A study of the interaction of diethylzinc with the Aerosil surface

A. A. Oleinik,* V. A. Dodonov, G. N. Lysenko, and O. N. Druzhkov

N. I. Lobachevsky Nizhnii Novgorod State University,
23 prosp. Gagarina, Nizhnii Novgorod, Russian Federation.
Fax: +7 (831) 265 8592

The interaction of diethylzinc with Aerosil has been examined by IR spectroscopy and mass spectrometry. The reaction involves both free hydroxyl groups and siloxane groups of the surface resulting in the formation of ≡Si—O—Zn—Et and ≡Si—Et fragments. At temperatures above 300 °C, these structures undergo decomposition with the recovery of ≡Si—OH groups on the Aerosil surface and liberation of metallic zinc.

Key words: diethylzinc; Aerosil; IR spectroscopy; mass spectrometry.

The interaction of organometallic compounds with Aerosil affords surface heterosiloxane fragments containing a Si—O—M group, where M is a metal atom. The interest in the latter is caused, on the one hand, by the demand for submicron films, and, on the other hand, by the possibility of forming sublayer structures that increase the adhesion of a coating. In addition, the active sites arising during thermal decomposition of the surface metal-containing fragments may be used as efficient catalysts of the coordination polymerization of olefins.

It has been shown previously[1] that the interaction of dimethyl- and diethylcadmium with Aerosil at 20 °C involves both the free hydroxyl and siloxane groups on the surface and gives the structures ≡Si—O—Cd—C≡ and ≡Si—H. When the temperature increases to 200 °C, Cd—H fragments are formed, and at 500 °C, the surface ≡Si—O—H groups are recovered with the liberation of metallic Cd. It has been of interest to study the behavior of alkyl derivatives of another Group II metal, zinc, which are Lewis acids, as are the cadmium analogs, and can also be used for directed formation of reactive organometallic surface compounds. The purpose of the present work has been to study the interaction of diethylzinc with the surface of Aerosil.

Experimental

Degussa Aerosil with a specific surface area of 175 m^2 g^{-1} was used as the adsorbent. For spectroscopic study, it was pressed into pellets (7 and 12 mg cm^{-2}) under a pressure of 200 kg cm^{-2}. Prior to adsorption, the Aerosil was calcined in air at 300 °C for 1 h and then evacuated ($1.3 \cdot 10^{-3}$ Pa) at 600 °C for 3 h. The adsorption of diethylzinc was carried out at 20 °C for a period of 30 min in a cell described previously.[2] No changes in the IR spectrum of a modified sample during its evacuation at 20 °C for 30 min was observed.

IR spectra were recorded on an IR-75 spectrometer using an IBM PC/AT 386 computer; mass spectra were obtained on a MI-1305 mass spectrometer. Diethylzinc was prepared and purified by the previously reported procedure.[3]

Results and Discussion

According to IR spectroscopy data, when a cell with Aerosil is filled with Et_2N vapor, the absorption band (AB) at 3750 cm^{-1} caused by vibrations of the free hydroxyl groups of the Aerosil surface disappears, and a set of bands in the 3100—2800 cm^{-1} region corresponding to C—H stretching vibrations (*cf.* Ref. 4) simultaneously arise. In addition, we detected AB in the 1600—1350 cm^{-1} region associated with bending vibrations of the C—H bonds of the ethyl group (Fig. 1, spectrum *2*), AB due to stretching and asymmetric vibrations of the Zn—C bonds (612 and 569 cm^{-1}, respectively), and an AB at 523 cm^{-1}, which may correspond to vibrations of the O—Zn—C fragment on the surface. According to mass spectrometric analysis, ethane (79.5 mol. %), butane (1.9 mol. %), and butene (1.1 mol. %) are evolved to the gas phase during adsorption.

Gaseous $ZnCl_2$ is known[5] to react with silica gel only at 450—600 °C to afford a tetrahedral complex involving the O atoms on the silica gel surface; no substitution of Zn^{2+} ions for the H^+ ions of the OH groups occurs in this reaction. However, the reaction of diethylzinc with Aerosil proceeds even at room temperature and involves the replacement of the OH-group protons and evolution of ethane into the gas phase according to Eq. (1).

$$\equiv\text{Si—O—H} + \text{Et}_2\text{Zn} \xrightarrow{20\ ^\circ\text{C}} \equiv\text{Si—O—Zn—Et} + \text{EtH} \qquad (1)$$

When hydrolysis of the Aerosil modified with diethylzinc is carried out, the AB at 2920 and 2860 cm^{-1} associated with vibrations of the C—H bonds of the

