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Infrared Spectroscopic Study of the Adsorption of Nitro Compounds and Amines on Cobalt Oxide

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The adsorption of nitrobenzene on unsupported and SiO_2-supported Co_3O_4 and a range of adsorbed reaction products of nitrobenzene are studied by infrared spectroscopy. Products observed after adsorption of nitrobenzene on Co_3O_4 are aniline, azoxybenzene, and cyclohexylamine (reduction products) at lower temperatures and carbonates and cyanates (oxidation products) at higher temperatures. One of the supported cobalt oxides appears to be very different from the pure Co_3O_4, probably due to cobalt silicate formation during its synthesis. With all samples, the surface reactivity and adsorption of gases are mostly related to hydroxyl groups, but Lewis acid sites are also present on the surface.

INTRODUCTION

The selective reduction of nitrobenzene to nitrosobenzene is important to the chemical industry, since nitrosobenzene is an intermediate in the production of antioxidants, photolacquers, and insecticides. From a more fundamental point of view the reaction is interesting because of the two chemically identical oxygen atoms in the NO_2 group, only one is removed. Interaction of nitrobenzene with oxides has already been studied from the point of view of surface chemistry (1) and catalysis by the so-called Mars–van Krevelen mechanism. In this mechanism, lattice oxygen is used for catalytic oxidation of the organic reactant, or in the case of catalytic reduction, oxygen from the reactant is used to replenish vacancies in the oxidic lattice (2). While the infrared studies revealed that nitrobenzene is coordinated to the surface cations through the NO_2 group, electron spin resonance indicates a possible interaction through the phenyl ring (3).

The easiest catalytic conversion of nitrobenzene is that to aniline. This conversion is induced by metals (4–8), metal carbonyl clusters (9–15), and some organometallic compounds (16, 17). More difficult but also more desirable is a selective reduction of nitrobenzene to nitrosobenzene, which is indeed possible with some transition metal oxides (18, 19), whereas MgO, for example, produces aniline (20).

The collection of molecules whose adsorption is relevant in relation to the reduction reactions of nitrobenzene comprises also aliphatic nitro and amino compounds, since these also are potential products of surface and catalytic reactions of nitrobenzene. Some aliphatic nitro compounds form nitronate species on adsorption (21, 22). In this article, particular attention is paid to the adsorption of aniline which is both a product of the reaction of interest and a suitable probe of the acid–base properties of surfaces. Extended literature on the adsorption of aniline on oxides can be found in Refs. (23–33).

In this paper a study of the adsorption of nitrobenzene and of some of its possible products on various kinds of cobalt oxide is presented. The first sample used is pure Co_3O_4 which has a spinel structure like that of Mn_3O_4 studied earlier (1). Since it is impossible to study pure Co_3O_4 in its oxidized state (see below), two supported cobalt oxides were prepared, with 5 and 50 wt% cobalt oxide on silica. The former was made by incipient wetness impregnation of the silica with a cobalt complex. The advantage of this method is that the active component is deposited on the silica surface without altering it. However, this method is not useful for high loadings. The 50% cobalt oxide on SiO_2 was made by slow deposition of cobalt hydroxide from a cobalt nitrate solution. It was necessary to make a 50% supported sample, because on the 5% supported sample, a direct contact between adsorbed molecules and the carrier could play a role in the overall behavior of the catalyst.

METHODS

The cobalt oxide samples used in this study were prepared as follows. (1) Pure Co_3O_4 was made by the decomposition of $Co(OH)_2$ obtained by the precipitation of cobalt(II) nitrate with NaOH solution at pH 9. After synthesis the hydroxide obtained was washed thoroughly with distilled water. Synthesis from NH_4OH failed to produce IR-transparent samples. (2) 50% Co_3O_4 loaded on silica was made by a homogeneous deposition precipita-

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TABLE 1

Specific Surface Area (SSA) and Morphology of the Oxides Used in This Study

Sample	SSA (m^2/g)	Particle size (Å)	Morphology
Co_3O_4 pure	18	350–500	Spheres
Co_3O_4/SiO_2 5%	180	175–225 (Si spheres) 40 (Co_3O_4 spheres)	Small cobalt oxide spheres on large silica spheres
Co_3O_4/SiO_2 50%	270	Thickness: 25–75 Length: variable	Fiberlike structure, irregular.

tion method (34). A 0.5 *M* ammonium hydroxide solution was added at a flow of 20 ml/h to a stoichiometric mixture of cobalt nitrate and 10 g SiO_2 until a pH of 8.5 was reached. (3) Five percent Co_3O_4 on SiO_2 was prepared by incipient wetness impregnation of SiO_2 by cobalt–EDTA solution. The Co–EDTA complex was formed by adding cobalt nitrate to a H–EDTA solution. All preparations were carried out at room temperature. All samples were heated in air at 600°C for 8 h to remove remaining nitrate and EDTA.

The purity of the Co_3O_4 was confirmed by powder X-ray diffraction (XRD). XRD of the two supported cobalt oxide samples showed no diffraction peaks, indicating good dispersion of the support on the carrier. The specific surface area of the samples was determined by nitrogen adsorption (BET method), and the samples were also characterized by means of electron microscopy. Results are shown in Table 1.

About 50 mg of each sample was pressed to pellets of 2.8-cm diameter using a pressure of 1×10^7 Pa. The pellets were placed in an infrared transmission cell equipped with CaF windows and connected to a conventional vacuum system. This cell can be heated to 675 K and cooled to 77 K. Spectra were recorded between 2400 and 1200 cm^{-1} on a Mattson Galaxy 3000 FTIR spectrometer. Spectra were recorded with a resolution of 2 cm^{-1}.

