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

II. Isopropylamine and Cyclohexylamine

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The adsorption of isopropylamine and cyclohexylamine on Al_2O_3 and Fe_2O_3, and of isopropylamine on SiO_2, MgO, and CaO has been studied by infrared spectroscopy and temperature-programmed desorption (TPD). Surface complexes are formed at beam temperature as a result of hydrogen bonding and dissociative adsorption on SiO_2, and formation of coordination bonds between amine molecules and Lewis-acidic surface sites on the other oxides. With increasing temperature during TPD, in addition to the unchanged amines, products desorb, which indicates the occurrence of C–N bond breakage and dehydrogenation reactions.

INTRODUCTION

In Part I we reported on the adsorption of diethylamine and triethylamine at the oxide/vapour interfaces (*1*). We studied the infrared (IR) spectra of the surface complexes formed at beam temperature, and by temperature-programmed desorption (TPD), the chemical transformations of the adsorbed amine molecules with increasing temperature. We considered the nature of the oxide surface centres on which these reactions occur, having regard also to results from various experimental techniques already published in the literature. For aliphatic amines in which the N atom is attached to a primary carbon atom (e.g., *n*-butyl-, diethyl-, triethylamine), the main high-temperature reaction on oxides possessing Lewis-acidic surface centres is the formation of the corresponding nitriles (e.g., butyronitrile, acetonitrile) by dehydrogenation only (*n*-butylamine) or dehydrogenation and dealkylation (di-, triethylamine). Knowing this, we were interested in studying amines in which the amino group is located on a secondary carbon atom, and we report here results for isopropylamine and cyclohexylamine.

EXPERIMENTAL

Oxides were obtained in different ways: CaO (MgO) by vacuum decomposition (1023 K, $1 \cdot 10^{-3}$ Pa) of pressed disks of $CaCO_3$ ($MgCO_3$); α-Fe_2O_3 also by vacuum decomposition (573 K, $1 \cdot 10^{-3}$ Pa) of pressed disks of goethite (α-FeOOH, prepared from $Fe(NO_3)_3 \cdot 9H_2O$); Al_2O_3 and SiO_2 were commercially available products (Aluminiumoxid C: mixed ($\delta + \gamma$) phase, Aerosil 300; both from Degussa). The amines were purified by distillation and degassed immediately before use in the adsorption experiments.

Infrared spectra were recorded in the range 4000–1200 cm^{-1} by a Specord 75 IR spectrometer (VEB Carl Zeiss, Jena) coupled with a KRS 4200 computer (VEB Robotron). For monitoring the desorption and identification of the desorption products, a CH8 mass spectrometer (Varian Mat) was connected to the TPD apparatus. Samples were initially activated under vacuum ($p = 1 \times 10^{-3}$–6×10^{-4} Pa) for 2 h: SiO_2, Al_2O_3

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TABLE 1

Wavenumbers (cm^{-1}) of Infrared Bands of Gaseous Isopropylamine, Isopropylamine after Adsorption on Oxides at Beam Temperature, and Adsorbed Reaction Products Formed at Elevated Temperatures

Gaseous isopropylamine	Wavenumber (cm^{-1})					Assignment
	SiO_2	CaO	MgO	Fe_2O_3	Al_2O_3	
—	3550	—	—	—	—	$\nu_{as}(NH_2)^a$
—	3450	—	—	—	—	$\nu_s(NH_2)^a$
—	3423[b]	—	—	—	—	ν(NH)/sec. amine
3429	3356	3326	3322	3310	3308	$\nu_{as}(NH_2)$
3332	3291	3256	3248	3223	3211	$\nu_s(NH_2)$
3196	—	3140	3128	3126	3113	$2\delta(NH_2)$
—	—	1656	1652	—	1654	ν(C=N)/imine
1616	1588	1590	1588	1579	1576	$\delta(NH_2)$
—	—	—	—	1544	1560	$\nu_{as}(COO^-)$
—	1550	—	—	—	—	$\delta(NH_2)^a$
—	—	—	—	1436	1474	$\nu_s(COO^-)$

[a] Surface NH_2 groups.

