chem.* **79,** 761 (1975).
32. Marx, G., and Fink, P., *Wiss. Zeitschr. Friedrich-Schiller-Univ. Jena* **26,** 743 (1977).
33. Morterra, C., Chiorino, A., Ghiotti, G., and Garrone, E., *J. Chem. Soc. Faraday Trans. 1* **75,** 271 (1979).
34. Kawakami, K., and Yoshida, S., *J. Chem. Soc. Faraday Trans. 2* **81,** 1129 (1985).
35. Fleisher, M. B., Golender, L. O., and Shimanskaja, M. V., *React. Kinet. Catal. Lett.* **24,** 25 (1984).
36. Hogan, P., and Pasek, J., *Collect. Czech. Chem. Commun.* **39,** 3696 (1974).
37. Layer, R. W., *Chem. Rev.* **63,** 489 (1963).
38. Klostermann, K., Dissertation B, Jena, 1979.
39. Greenler, R. G., *J. Chem. Phys.* **37,** 2094 (1962).
40. Krietenbrink, H., and Knözinger, H., *Z. Phys. Chem. N.F.* **102,** 43 (1976).
41. Benzinger, J. B., and Larson, L. R., *J. Catal.* **77,** 550 (1982).
42. Busca, G., and Lorenzelli, V., *Mater. Chem.* **6,** 175 (1981).
43. Busca, G., and Lorenzelli, V., *J. Chem. Soc. Faraday Trans. 1* **78,** 2911 (1982).
44. Busca, G., Lorenzelli, V., Zerlia, T., and Girelli, A., *J. Catal.* **88,** 131 (1984).
45. Kung, M. C., Cheng, W. H., and Kung, H. H., *J. Phys. Chem.* **83,** 1737 (1979).
46. Stein, K. C., Feenan, J. J., Thompson, G. P., Shultz, J. F., Hofer, L. J. E., and Anderson, R. B., *Ind. Eng. Chem.* **52,** 671 (1960).
47. Kawakami, K., and Yoshida, S., *J. Chem. Soc. Faraday Trans. 1* **80,** 921 (1984).
48. Morris, R. M., Kaba, R. A., Groshens, T. G., Klabunde, K. J., Baltisberger, R. J., Woolsey, N. F., and Steenberg, V. T., *J. Amer. Chem. Soc.* **102,** 3419 (1980).
49. Koubowetz, F., Noller, H., and Latzel, J., *Z. Naturforsch. B* **31,** 922 (1976).
50. Zecchina, A., and Stone, F. S., *J. Catal.* **101,** 227 (1986).
51. Lercher, J. A., Colombier, Ch., and Noller, H., *Z. Phys. Chem. N.F.* **131,** 111 (1982).
52. Vinek, H., *Z. Phys. Chem. N.F.* **120,** 119 (1980).
53. Zecchina, A., Coluccia, S., and Morterra, C., *Appl. Spectrosc. Rev.* **21,** 259 (1985).
54. Sheets, R. W., and Blyholder, G., *J. Catal.* **67,** 308 (1981).
55. Inamura, K., Inoue, Y., and Ikeda, S., *Surf. Sci.* **155,** 173 (1985).