As a result of the property of Co_3O_4 to absorb an excess of oxygen, which makes the oxide a p-type semiconductor, the pure, fresh oxide is nontransparent to IR radiation. After *in situ* pretreatment by 100 Torr (1 Torr ≡ 133.3 Pa) hydrogen at 200°C for 15 min, a transparent window appears between 3500 and 600 cm^{-1} (35). The supported cobalt oxides were already transparent when used as such and were measured with and without prereduction. If no reduction was carried out, the samples were evacuated at 200°C for 1 h.

The cobalt nitrate used in this work was $Co(NO_3)_2 \cdot 6H_2O$ from Merck, Germany, 99% pure. The EDTA (Titriplex II) was from Merck, Germany, 99.4% pure, and the SiO_2 was Aerosil 200 from Degussa, Germany. The nitrobenzene used was from J. T. Baker Chemicals B.V., The Netherlands, 99% pure; the aniline from Merck, Germany, 99% pure; the cyclohexylamine from Fluka, Switzerland, 95.5% pure; and the nitrocyclohexane from Aldrich Chemical Company Inc., 97% pure. The compounds used to characterize the oxide surfaces were pyridine from J. T. Baker Chemicals B.V., >95% pure, and CO from Messer Griesheim, 99.99% pure.

RESULTS

Characterization of the Oxides by Infrared Spectroscopy and CO and Pyridine Adsorption

Adsorption of carbon monoxide and pyridine was monitored to gain information on the valencies of the exposed cobalt ions and on the acid sites on the oxide surfaces. Pure Co_3O_4 could be used only in reduced form because otherwise it would not be transparent. The 50% Co_3O_4 sample was measured in the calcined and reduced states. Results are shown in Table 2.

In all cases the bands arising from hydrogen-bonded pyridine have the highest intensity immediately after gas admission, but after evacuation the bands of pyridine bound to Lewis acid sites dominate the spectra. Bands

TABLE 2

Infrared Absorption Bands (in cm^{-1}) of Pyridine Adsorbed on Pure and Supported Cobalt Oxide

Co_3O_4 pure (red.)	Co_3O_4/SiO_2 50% (red.)	Co_3O_4/SiO_2 50% (calc.)	Assignment
1597	1609	1607	Lewis
1580	1597	1596	Hydrogen bond
1775	1578	1578	Lewis
1483	1489	1491	Lewis
1482	1487	1491	Hydrogen bond
1442	1449	1450	Lewis
1439	1445	1447	Hydrogen bond

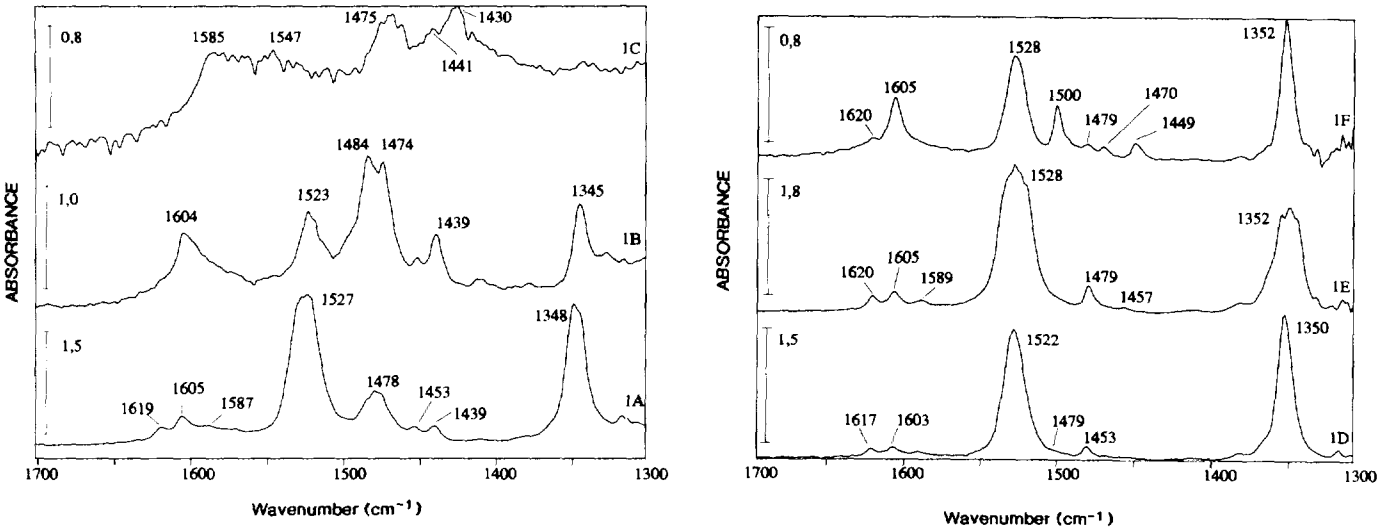

FIG. 1. Nitrobenzene adsorbed on pure Co_3O_4 at (a) 300 K, 10^{-4} Torr, (b) 373 K, 10^{-5} Torr, and (c) 473 K, 10^{-5} Torr; on (d) 50% Co_3O_4/SiO_2 at 300 K, 10^{-4} Torr; and on 5% Co_3O_4/SiO_2 at 300 K (e) 10 min after adsorption at 10^{-4} Torr and (f) 8 h after adsorption at 10^{-5} Torr. Numbers adjacent to vertical bars quantify the absorbance scale for each spectrum.

arising from pyridinium ions were not observed. The assignments in Table 2 are based on Ref. (36). As can be seen in Table 2, reduction or calcination has only marginal influence on the sites of the 50% Co_3O_4/SiO_2. The band positions of pyridine adsorbed on pure Co_3O_4 differ from those of the supported cobalt oxide. On the supported cobalt oxide the pyridine bands are more intense than on the pure cobalt oxide, but this results rather from the higher specific surface area than from a substantial difference in the nature of the acid sites. Worthy of note is that pyridine is very strongly bound to the surface on all samples.