[b] ν(NH), which seems high relative to that of a secondary amine in the gas phase; however, literature data (IR spectra of compounds R_3SiNHR' (*16, 17*)) show that such high values can be observed if NH groups are attached to Si.

at 973 K; MgO, CaO at 1023 K; Fe_2O_3 at 573 K for IR and 738 K for TPD (lower for IR because during vacuum treatment at $T >$ 573 K, reduction of Fe_2O_3 to Fe_3O_4 begins to cause a dramatic loss of IR transparency). All other experimental conditions and procedures were the same as those in Part I (*1*).

RESULTS

Tables 1 and 3 summarize the wavenumbers of the NH infrared bands of both amines investigated after adsorption on the various oxides and subsequent evacuation at beam temperature, as well as the bands of adsorbed reaction products formed at elevated temperatures. Therefore, only the most important infrared spectra are cited in the text. The main desorption products and the temperatures of their desorption maxima are given in Tables 2 and 4.

Isopropylamine

In the main, the shapes of the TPD curves of isopropylamine/oxide systems (Fig. 1) are similar to those of the *n*-butylamine, diethylamine/oxide systems (*1–3*). The first maximum in each case (SI, AI, FI, MI) is again caused by desorption of the unchanged amine. However, essential differences from amines in which the N atom is attached to a primary carbon can be de-

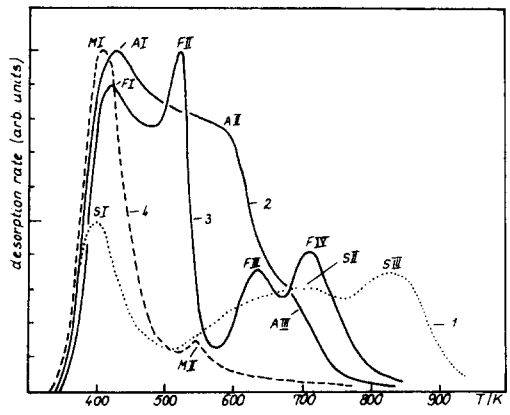


FIG. 1. Thermal desorption curves of the isopropylamine/oxide systems. (1) SiO_2, (2) Al_2O_3, (3) Fe_2O_3, (4) MgO.

TABLE 2

Desorption Products Obtained after Adsorption of Isopropylamine on Oxides

Desorption product	Temperature of the desorption maximum (K)				
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO
Isopropylamine	403 703	433	423	413	413
Propylene	803	588	523	—	—
Ammonia	—	588 (658)	523	—	—
Acetone	—	(588)	523	—	—
Propadiene	—	(658)	—	—	—
Acetonitrile	843	698	—	548	548
Methane	843	698	—	548	548
Hydrogen cyanide	883	—	—	—	—
Water	—	—	638 (708)	—	—
Carbon dioxide	—	—	638 708	—	—

Note. Parentheses signify product present only in small amount.

tected in desorption products evolved at higher temperatures (Table 2). Thus, in the case of Al_2O_3, the infrared band at 1654 cm^{-1} (ν(C=N) of adsorbed imine species; ν(NH) cannot be detected because of its small intensity) which appears after heating at ca. 553 K (Fig. 2) indicates a partial dehydrogenation of isopropylamine molecules coordinatively bonded to strong Lewis acid sites on the solid surface, but the main desorption products (Fig. 1) are propylene and NH_3 (TPD maximum AII) and methane and acetonitrile (TPD maximum AIII). The vital point is that formation of imine species begins already at ca. 553 K, but, contrary to *n*-amines, for instance, their thermal degradation only occurs between 653 and 753 K (TPD maximum AIII). After heating at 753 K, two weak infrared bands of carboxylate species remain visible (1560, 1474 cm^{-1}, Fig. 2) which indicate that Al_2O_3 is capable of oxidizing small amounts of adsorbed hydrocarbons (e.g., see Ref. (*4*)).