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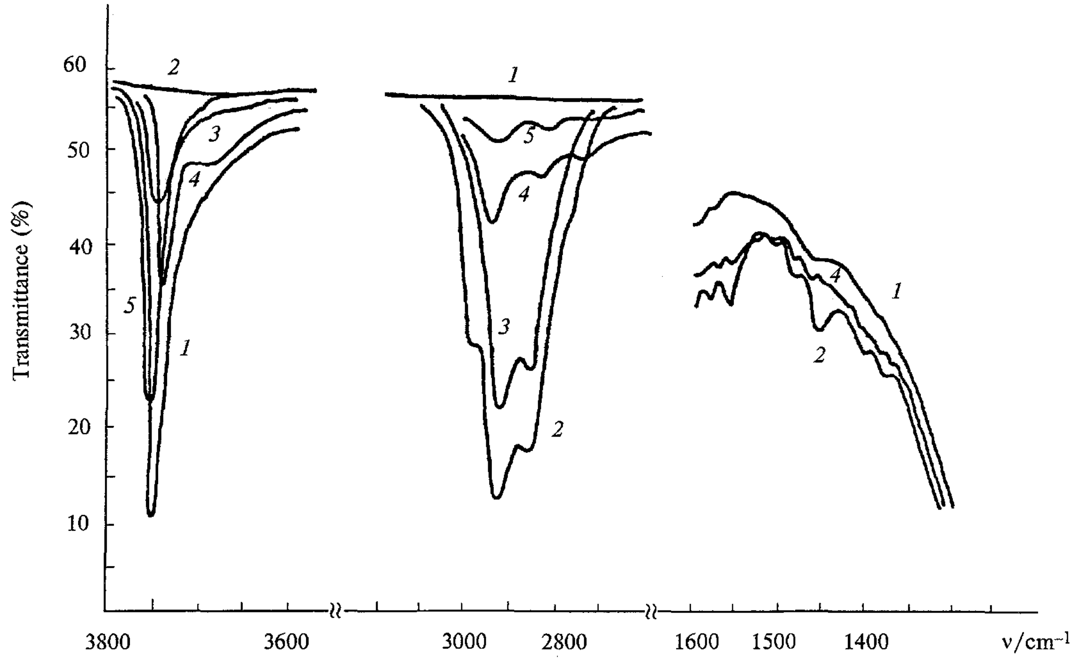
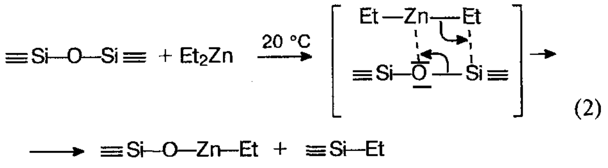


Fig. 1. IR spectra of Aerosil evacuated at 600 °C (*1*), treated thereafter with diethylzinc at 20 °C for 30 min (*2*), and then evacuated at 300 °C (*3*), 400 °C (*4*), and 600 °C (*5*) for 30 min.

methylene groups and the AB at 2960 and 2900 cm^{-1} corresponding to vibrations of the methyl C—H bonds are retained in the IR spectrum after the adsorption of water (Fig. 2, spectrum *2*). Therefore, we believe that the adsorption of diethylzinc on the Aerosil involves the formation of ≡Si—Et fragments according to Eq. (2); these fragments are not hydrolyzed.



$$\equiv Si{-}O{-}Si\equiv + Et_2Zn \xrightarrow{20\ ^\circ C} \left[\begin{matrix} Et{-}Zn{-}Et \\ \equiv Si{-}\underline{O}{-}Si\equiv \end{matrix}\right] \longrightarrow \equiv Si{-}O{-}Zn{-}Et + \equiv Si{-}Et \qquad (2)$$

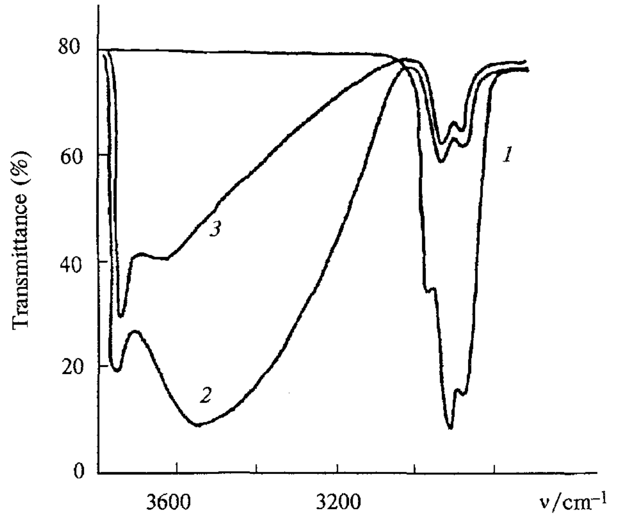


Fig. 2. IR spectra of Aerosil modified with diethylzinc at 20 °C (*1*), treated thereafter with water vapor at 20 °C (*2*), and then evacuated at 300 °C for 30 min (*3*).