The difference between the pure and 50% supported samples is confirmed by CO adsorption: both on reduced and calcined 50% cobalt oxide supported on silica, the CO spectrum consists of one single band at 2177 cm^{-1}, which disappears on evacuation. This band can be ascribed to CO weakly adsorbed on Co^{3+} ions (35). With the reduced pure Co_3O_4, the only band visible is at 2140 cm^{-1}. This is the gas-phase frequency of CO. Probably the large number of hydroxyl groups on the prereduced oxide surface prevents any strong interaction of CO with cobalt oxide. Evidence for the presence of cobalt metal atoms (potentially formed by the hydrogen pretreatment) is not found.

Adsorption of Nitrobenzene

Figures 1A–C show the spectra of nitrobenzene adsorbed on pure cobalt oxide at different temperatures from room temperature to 473 K. Figure 1A shows the spectrum of nitrobenzene just after gas admission. No product formation could be observed under these conditions. As can be seen in Table 3, the infrared bands of nitrobenzene adsorbed on Co_3O_4 are almost identical to those of liquid nitrobenzene (37). After the sample is heated to 373 K the spectrum shows bands of aniline (peaks at 1604 and 1484 cm^{-1}) and azoxybenzene, C_6H_5–N(O)=N–C_6H_5 (peaks at 1474 and 1439 cm^{-1}). This behavior is very similar to that of nitrobenzene adsorbed on Mn_3O_4, where azoxybenzene was also identified by IR spectra (1). Aniline and nitrosobenzene are the main products of (auto)reduction on various oxides (18). At 473 K the spectrum still shows bands of azoxybenzene (1475 and 1441 cm^{-1}), but the most striking feature is a strong peak at 2186 cm^{-1}, belonging to either a cyanide

TABLE 3

Bands Observed in the Infrared Spectrum of Nitrobenzene Adsorbed at Ambient Temperature on Various Cobalt Oxides (in cm^{-1}) and Their Assignments[a]

Liquid phase (37)	Co_3O_4	Co_3O_4/SiO_2 50%	Co_3O_4/SiO_2 5%	Assignment
	1619 w	1617 w	1620 w	8a
1608	1605 w	1603 w	1605 w	8a
1588	1587 w			8b
1525	1527 vs	1522 vs	1528 vs	$\sigma_{as}NO_2$
1478	1478 s	1479 w	1479 m	19a
	1453 w	1453 w	1457 vw	19b
	1439 w			
1348	1348 vs	1350 vs	1352 vs	σ_sNO_2

[a] The assignments of the ring vibrations are presented in the Wilson notation (38).

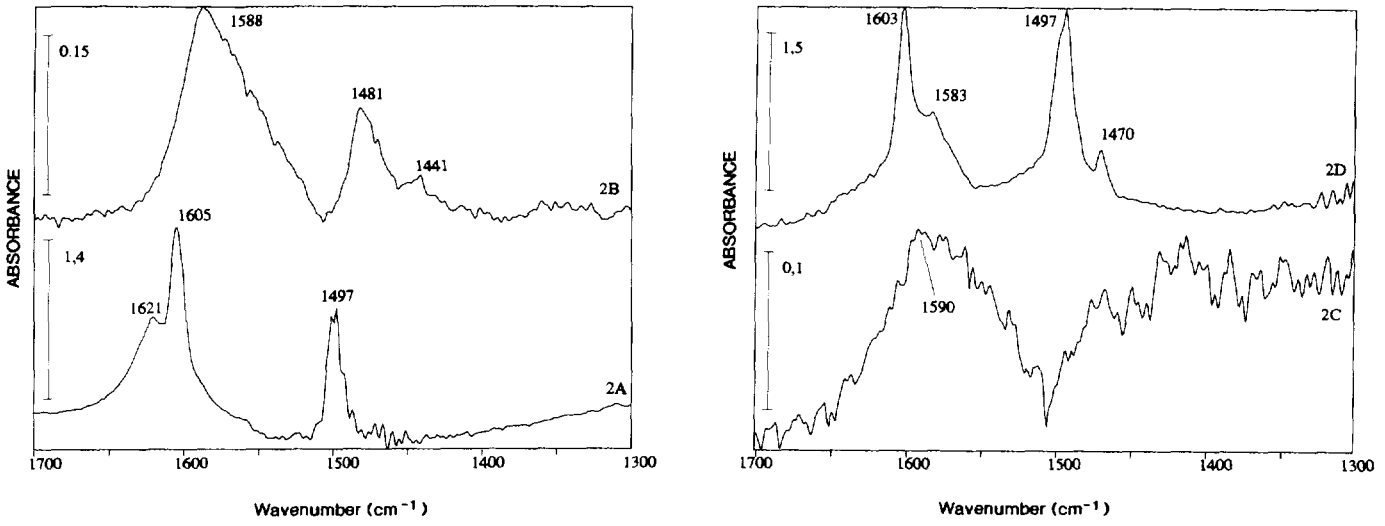

FIG. 2. Aniline adsorbed on pure Co_3O_4 at (a) 300 K, 10^{-4} Torr, (b) 373 K, 10^{-5} Torr, and (c) 473 K, 10^{-5} Torr and on (d) 50% Co_3O_4/SiO_2 at 300 K, 10^{-4} Torr.