In addition to contributions from propylene and NH_3 (as in the case of Al_2O_3) the TPD maximum FII of the system isopropylamine/Fe_2O_3 is caused by the desorption of marked amounts of acetone. This is the only case of all the investigated amine/Fe_2O_3 systems in which an oxidation prod-

TABLE 3

Wavenumbers (cm^{-1}) of Infrared Bands of Gaseous Cyclohexylamine, Cyclohexylamine after Adsorption on Oxides at Beam Temperature, and Adsorbed Reaction Products Formed at Elevated Temperatures

Wavenumber (cm^{-1})			Assignment
Gaseous cyclohexylamine	Al_2O_3	Fe_2O_3	
3395	3304	3310	$\nu_{as}(NH_2)$
3324	3213	3216	$\nu_s(NH_2)$
—	3102	3122	$2\delta(NH_2)$
—	3064	3062	ν(=CH)/aniline
—	3032	3025	ν(=CH)/aniline
—	1648	—	ν(C=N)/imine
—	1589	1575	ν(C=C)/aniline
1614	1574	1578	$\delta(NH_2)$
—	1486	1474	ν(C=C)/aniline

TABLE 4

Desorption Products Obtained after Adsorption of Cyclohexylamine on Oxides

Desorption product	Temperature of the desorption maximum (K)	
	Al_2O_3	Fe_2O_3
Cyclohexylamine	433	423
Ammonia	598	513
Cyclohexene	598	513
Cyclohexanone	—	523
1,3-Cyclohexadiene	(653)	—
Propylene	—	513
Aniline	673	533
Water	—	533 698
Carbon dioxide	—	718

Note. Parentheses signify product present only in small amount.

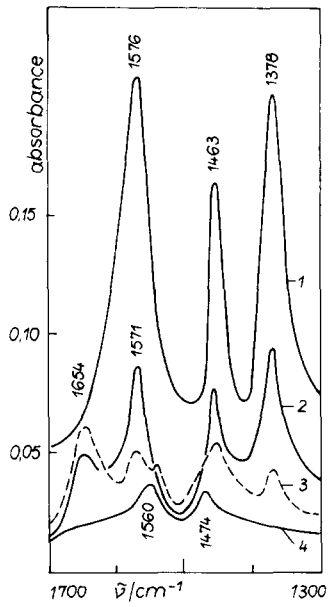


FIG. 2. Infrared spectra of Al_2O_3 after adsorption of isopropylamine from the vapour phase and subsequent evacuation at (1) beam temperature, (2) 558 K, (3) 628 K, (4) 753 K.

uct different from CO_2 and H_2O desorbs. The infrared spectra are characterized mainly by the NH_2 bands listed in Table 1, and with the beginning of the above-mentioned desorption of reaction products (ca. 463 K) formation of adsorbed carboxylate species can be detected (bands at 1544 and 1436 cm^{-1}), together with a progressive loss in overall spectral transmission.

For MgO, there is desorption of unchanged isopropylamine (TPD maximum MI). In the maximum MII temperature range, only acetonitrile and methane could be detected as gaseous reaction products (also by the use of CaO as adsorbent). This is surprising because in most other amine/oxide systems the same main reaction products are formed on all oxides possessing Lewis-acidic surface centres. Therefore in this system, breakage of C–C bonds seems to be favoured against breakage of C–N bonds. Infrared spectra recorded after adsorption of isopropylamine and evacuation at ca. 523 K show, in addition to CH absorptions, only bands at 1652 cm^{-1} (MgO) and 1656 cm^{-1} (CaO), respectively, of imine species; NH_2 bands of adsorbed unchanged amine are no longer visible.

