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Alumina–Organic Interaction: Oxidation of Aromatic Compounds on Alumina Surface

M. DEFLIN,* I. M. ELTANTAWY,† AND M. BAVEREZ*

* *E.N.S.I.C., Nancy, France, and † Department of Soil and Agricultural Chemistry, Mansoura University, Mansoura, Egypt*

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An infrared spectroscopic study of toluene, benzyl alcohol, and benzaldehyde adsorbed on alumina surfaces showed that these compounds were irreversibly adsorbed in the temperature range from 190 to 400°C. The retained compounds were transformed into the benzoate form in the absence of oxygen, confirming that alumina is capable of oxidizing such compounds. The formation of an alumina–toluene complex (200–360°C) through a π-electron interaction was observed in this study.

Redox properties of aluminas and aluminosilicates have been discussed extensively (*1–5*). Lewis acid sites, transition metal ions, and structural Fe^{3+} are the main oxidizing sites observed on alumina and aluminosilicate catalysts.

Oxidation of organic compounds on the alumina surface is well known; however, very little is known about the oxidation of aromatic substances. It is the aim of this investigation to study the oxidation of aromatic species such as toluene, benzyl alcohol, and benzaldehyde on the alumina surface under various experimental conditions.

EXPERIMENTAL PROCEDURES

Materials. $A < 40\ \mu$ alumina was separated from industrial alumina supplied by Pechiney St. Gobain Co. Na (0.44%) and Fe (0.013%) were the main impurities present in this alumina. Self-supporting films were obtained by a pelleting technique (5 t/cm^2), and about 14 mg of sample was present in a 15-mm-diameter disk. Toluene, benzyl alcohol, benzaldehyde, and benzoic acid were high-grade reagents (Fluka) and were well degassed by freeze–evacuate–thaw cycles.

Procedure. A Beckman IR 9 double-beam infrared spectrometer equipped with a prism-grating system was used to record the infrared spectra. The cell utilized was stainless steel fitted with calcium fluoride windows and a heating coil. The temperature was controlled by a thermocouple connected to a galvanometric regulator. The windows were water cooled and the cell was vacuum tight. The alumina film was placed in a sample holder and then inserted into the center of the cell. To remove the strongly held organic impurities and to reactivate the surface of the alumina, the cell was attached to a vacuum line and heated at 600°C for 5 hr at a pressure of 10^{-4} mm Hg and subsequently in an oxygen atmosphere (300 mm Hg) for 5 hr. Further heating was done at 700°C for 12 hr at a pressure of 10^{-4} mm Hg. The infrared spectra of the pretreated film were

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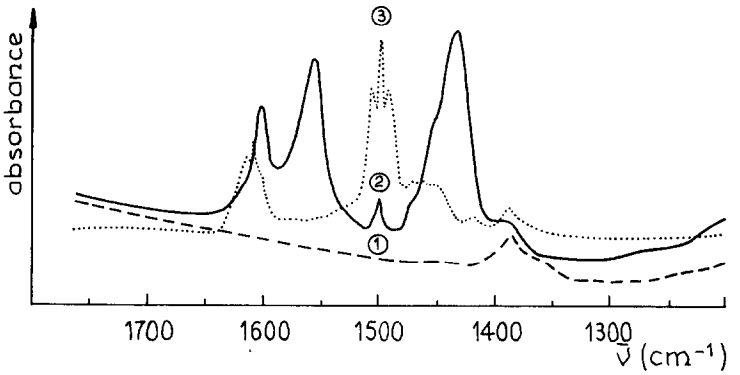

FIG. 1. Infrared spectra of: (1) alumina; (2) toluene adsorbed on alumina; (3) toluene vapor.

recorded under reduced pressure after cooling the cell to 130°C. The adsorbate was introduced in a vapor phase by connecting the evacuated cell to the organic liquid container at a temperature set for the adsorption. Before recording the spectra the cell was degassed and cooled to the recording temperature (130°C).

RESULTS AND DISCUSSION

The infrared spectra for the toluene vapor and the toluene adsorbed to the alumina surface are given in Fig. 1. Spectra of alumina kept in contact with a toluene vapor pressure of 10 mm Hg at 260°C showed that some toluene may be oxidized to benzoate in the absence of oxygen, as indicated by the appearance of the 1600-, 1500-, and 1455-cm^{-1} bands ascribed to ring breathing modes and the 1555- and 1435-cm^{-1} bands assigned to the stretching vibrations of the COO^- group. Band assignment was based on the spectra index and published work (*6*, *7*). Further evacuation at reaction temperature overnight did not show any effect on the intensities of these bands, showing that the adsorbed species were strongly held on the alumina surface. The spectra obtained for toluene adsorbed on alumina in the temperature range from 190 to 400°C were similar, and hence, this may be considered as the optimum temperature range for this reaction.

Further experimental studies showed that this oxidation reaction cannot be attributed to traces of oxygen gas and that the alumina surface is mainly responsible for this oxidation process.