(C≡N), a cyanate (O–C≡N), an isocyanate (–N=C=O) or an isonitrile (–N≡C). This surface species is stable up to 573 K. At 573 K the low-frequency part of the spectrum shows peaks that can be ascribed to bidentate carbonates (~1580, ~1240, and 1026 cm^{-1}).

Figure 1D shows the spectrum of nitrobenzene adsorbed on the 50% Co_3O_4/SiO_2. This sample was studied both in the reduced state and the unreduced state. In both cases aniline was formed, but much less than on the pure Co_3O_4, and aniline formation was least on the unreduced sample. In contrast to the pure cobalt oxide, no C≡N species or azoxybenzene was seen.

Figures 1E and 1F show the spectra obtained with 5% cobalt oxide on SiO_2 (prereduced) after exposure to 10^{-2} Torr nitrobenzene at room temperature for 10 min and 8 h, respectively. With this sample, heating decreased the amount of nitrobenzene adsorbed so much that no well-developed spectra could be observed. However, a reaction followed at room temperature provided some interesting information as well. The products observed are aniline (1605 and 1500 cm^{-1}) and cyclohexane or cyclohexene (a small but sharp peak at 1449 cm^{-1}).

Adsorption of Aniline

Figures 2A–C show the spectra of aniline adsorbed on pure Co_3O_4 at several temperatures from room temperature to 473 K. In comparison with liquid aniline, the ring vibrations are only very slightly shifted (Table 4) after adsorption at 300 K on cobalt oxide. At 373 K bands appearing at 1481 and 1442 cm^{-1} indicate the formation of azoxybenzene. Bands at 1588, ~1260, and ~1020 arise probably from a bidentate carbonate species. These bands are still present at 473 K, together with again a C≡N species (2177 cm^{-1}). The C≡N triple bond is observed at a somewhat lower wavenumber than in the case of nitrobenzene adsorption.

Figure 2D shows the spectrum of aniline adsorbed on 50% cobalt oxide supported on silica. Again, the ring vibrations are not very different from those of liquid aniline. Since aniline does not desorb from the oxide on evacuation, adsorption is obviously not weak, but on heating the sample aniline desorbs completely below 473 K, without a detectable reaction to any other product.

The adsorption of aniline on 5% Co_3O_4 on silica gave the same results: easy desorption on mild heating and no visible product formation. In contrast to nitrobenzene, the aniline aromatic ring was not detectably hydrogenated.

Adsorption of Cyclohexylamine

Apart from a small difference in $\delta(NH_2)$, the spectrum obtained with the pure Co_3O_4 is the same as that on the supported cobalt oxide. In comparison with the gas-phase

TABLE 4

Wavenumbers of Absorption Bands of Aniline Adsorbed on Pure and Supported Cobalt Oxides (in cm^{-1}) and Band Assignments

Liquid phase (39)	Co_3O_4	Co_3O_4/SiO_2 50%	Assignment
1618	1621 s		δNH_2
1600	1605 vs	1603 vs	8a
		1583 s	δNH_2
1500	1497 vs	1497 vs	19a
		1470 m	19b

spectrum, the NH_2 deformation band has shifted downward by 23 cm^{-1} and has increased in intensity: it is about twice as strong as the CH_2 scissoring band, which in the free molecule is roughly the same intensity (Table 5). Heating the sample leads to slow desorption of cyclohexylamine, but not to the appearance of new infrared absorption bands.

Adsorption of Nitrocyclohexane

The adsorption of nitrocyclohexane on cobalt oxide was studied to see how the possible formation of nitrocyclohexane from nitrobenzene would manifest itself in the IR spectra (Table 6). The experiments were carried out on pure cobalt oxide (reductive pretreatment) and on 50% cobalt oxide on SiO_2 (heated in air). The spectrum of nitrocyclohexane adsorbed on pure Co_3O_4 is shown in Fig. 3D. Like nitrobenzene on this sample, nitrocyclohexane reacts to its corresponding amine. The formation of cyclohexylamine occurs so fast that even at ambient temperature, immediately after admission of nitrocyclohexane to the sample, it is impossible to detect N–O vibrations and the spectrum is dominated by the strong amine δNH_2 vibration at 1600 cm^{-1}. Heating the sample leads to slow desorption of the adsorbate, but not to formation of other products.

The spectra of nitrocyclohexane adsorbed on 50% cobalt oxide on SiO_2, at ambient temperature, 1, 10, and 20 min after admission of the gas to the sample, are shown in Figs. 3A–C. The first spectrum shows only the nitrocyclohexane bands. After 10 min, an intermediate band at 1622 cm^{-1} arises, which is ascribed to $\rangle C{=}N$ of cyclohexanenitronate $O_2N{=}C_6H_{10}$. Nitronate formation from a nitro compound was observed by Angevaare (1) on adsorption of nitromethane and nitropropane on Mn_3O_4. After 20 min a shoulder at 1672 cm^{-1} grows on the band mentioned. This frequency corresponds to the frequency expected for cyclohexyloxime ($HO{-}N{=}C_6H_{10}$) or cyclohexylimine ($H{-}N{=}C_6H_{10}$) (40). Since the sample was not reduced before measurement, an oxime seems to be more likely.