After adsorption of isopropylamine on SiO_2 and subsequent evacuation at beam temperature, the infrared spectrum shows bands of both hydrogen-bonded (3356, 3291, 1588 cm^{-1}; the broad absorption of perturbed SiOH groups is situated in the 2800- to 3000-cm^{-1} range, but is overlapped by CH bands) and dissociatively adsorbed (3423, 1402 cm^{-1}) amine molecules (Fig. 3). These bands successively disappear with increasing temperature, and in the TPD maximum SIII temperature range (803–903 K) three new absorptions become visible at ca. 3550, 3450, and 1550 cm^{-1} (Fig. 3, curves 5 and d). In accordance with published data (*5, 6*), the latter phenomena indicate the formation of surface NH_2 groups ($\equiv$Si–NH_2). These results of the system isopropylamine/SiO_2 have been discussed in an earlier publication (*7*).

Cyclohexylamine

In this case only Al_2O_3 and Fe_2O_3 were used as adsorbents. The fundamental reaction behavior of cyclohexylamine mole-

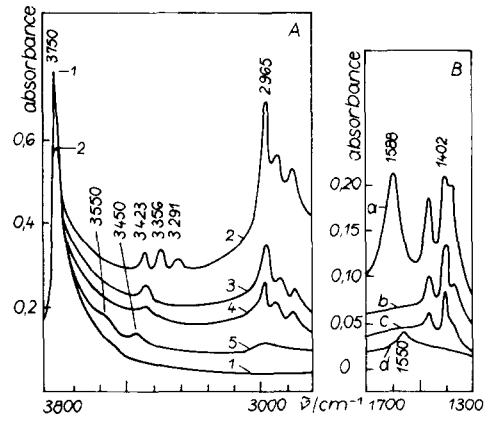


FIG. 3. (A) Infrared spectra of isopropylamine/SiO_2: (1) SiO_2 under vacuum; (2 to 5) after adsorption of isopropylamine from the vapour phase and subsequent evacuation at (2) beam temperature; (3) 513 K; (4) 743 K; (5) 923 K. (B) Difference spectra: (a) = (2) − (1), (b) = (3) − (1), (c) = (4) − (1), (d) = (5) − (1).

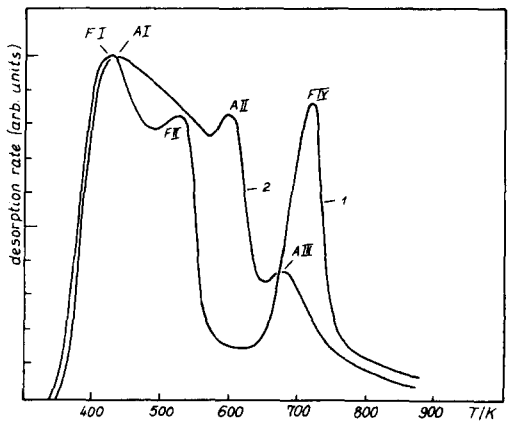


FIG. 4. Thermal desorption curves of the cylohexylamine/oxide systems. (1) Fe_2O_3; (2) Al_2O_3.

cules coordinatively bonded to strong Lewis acid sites of Al_2O_3 manifests itself by the desorption mainly of NH_3, cyclohexene (TPD maximum AII) and aniline (TPD maximum AIII; Fig. 4, Table 4). From the infrared spectra it can be seen that desorption of exclusively unchanged cyclohexylamine up to ca. 533 K is accompanied only by a reduction in the intensity of all bands (Fig. 5). With the beginning of NH_3 and cyclohexene desorption, a new absorption appears at 1648 cm^{-1} (ca. 553 K) which first becomes stronger (573 K) and then disappears in the TPD maximum AII temperature range, together with the residual NH_2 bands of unchanged amine. Finally, desorption of aniline causing TPD maximum AIII can obviously be connected with the relatively weak infrared bands which appear after heating to 633 K, because the latter are almost completely identical to those of aniline adsorbed on Al_2O_3 (Ref. (*8*), Fig. 5B).