Raising the temperature above that of the adsorption removes some of the adsorbed species. Analysis of the evolved products showed that toluene was the prominent phase up to 400°C. It was concluded that some toluene molecules are strongly held on the alumina surface through π–electron interaction. Such molecules could be oxidized to the benzoate form immediately upon introducing O_2. Indeed, the intensities of the 1555- and 1435-cm^{-1} bands were greatly increased by introducing O_2, confirming the presence of fixed toluene molecules which were oxidized by oxygen to form benzoate in addition to the benzoate formed in the absence of oxygen. Toluene molecules were fixed on the alumina by the π mechanism in the temperature range 200 to 360°C.

If, indeed, the toluene was transformed to benzoate on the alumina surface, similar reactions may be expected from the adsorption of benzylic alcohol, benzaldehyde, and benzoic acid. The spectra of benzylic alcohol, benzaldehyde, and benzoic acid adsorbed on the alumina at 190°C under saturated vapor pressures are shown in Fig. 2. The spectra were very similar to that of adsorbed toluene, confirming that toluene, benzylic alcohol, and benzaldehyde were oxidized to the benzoate form. The

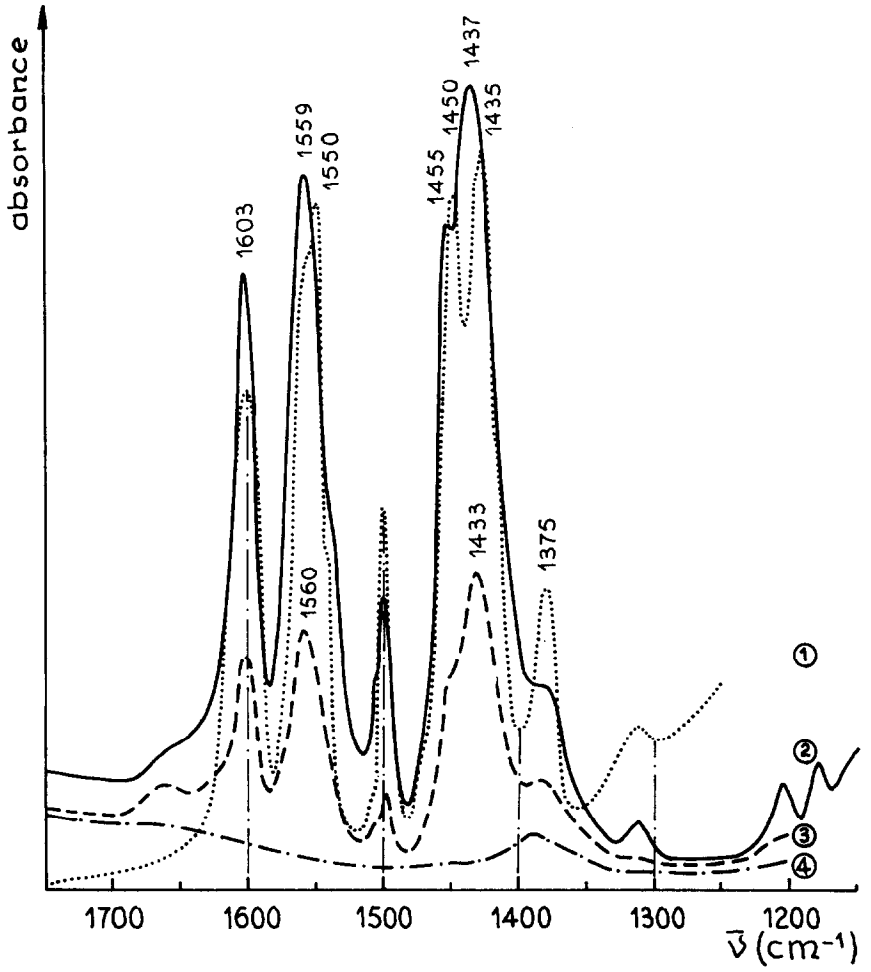

FIG. 2. Infrared spectra of: (1) benzylic alcohol adsorbed on alumina; (2) benzaldehyde adsorbed on alumina; (3) benzoic acid adsorbed on alumina; (4) alumina.

transformation of benzoic acid on the alumina surface was limited to the ionization process. This process occurred even at ordinary temperatures when benzoic acid was mixed with alumina to make a self-supporting film. It is obvious that toluene, benzylic alcohol, benzaldehyde, and benzoic acid adsorbed on the alumina were converted to a strongly held benzoate form.

An ESR study was conducted to provide a better understanding of the surface properties of the alumina and the mechanisms of reactions reported in this investigation.

REFERENCES

1. Flockhart, B. D., Naccache, C., Scott, J. A. N., and Pink, R. C., *Chem. Commun.* 238 (1965).
2. Flockhart, B. D., Scott, J. A. N., and Pink, R. C., *Trans. Faraday Soc.* **62**, 730 (1966).
3. Flockhart, B. D., Leith, I. R., and Pink, R. C., *J. Catal.* **9**, 45 (1967).
4. Furukawa, T., and Brindley, G. W., *Clays Clay Miner.* **21**, 279 (1973).
5. Eltantawy, I. M., and Baverez, M., *Clays Clay Miner.* **26**, in Press (1978).
6. Little, L. H. (1966) "Infrared Spectra of Adsorbed Species." Academic Press, New York/London.
7. Bellamy, L. J. (1975) "The Infrared Spectra of Complex Molecules." Chapman and Hall, London.