TABLE 5

Wavenumbers of IR Bands Observed with the Adsorption of Cyclohexylamine on Pure and Supported Cobalt Oxide (in cm^{-1})

Liquid phase (41)[a]	Co_3O_4	Co_3O_4/SiO_4 50%	Assignment
1595	1604 s	1591 vs	$\delta(NH_2)$
1614 (gas)[b]			
1466	1466 m	1465 m	$sc(CH_2)$
1450	1450 s	1451 s	$sc(CH_2)$

[a] Liquid-phase data are from the Aldrich Library of Infrared Spectra. The band positions were read from the spectrum in micrometers with a precision of 0.01 μm, which corresponds to 3 cm^{-1} for the part of the infrared spectrum relevant for this study.

[b] For a good comparison between adsorbed and isolated cyclohexylamine, the gas-phase δNH_2 frequency is also given, because in the liquid phase this band is already shifted due to intermolecular hydrogen bonding (32, 48).

TABLE 6

Observed IR Bands (in cm^{-1}) of Nitrocyclohexane Adsorbed on 50% Cobalt Oxide Supported on Silica and Assignments of the Bands

Liquid phase (41)[a]	Co_3O_4/SiO_2 50%	Assignment
2945	2949 s	$\sigma C{-}H$
2873	2870 s	$\sigma C{-}H$
1543	1544 vs	$\sigma_{as}N{-}O_2$
1450	1450 m	$scCH_2$
1380	1380 s	$\sigma_sN{-}O_2$

[a] Liquid-phase values from the Aldrich Library of Infrared Spectra, with a precision of 3 cm^{-1}.

DISCUSSION

Adsorption Mode and Products of Nitrobenzene

The behavior of nitrobenzene adsorbed on Co_3O_4 is very similar to the behavior of nitrobenzene on Mn_3O_4 (1). The main difference observed by infrared spectroscopy is the production on Co_3O_4 of aniline *immediately* after adsorption of nitrobenzene. However, it is known from catalytic experiments (19) that aniline is the most important side product of the interaction of nitrobenzene with Mn_3O_4, but its formation starts only after an induction period following the admission of nitrobenzene to the sample. Probably the large amount of aniline formed on cobalt oxide is due to the reductive pretreatment (necessary to make the sample transparent): a part of the hydrogen used is stored on the oxide, most probably in the form of surface hydroxyl groups, and can thus lead to the nonselective reduction of nitrobenzene. This idea is confirmed by catalytic experiments in which yields of various products were monitored in reaction on prereduced and calcined cobalt oxides. Just after the initiation of the reaction the reduced catalyst produced more aniline than the calcined catalyst. However, in the steady state the two catalysts showed the same activities and selectivities toward aniline and other products.

The infrared absorption bands of nitrobenzene chemisorbed on pure Co_3O_4 are similar to those of liquid nitrobenzene (Table 3) and of nitrobenzene adsorbed on Mn_3O_4 (1). It has been suggested by several authors (1, 3, 42) that nitrobenzene might be adsorbed on an oxide surface

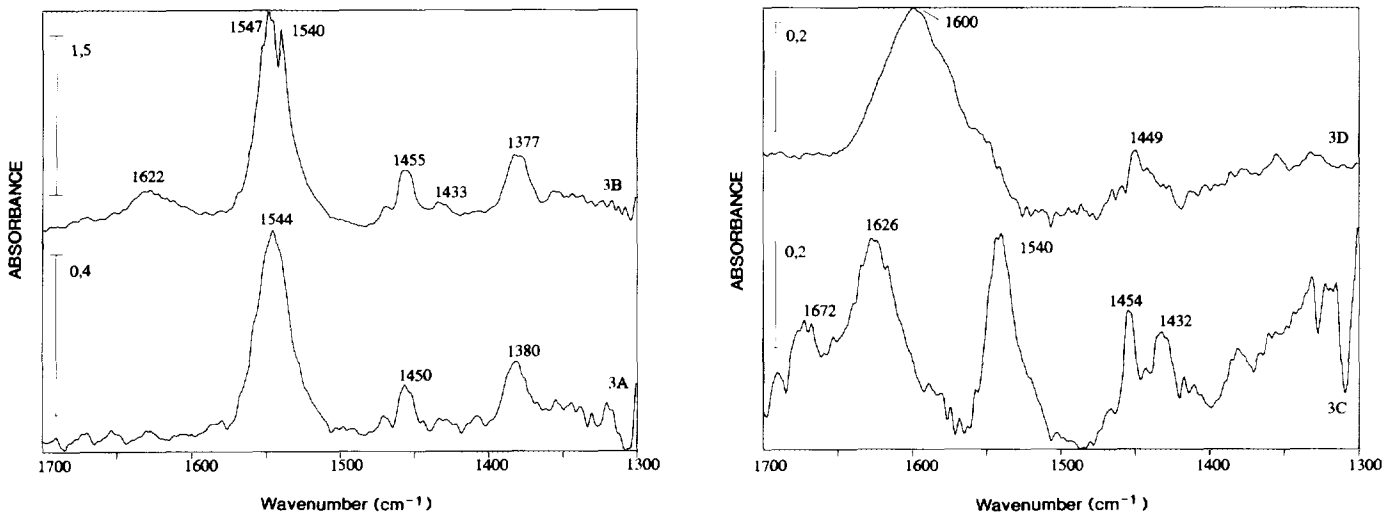

FIG. 3. Nitrocyclohexane at 300 K adsorbed on 50% Co_3O_4/SiO_2 (a) 1 min after adsorption at 10^{-4} Torr (b) 10 min after adsorption at 10^{-4} Torr, and (c) 20 min after adsorption at 10^{-5} Torr; and on (d) Co_3O_4 at 300 K, 10^{-4} Torr.