The high-temperature behavior of the system cyclohexylamine/Fe_2O_3 is determined by the aniline formation reaction to a much higher degree. This can be clearly seen from the infrared spectra (Fig. 6). Already after heating at ca. 493 K all absorptions of adsorbed unchanged cyclohexylamine disappeared, whereas the series of newly formed bands (3062, 3025, 1575, 1474, 1245 cm^{-1}) can be attributed to adsorbed aniline, compared to those of the system aniline/Fe_2O_3 after evacuation at 493 K (3061, 3023, 1575, 1472, 1243 cm^{-1}) (*8*). This is confirmed by desorption of aniline, which shows a maximum at ca. 533 K. Simultaneously with this process of aniline formation and desorption, a strong loss in overall spectral transmission occurs, thus hindering the recording of additional IR spectra at still higher temperatures. This loss in IR transparency is attributed to the change in the composition of the Fe_2O_3 sample toward that of magnetite, caused by

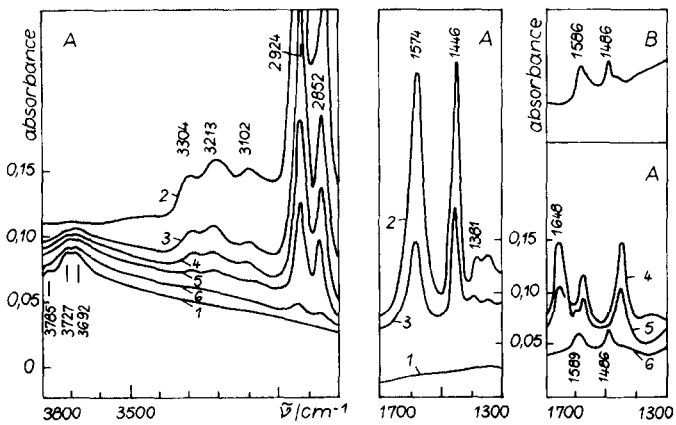


FIG. 5. (A) Infrared spectra of cyclohexylamine/Al_2O_3: (1) Al_2O_3 under vacuum; (2 to 6) after adsorption of cyclohexylamine from the vapour phase and subsequent evacuation at (2) beam temperature; (3) 533 K; (4) 553 K; (5) 573 K; (6) 633 K. (B) Infrared spectrum of Al_2O_3 after adsorption of aniline from the vapour phase and subsequent evacuation at 603 K.

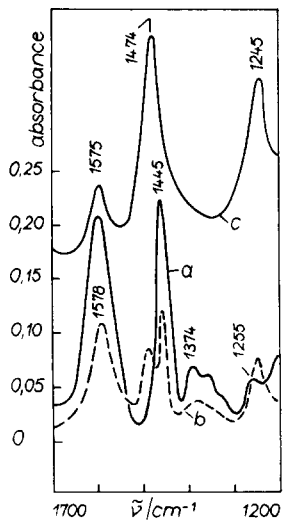


FIG. 6. Infrared spectra of cyclohexylamine/Fe_2O_3. Spectra were measured of (1) Fe_2O_3 under vacuum; (2, 3, 4) after adsorption of cyclohexylamine from the vapour phase and subsequent evacuation at (2) beam temperature; (3) 473 K; (4) 513 K. Curves shown are the difference spectra: (a) = (2) − (1), (b) = (3) − (1), (c) = (4) − (1).

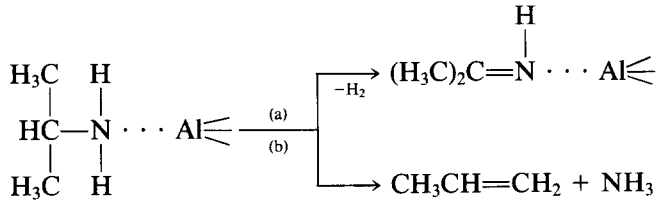
the occurrence of oxidation reactions on the solid surface (formation of cyclohexanone; hydrogen evolved in great amounts by dehydrogenation of cyclohexylamine (*5*) reacts with lattice oxygen, causing strong desorption of H_2O at 533 K). In addition, desorption of NH_3 begins at ca. 473 K, indicating that breakage of NH bonds occurs (main reaction in the case of Al_2O_3). As complementary products, cyclohexanone and propylene, as well as small amounts of cyclohexene, can be detected in the gas phase.