In order to study the reactivity of the structures formed during modification of the Aerosil surface with diethylzinc we carried out thermolysis of the samples at 300—600 °C with continuous evacuation. According to the IR spectroscopy data, increasing the temperature in the above-mentioned range results in gradual restoration of the AB associated with the vibrations of free OH groups (at 3750 cm^{-1}), and gradual disappearance of the bands in the 3100—2800 cm^{-1} and 1600—1350 cm^{-1} regions corresponding to the vibrations of the organic radical in the adsorbed molecules (see Fig. 1, spectra *3*—*5*). Based on the data of mass spectrometric analysis, ethane (50.2 mol. %), butane (34.1 mol. %), and butene (3.6 mol. %) evolve in the gas phase during thermolysis. The decomposition of zinc-containing surface fragments probably occurs according to reaction (3) with the recovery of the free hydroxyl groups of the surface and the liberation of metallic Zn.

$$\equiv Si{-}O{-}Zn{-}Et \xrightarrow{300-600\ ^\circ C} \equiv Si{-}O{-}H + Zn + C_2H_6 + C_4H_{8(10)} \qquad (3)$$

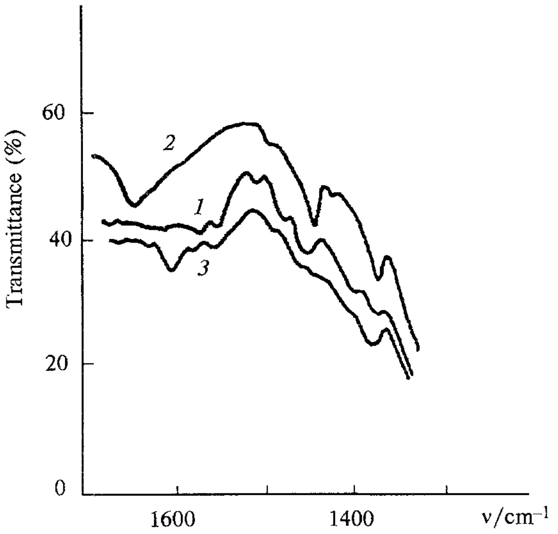


Fig. 3. IR spectra of Aerosil modified with diethylzinc at 20 °C (*1*), treated thereafter with pyridine at 20 °C (*2*), and then evacuated at 200 °C for 30 min (*3*).

We attribute the absence of ethylene in the reaction products to its coordination transformations on the metal-containing site. The presence of ethane, butane, and butene in the gas phase also apparently results from transformations of hydrocarbon radicals in the coordination sphere of zinc.

In order to study the acidity of the surface of Aerosil modified with diethylzinc we analyzed it for the presence of Brønsted and Lewis acid sites using the adsorption of pyridine vapor (a known test for acid sites on surfaces of various carriers). The IR spectrum of the adsorbed pyridine exhibits AB at 1630 and 1450 cm^{-1} associated with pyridine coordinated by the Lewis acid sites of the surface (Fig. 3, spectrum *2*). When the sample is heated above 200 °C, these AB disappear (see Fig. 3, spectrum *3*). The fact that the IR spectrum displays no AB at 1540 cm^{-1} typical of the pyridinium cation indicates that the surface of the sample modified with diethylzinc contains no Brønsted acid sites.

Therefore, one may conclude that modification of Aerosil with diethylzinc results in the formation of the ≡Si—O—Zn—Et and ≡Si—Et surface structures and Lewis acid sites on the surface. At temperatures ≥300 °C, free hydroxyl groups are restored and metallic Zn is liberated.

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References

1. V. A. Dodonov, A. A. Oleinik, M. B. Molotovshchikova, G. N. Lysenko, and O. N. Druzhkov, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1717 [*Russ. Chem. Bull.*, 1993, **42**, 1639 (Engl. Transl.)].
2. A. V. Kiselev and V. I. Lygin, *IK-spektry poverkhnostnykh soedinenii i adsorbirovannykh veshchestv* [*IR spectra of Surface Compounds and Adsorbed Substances*], Nauka, Moscow, 1972 (in Russian).
3. N. I. Sheverdina and K. A. Kocheshkov, in *Metody elementoorganicheskoi khimii. Tsink. Kadmii* [*Methods of Organometallic Chemistry. Zinc. Cadmium.*]; Nauka, Moscow, 1964, 13, 150 (in Russian).
4. Yu. M. Artem'ev, S. V. Kurganov, and M. A. Artem'eva, *Vestn. Leningr. Un-ta. Ser. 4: Fizika, Khimiya* [*Journal of Leningrad University. Div. 4: Physics, Chemistry*], 1991, **4**, 62 (in Russian).
5. N. A. Stepanova, V. M. Smirnov, S. I. Kol'tsov, and V. B. Aleskovskii, *Zh. Prikl. Khim.*, 1977, **50**, 465 [*J. Appl. Chem. USSR*, 1977, **50** (Engl. Transl.)].

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