either in a parallel (adsorption by the phenyl ring) or in a perpendicularly oriented (adsorption by the nitro group) mode. A way to distinguish between the two species by use of infrared spectroscopy has not yet been found. However, the reduction of the nitrobenzene phenyl ring on the 5% cobalt oxide on silica (after a hydrogen pretreatment) is an indication that some molecules are adsorbed parallel to the oxide surface. It is important to note that the peak at 1449 cm^{-1} assigned above to a cyclohexyl ring cannot be a misinterpreted azoxybenzene band (azoxybenzene has a strong absorption at 1439 cm^{-1}) because the strongest azoxybenzene band (1475 cm^{-1}) is not present in the spectrum.

The hydrogenation of a phenyl ring by an oxide may be surprising, but, although most catalysts used for hydrogenation of aromatics are metals, hydrogenation by oxides is not an unknown phenomenon in catalysis. For instance, the activation of hydrogen on zinc oxide occurs dissociatively, with one H atom adsorbing on Zn and one on O (43):

$$H_2 + \text{Zn–O} \rightarrow \begin{matrix} H & H \\ | & | \\ \text{Zn–O} \end{matrix}$$

The former is only weakly adsorbed and will move soon to a neighboring O ion to form another surface OH group. Thus it is very well possible that the reductive pretreatment applied produces additional and reactive OH groups.

The question now is, What happens after reduction of the phenyl ring? We have seen that the adsorption of aniline on cobalt oxide does not lead to the appearance of a CH_2 scissoring vibration in the spectrum. This is an indication that ring hydrogenation takes place only with nitrobenzene, but not with aniline. A possible product expected from hydrogenation of nitrobenzene on the phenyl ring is nitrocyclohexane. Experiments with nitrocyclohexane on the same (prereduced) sample revealed that this molecule reacts to cyclohexylamine immediately after adsorption on the oxide surface. Hence it can be assumed that the band observed at 1449 cm^{-1} on nitrobenzene adsorption arises from cyclohexylamine, and that the other strong cyclohexylamine band, the δNH_2 vibration at 1600 cm^{-1}, is masked by the aniline 8a ring vibration.

The third product of nitrobenzene adsorbed on cobalt oxide, azoxybenzene, is a condensation product of fragments of two nitrobenzene molecules. It contains only one oxygen atom, and therefore it is a reduction product. More on the production of azoxybenzene from nitrobenzene can be found in Refs. (1, 18).

Adsorption Mode and Products of Aniline

It is well known that on surfaces covered with hydroxyl groups, amines are often bound to the oxide via a hydrogen bond between the NH_2 group and a surface OH group. This kind of bonding causes a shift in the N–H stretching and NH_2 deformation vibrations. However, the oxides used in this study are not transparent in the N–H stretching region of the infrared spectrum. The δNH_2 band of aniline is not resolvable due to its overlap with the strong 8a ring vibration. With pure Co_3O_4 a shoulder at the high-frequency side of the 8a ring vibration band is observed at the position expected for δNH_2 (1621 cm^{-1}). Since physisorbed molecules often have the same infrared spectrum as in the liquid state and since the mentioned shoulder

disappears easily on evacuation of the sample, it must arise from physically adsorbed aniline. Although we could not obtain the evidence by means of infrared spectroscopy, we have the following good reasons to believe that aniline is bound to cobalt oxide through the NH_2 group:

1. That part of the aniline which is not associated with the shoulder at 1621 cm^{-1} is chemisorbed on the surface; it does not desorb on evacuation and heating of the sample to 373 K. The δNH_2 band has probably shifted down to a complete overlap with the 8a ring vibration in the adsorption mode.
2. In contrast to nitrobenzene, hydrogenation of the phenyl ring of aniline does not occur. Probably this is due to the perpendicular adsorption mode of the aniline phenyl ring toward the surface. Electronic effects are not likely to account for the difference between nitrobenzene and aniline concerning hydrogenation, since the electronic structures of the two molecules make aniline a better candidate for electrophilic attack of the ring from acid surface OH protons (44).
3. The high electron density near the nitrogen atom in aniline (44) makes it possible for this molecule to bind to the surface through the amino group, either by electron donation to Lewis acid sites or by hydrogen bonding to a surface OH group with the amino N as proton acceptor.
4. On a number of oxides, aniline was found to be adsorbed via the amino group (25, 26).

These arguments emphasize the importance of hydroxyl groups for the adsorption of aniline. However, an important question to be answered is whether aniline is also adsorbed on Lewis acid sites, since pyridine adsorption proved these sites to be present on the surface. In the literature, typical infrared data for aniline adsorbed on Lewis acid sites are hardly found. In a review article (45), Knözinger concludes that amines cannot be considered in general as ideal probes for the characterization of surface acidity. In Ref. (46), however, a relationship is proposed between the strength of Lewis acid sites on alumina and the intensity ratio of the ring vibrations at about 1600 and 1500 cm^{-1}. The $I_{\nu 1600}/I_{\nu 1500}$ ratio varies between 1.5 and 1.0, where a value of 1.0 indicates the strongest Lewis acid sites. In the spectrum of aniline adsorbed on pure Co_3O_4 it is impossible to determine the intensity ratio of the two bands because of the presence of shoulders arising from physically adsorbed aniline at room temperature and an overlap with the δNH_2 band. The azoxybenzene band arising at higher temperatures also disturbs the observation. However, a band observed at 1575 cm^{-1} with aniline adsorbed on Lewis acid sites (46) is missing in our spectrum and therefore we consider this kind of adsorption on Co_3O_4 to be unlikely. The absence of an indication that aniline is adsorbed on Lewis sites adds further support to the hypothesis stated above that aniline is adsorbed by hydrogen bonding on surface hydroxyl groups.