DISCUSSION

The results for adsorption of both isopropylamine and cyclohexylamine at beam temperature are broadly similar to those for *n*-butylamine (*2, 3*) or diethylamine (*1*). There occur hydrogen bonding between amines and surface hydroxy groups (mainly on SiO_2; partly on the other oxides), dissociative adsorption (on SiO_2 only), and formation of coordinative bonds between amines and Lewis sites of different acidity (on Al_2O_3, Fe_2O_3, MgO, CaO). The following discussion therefore concentrates upon the high-temperature behaviour of the amine/oxide systems.

Isopropylamine

Due to the structure of isopropylamine, formation of nitrile is not possible on strong Lewis acid sites without breakage of C–C bonds. This is clearly seen from the desorption products of the isopropylamine/Al_2O_3 system between 553 and 753 K (TPD maxima AII, AIII; Table 2). In principle there are two ways to interpret the IR results as regards reaction mechanism. Thus, formation of imine species on the Al_2O_3 surface is indicated by a new C=N absorption at 1654 cm^{-1}, the intensity of which first is considerably smaller than those of the $\delta(NH_2)$ of adsorbed unchanged isopropylamine (at 558 K: Fig. 2, curve 2)). Heating to temperatures higher than 588 K (maximum of the NH_3, propylene desorption) causes an increase in the intensity of the imine absorption, whereas the intensity of $\delta(NH_2)$ is strongly reduced (at 628 K; Fig. 2, curve 3). From this it is possible to conclude that two reactions occur in the temperature range of the maximum AII which, both starting from amine molecules bonded to strong Lewis acid sites, lead to the desorption of propylene and NH_3 by C–N bond breakage and to the formation of adsorbed imine species (dehydrogenation), respectively:

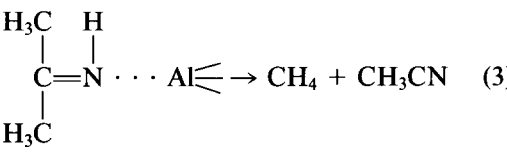


(1)

On the other hand, Sedlaček and Koubek (*9*) from their work on the reaction of isopropylamine on Al_2O_3 at ca. 573 K derived a reaction scheme which also would be consistent with our infrared and TPD results:

$$\begin{aligned}(CH_3)_2CHNH_2 &\rightarrow (CH_3)_2C{=}NH + H_2\\ (CH_3)_2C{=}NH + (CH_3)_2CHNH_2 &\rightarrow (CH_3)_2C = NCH(CH_3)_2 + NH_3 \qquad (2)\\ (CH_3)_2C{=}NCH(CH_3)_2 &\rightarrow (CH_3)_2C{=}NH + CH_3CH{=}CH_2.\end{aligned}$$

However, for the latter a permanent excess of amine would be necessary on the oxide surface, and this is not realized in our experiments (TPD runs start after adsorption and subsequent evacuation for several hours at room temperature). In the temperature range of TPD maximum AIII, desorption of acetonitrile and methane implies the occurrence of still another reaction. The IR spectra show that the band at 1654 cm^{-1} completely disappears during this desorption (743 K; Fig. 2, curve 4). That means the process starts from adsorbed imine species:



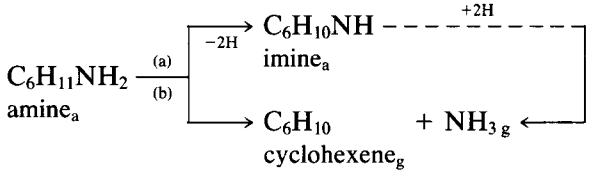
On Fe_2O_3 the same main reaction occurs as in the case of Al_2O_3, because desorption of propylene and NH_3 can be detected in the TPD maximum FII temperature range (according to Eq. (1b)). However, neither formation of imine species nor the desorption reaction (Eq. (3)) is observable. As already mentioned, the TPD maximum FII is also caused by the desorption of acetone in considerable amounts. This phenomenon shows that oxidation which in the case of amines with NH_2 groups located on a primary carbon atom leads to the formation of adsorbed carboxylate species chiefly stops at the stage of ketone by the use of isopropylamine, because C–C bond breakage would be necessary to continue this reaction (*10*). However, it must be noted that small amounts of carboxylate species are formed, too, which cause desorption of CO_2 and H_2O (TPD maxima FIII, FIV), but no further information is available regarding this reaction. The only reaction which can be detected in the systems isopropylamine/MgO(CaO) becomes apparent by the desorption of acetonitrile and methane in the temperature range of TPD maximum MII(CII). The reaction pathway should be describable by a scheme consisting of Eq. (1a) followed by Eq. (3), because adsorbed imine intermediates can be detected. The dominance of these reactions on alkaline earth oxides (contrary to Al_2O_3 and Fe_2O_3) possibly results from their more pronounced basic character, i.e., the higher negative charge on the lattice oxygen atoms (*11*). Methyl groups of isopropylamine molecules coordinatively bonded to the relatively weak Lewis-acidic centres of MgO and CaO are in closer proximity to the oxide surface than those in the case of *n*-amines. Therefore, a secondary interaction is possible between methyl groups and surface oxygen, which becomes stronger with increasing basic character of the oxide, and thus may be the reason for a favoured breakage of C–C bonds in comparison with C–N bond breakage.

Dissociative adsorption of isopropylamine at beam temperature (as in the well-known case of NH_3 adsorption) leading to NH_2 species on MgO could not be detected.

Cyclohexylamine

Comparable with isopropylamine, the main high-temperature reaction of the system cyclohexylamine/Al_2O_3 consists of C–N bond breakages of amine molecules coor-

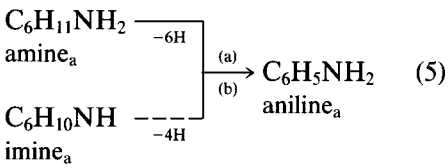
dinatively bonded to strong Lewis acid sites. This is shown by the desorption of cyclohexene and NH_3. Contrary to isopropylamine these two products seem to be formed from both adsorbed cyclohexylamine molecules and imine intermediates, because the IR bands of both species completely disappear in the temperature range of the corresponding TPD maximum. Moreover, no additional decomposition products of the adsorbed imine species (acetonitrile and methane in the case of isopropylamine) are detectable. Possibly the two missing H atoms for the proposed chemical transformation of imine species come from dehydrogenation to aniline, which starts in this temperature range. Therefore a reaction scheme similar to Eq. (1) can be formulated,



(4)

where the subscripts a and g indicate adsorbed and gaseous, respectively.

In spite of the lack of detailed experimental results, participation of both amine and imine species must be taken into consideration in the undoubtedly detected formation of adsorbed aniline:



(5)

Occurrence of reaction (5) is not surprising; other authors also report such dehydrogenations of cyclic substances on oxides (*12, 13*) and metals (*14, 15*) at elevated temperatures.