The observation of azoxybenzene as a product of aniline is interesting, since this molecule does contain an oxygen atom, whereas the reactant does not. This oxygen atom must therefore originate from the cobalt oxide, an indication that a feature of the Mars–van Krevelen mechanism (2) is operative.

The "(iso)cyanate" peak, which was found both in the case of nitrobenzene and in the case of aniline adsorbed on pure cobalt oxide, is probably an isolated C≡N species. Its frequency is nearer to the C≡N frequencies of inorganic cobalt cyanide complexes (around 2140 cm^{-1}) (47), than those of organic cyanides and nitriles which absorb in the region around 2250 cm^{-1}. The difference in peak position between the sample exposed to nitrobenzene (2186 cm^{-1}) and the one exposed to aniline (2178 cm^{-1}) can result from a higher degree of surface reduction in the latter case.

The spectrum of aniline chemisorbed on 50% supported cobalt oxide looks very much like the spectrum of aniline on alumina (46). There are four peaks at 1603, 1583, 1497, and 1470 cm^{-1} (alumina: 1605, 1575, 1494, and 1470 cm^{-1}), indicating adsorption of aniline on Lewis sites. The different chemisorption of aniline on the two samples of cobalt oxide is in agreement with the results obtained with OC and pyridine adsorption: the supported oxide is different from pure Co_3O_4 and its behavior is independent of oxidative or reductive pretreatment.

Adsorption Modes of Cyclohexylamine

Sokoll *et al.* (32) observed the dissociation of cyclohexylamine into NH_3 and cyclohexene on iron oxide and aluminum oxide, but on the oxides used in this study, cyclohexylamine is not transformed measurably to any products. It is, however, chemisorbed on the oxide surface, since it does not desorb from the surface until a temperature of 373 K. Amine can potentially be bound to the oxide by a hydrogen bond between the amino group and a surface hydroxyl group. Theoretically, this kind of interaction can take place in two ways: the amino group can act either as a proton donor or as a proton acceptor. In both cases the N–H stretching vibrations are expected to shift down, but in the first case the NH_2 deformation vibration is expected to shift to a higher wavenumber and decrease in intensity, and in the second case exactly the opposite is to be expected (48). This shift is very clearly demonstrated in the spectrum of cyclohexylamine adsorbed on the 50% Co_3O_4/SiO_2: the δNH_2 vibration has shifted to a lower wavenumber by 23 cm^{-1} and the intensity of absorption increased. In most cases the δNH_2 peak has about the same intensity as the CH_2 scissoring band (broader but less high), but in this case it is about twice

as strong. Thus the amine group most probably acts as a proton acceptor. On pure cobalt oxide the effect is less clearly expressed; the frequency shift amounts only to 10 cm^{-1}, the intensity difference is less spectacular, but it is visible.

Cyclohexene [scCH_2 at 1437 cm^{-1} (49)], which is a possible product of cyclohexylamine adsorption on Lewis acid sites (32), was not observed. This may be due to the fact that cyclohexene reacts or desorbs fast from the oxides used in this study, as was revealed by additional experiments in which cyclohexene was adsorbed on cobalt oxides. However, the hydrogenating activity of the oxide offers also an explanation: if cyclohexene reacted to cyclohexane it would also desorb too fast to be observed.

Adsorption Modes and Reactions of Nitrocyclohexane

On pure, prereduced Co_3O_4, the reaction of nitrocyclohexane to cyclohexylamine is so fast that it is impossible to observe the adsorption of the nitro compound alone. Since hydrogenation of the phenyl ring takes place on prereduced cobalt oxide only, we can rule out the formation of nitrocyclohexane as a detectable product on any of the samples studied; reduction of the ring is always accompanied by reduction of the nitro group.

The absence of nitrocyclohexane in the spectrum is confirmed by the adsorption of this compound on supported cobalt oxide. As was expected, nitrocyclohexane reacted to its corresponding nitronate, which was stable on the surface up to a temperature of 330 K. The nitronate C=N stretching vibration at 1622 cm^{-1} was not observed in this study in the spectra of reacted nitrobenzene.

In contrast to pure Co_3O_4, on 50% Co_3O_4/SiO_2 nitrocyclohexane did not react so fast to the nitronate that its own adsorption mode on the oxide could not be observed. However, compared with the liquid phase, the infrared absorption bands are not relevantly shifted, so it is difficult to tell more about the adsorption mode of nitrocyclohexane on cobalt oxide. A splitting of the $N-O_2$ stretching band, which occurs after 10 min, but not after 1 min of adsorption time, indicates an interaction between the nitro group and the oxide surface.

Comparison of the Three Cobalt Oxides Studied

Several of the results obtained by this study indicate a difference between the supported 50% cobalt oxide on silica, on the one hand, and the pure Co_3O_4 (and probably the 5% cobalt oxide supported on silica), on the other hand. To start with, electron microscopy showed that the morphology of the 50% supported cobalt oxide (fibrous) is very different from that of the other two samples studied (spheres). Further, the adsorption of pyridine and carbon monoxide showed that reduction had negligible influence on the surface of the 50% supported oxide, whose reduced and oxidized states are practically identical, but different from those of pure Co_3O_4. Finally, and most important, the oxides have a different reactivity toward adsorbed nitrobenzene, as is shown schematically for pure Co_3O_4:

$$\begin{array}{ccc} & \nearrow & \Phi\text{-}NH_2\ (300\ K) \\ & & \downarrow \\ \Phi\text{-}NO_2 & \rightarrow & \Phi\text{-}N{=}N\text{-}\Phi\ (373\ K) \\ & & | \\ & & O \end{array} \qquad \textbf{(I)}$$

and above 473 K to C≡N species and carbonates

for 5% Co_3O_4/SiO_2:

$$\begin{array}{ccc} & \nearrow & \Phi\text{-}NH_2\ (300\ K) \\ \Phi\text{-}NO_2 & \rightarrow & C_6H_{11}NH_2\ (300\ K) \end{array} \qquad \textbf{(II)}$$

and for 50% Co_3O_4/SiO_2:

$$\Phi\text{-}NO_2 \rightarrow \Phi\text{-}NH_2 \qquad \textbf{(III)}$$

The explanation for the difference between pure Co_3O_4 and the supported cobalt oxides can probably be found in the preparation of the samples. The slow precipitation of cobalt hydroxide on silica starts with pH 4 and ends with pH 8.5. According to Ref. (50), SiO_2 can dissolve when the pH is higher than 5.5. Partial solution of the silica during the synthesis might lead to the formation of cobalt silicate instead of cobalt oxide. The supported 5% cobalt oxide on silica was made by incipient wetness impregnation by a Co–EDTA solution. The pH of this solution was about 5, but irrespective of the pH, the volume of liquids used is too small to dissolve enough silica to give a relevant amount of cobalt silicate. It can therefore be assumed that on calcination the Co–EDTA is turned into Co_3O_4 particles. For the surface reaction of nitrobenzene on the three cobalt oxides we propose the following hypothesis: on the 50% Co_3O_4/SiO_2 the nitrobenzene reacts, after molecular adsorption, with weakly adsorbed surface hydrogen (due to the reductive pretreatment) to aniline by a Langmuir–Hinshelwood type of mechanism. The cobalt oxide of the 5% Co_3O_4/SiO_2 is basically the same as pure Co_3O_4. On both samples not only aniline but also other products such as a cyclohexane on 5% Co_3O_4/SiO_2 (at room temperature) and azoxybenzene and a cyanate on pure Co_3O_4 (at higher temperatures) are formed, indicating that other mechanisms besides the Langmuir–Hinshelwood mechanism mentioned above occur on these oxides. Possibly the Mars–van Krevelen mechanism plays a role on these samples in the oxidation of aniline. Further, the same reactive OH groups that can

be generated on pure Co_3O_4 and 5% Co_3O_4/SiO_2 do not occur on 50% Co_3O_4/SiO_2, as is shown by the indifference of this sample toward reduction and by its different reduction activity in comparison with the other two samples.

CONCLUSIONS

The reactivity of each of the three cobalt oxides studied is greatly determined by their surface hydroxyl groups. Lewis acid sites are present too, but they play only a minor role on the 50% support cobalt oxide. With pure Co_3O_4, part of the hydrogen used for prereduction of the samples is stored on the surface, probably in the form of hydroxyl groups. This hydrogen participates subsequently in reactions like reduction of nitrobenzene to aniline and hydrogenation of the nitrobenzene phenyl ring to a cyclohexane ring. Amines are bound to the surface by hydrogen bonds to hydroxyl groups. Pure cobalt oxide is more reactive than the 50% supported cobalt oxide in all the reactions observed in this study (hydrogenation, reduction, and oxidation). Probably it contains more active surface hydroxyl groups.

As a result of different methods of synthesis, the 50% supported cobalt oxide differs from the other two cobalt oxides studied. Probably it contains cobalt silicate. The only product from nitrobenzene observed on this sample was aniline, a product that can be formed by a Langmuir–Hinshelwood-type mechanism. Aniline itself did not react on this sample to other products.

On Co_3O_4 in the pure and the 5% supported state, aniline, azoxybenzene, cyclohexylamine, carbonates, and a C≡N species were formed from nitrobenzene. The formation of cyclohexylamine from nitrobenzene shows that hydrogenation of the phenyl ring of nitrobenzene is possible on reduced cobalt oxide. Aniline reacted to azoxybenzene, a reaction that requires the removal of an oxygen atom from the oxide. This is an indication that, in contrast to the case of 50% Co_3O_4/SiO_2, the Mars–van Krevelen mechanism plays a role in the pure and the 5% supported Co_3O_4. The reduction products aniline and cyclohexylamine were formed at room temperature, whereas the products of total oxidation, carbonates and cyanates, were formed at higher temperatures. Obviously, the interaction of amines and nitro compounds with the surface occurs by more than one mechanism on this oxide.

Concerning the adsorption modes of nitrobenzene and its most important side product on Co_3O_4, it can be concluded that nitrobenzene is bound through the phenyl ring, which lies parallel to the surface, thus enabling its hydrogenation. Aniline is bound by hydrogen bonding between the amino group and a surface OH group, with the aniline phenyl ring pointing away from the surface.

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