In the case of the system cyclohexylamine/Fe_2O_3, dehydrogenation according to Eq. (5a) represents the main high-temperature reaction. This can be concluded from both the very intense IR bands and the strong desorption of aniline, as well as the appearance of only one TPD maximum (FIV, 718 K) of CO_2 and H_2O (oxidation of aromatic amines on Fe_2O_3 causes desorption of CO_2 and H_2O mainly in this temperature range, as will be described in a later publication). The second reaction, indicated by the desorption of NH_3 (according to Eq. (4b)) cannot be so clearly documented because only small amounts of cyclohexene desorb. However, in the TPD maximum FII temperature range, desorption of cyclohexanone and propylene occurs, too. Therefore the assumption can be made that the cyclohexene formed is mainly oxidized, but the oxidation stops at the stage of ketone, as was already discussed in the case of isopropylamine. Desorption of a little propylene shows that C–C bond breakage also occurs to a small extent, but IR bands of carboxylate species as another possible result of this process are not detectable. This can be due to the appearance of strong absorption of formed aniline and the resulting loss in overall spectral transmission (Fig. 6).

CONCLUSIONS

Adsorption of isopropylamine and cyclohexylamine on oxides results in the formation of the same surface complexes at beam temperatures as those formed in the case of diethylamine (*1*). However, when amines in which the NH_2 group is located on a secondary carbon atom are used, other surface reactions occur with increasing temperature. Thus, formation of the corresponding nitriles on oxides possessing Lewis-acidic surface centres is not possible

without breakage of C–C bonds. Therefore, chemical transformations dominate which include cleavage of C–N bonds leading to the desorption of NH_3 and the corresponding olefins (propylene and cyclohexene, respectively). In the case of isopropylamine, when compared to diethyl- and triethylamine, further differences are the formation of methane and acetonitrile via dehydrogenation and C–C bond breakage at higher temperature (on Al_2O_3, CaO, MgO) and desorption of acetone as the main oxidation product (on Fe_2O_3). Similar reactions occur using cyclohexylamine. However, in the latter case aniline is also formed by dehydrogenation. Thus, the results clearly show that the nature of the high-temperature reactions strongly depends on the molecular structure of the amines used, although the principal surface complexes formed at beam temperature are always identical.

REFERENCES

1. Sokoll, R., Hobert, H., and Schmuck, I., *J. Catal.* **121,** 153 (1990).
2. Marx, U., Sokoll, R., and Hobert, H., *J. Chem. Soc. Faraday Trans. 1* **82,** 2505 (1986).
3. Sokoll, R., Hobert, H., and Schmuck, I., *J. Chem. Soc. Faraday Trans. 1* **82,** 3391 (1986).
4. Gordymova, T. A., Budneva, A. A., and Davydov, A. A., *React. Kinet. Catal. Lett.* **20,** 113 (1982).
5. Morrow, B. A., Cody, I. A., and Lee, L. S. M., *J. Phys. Chem.* **79,** 2405 (1975).
6. Fink, P., and Plotzki, I., *Wiss. Z. Friedrich-Schiller-Univ. Jena* **27,** 691 (1978).
7. Rudakoff, G., Sokoll, R., Hobert, H., and Schmuck, I., *Z. Chem.* **27,** 150 (1987).
8. Sokoll, R., *Diss. B Jena* 1988.
9. Sedlaček, J., and Koubek, J., *Collect. Czech. Chem. Commun.* **48,** 755 (1983).
10. Busca, G., *React. Kinet. Catal. Lett.* **20,** 373 (1982).
11. Sanderson, R. T., "Inorganic Chemistry," Reinhold, New York, 1967.
12. Lycourghiotis, A., Katsanos, N. A., and Vattis, D., *J. Chem. Soc. Faraday Trans. 1* **75,** 2481 (1979).
13. Ledoux, M. J., and Sedrati, M., *J. Catal.* **83,** 229 (1983).
14. Gryasnov, V. M., Pavlova, L. F., Rivera, P., Rosen, A., and Chuarez, E., *Kinet. Katal.* **12,** 1197 (1971).
15. Cheung, H.-C., and Clearfield, A., *J. Catal.* **98,** 335 (1986).
16. Jarvie, S. W., and Lewis, D., *J. Chem. Soc.*, 4758 (1963).
17. Bürger, H., and Goetze, U., *Monatsh. Chem.* **99,** 155 (1968).