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SOME APPLICATIONS OF IRON(III) OXIDE AS A GAS CHROMATOGRAPHIC ADSORBENT

A. BETTI, G. LODI, C. BIGHI and F. DONDI

Istituto Chimico, University of Ferrara, Ferrara (Italy)

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SUMMARY

The behaviour of iron(III) oxide, α -Fe₂O₃, as a possible adsorbent in gas chromatography has been investigated, the activity being studied as a function of conditioning temperature. Variations in surface activity caused by water in the carrier gas, and also by very thin films of polyethylene glycol 20M deposited on the adsorbent, are described. Examples of separations of alkanes, alkenes, cycloalkanes, aromatic hydrocarbons, alcohols, esters and ketones are reported.

INTRODUCTION

We have previously reported some interesting characteristics of iron(III) oxide as an adsorbent in gas chromatography, in particular for the separation of light saturated and unsaturated hydrocarbons^{1,2}. This paper describes some further applications of this adsorbent, especially when water is present or other molecules are deposited on the surface.

EXPERIMENTAL

Iron(III) oxide was obtained as described previously¹. X-ray diffraction spectra of the sample confirmed that the only phase present is α -Fe₂O₃. The specific surface area, measured via adsorption of nitrogen using the Nelson and Eggertsen method³, was found to be 16 m²/g. The gas chromatograph used was a Fractovap GV Model 200 (Carlo Erba, Milan, Italy) with thermal conductivity or flame ionization detectors. The injector membranes were made of silicone rubber covered with polytrifluoroethylene (Hamilton, Reno, Nev., U.S.A.) and were heated at 200° in a stream of helium before use. Before entering the column, the gases were allowed to flow over active carbon and molecular sieves 5A. All compounds examined were pure products from J. T. Baker, Phillipsburgh, N.J., U.S.A.

The columns were conditioned as described below before determining gas chromatographic parameters.

TABLE I
RETENTION TIMES (t'_R) RELATIVE TO *n*-HEXANE AT 117.8°

Compound	t'_R	Boiling point (°C) (refs. 4 and 5)
Cyclopentane	0.24	49.3
<i>n</i> -Pentane	0.32	36.1
<i>trans</i> -2-Pentene	0.53	36.4
<i>cis</i> -2-Pentene	0.69	36.9
Methylcyclopentane	0.62	71.8
Cyclohexane	0.63	80.7
3-Methylpentane	0.74	63.3
2-Methylpentane	0.77	60.3
<i>n</i> -Hexane	1.00	68.7
2,2,3-Trimethylbutane	1.34	80.9
3,3-Dimethylpentane	1.49	86.0
2,2-Dimethylpentane	1.50	79.2
2,4-Dimethylpentane	1.65	80.5
2,3-Dimethylpentane	1.80	89.8
Methylcyclohexane	1.74	100.9
3-Methylhexane	2.27	91.8
2-Methylhexane	2.50	90.0
Benzene	2.30	80.1
<i>n</i> -Heptane	3.29	98.4
2,2,4-Trimethylpentane	3.74	99.2

RESULTS AND DISCUSSION

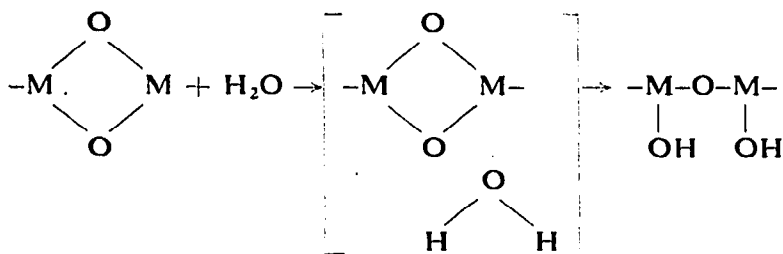
Table I lists the retention times of several hydrocarbons, relative to *n*-hexane, obtained at 117.8° following the techniques described by Kalaschnikova *et al.*⁶. The boiling points of the adsorbed species are also listed for comparison purposes. As expected, the order of elution of the alkanes and cycloalkanes (non-specific adsorbed species of type A in the classification of Kiselev and Yashin⁷) does not depend on their vapour pressures, but on their stereochemistry. The olefinic and aromatic hydrocarbons (group B in Kiselev and Yashin's classification) have interaction energies higher than those of aliphatic or alicyclic hydrocarbons with the same number of carbon atoms. Under the experimental conditions used, oxygenated compounds such as ketones, esters, ethers and alcohols give peaks that have marked tails, or become chemisorbed. In these cases, classification of the adsorbed species in the Kiselev and Yashin scheme is ambiguous.

The retention parameters given in Table I were obtained by first conditioning the material at 200° for 10 h in a stream of helium and then for 24 h at the temperature at which measurements were performed. This was found to be necessary as good reproducibility (better than 5%) in the retention parameters of the alkanes and the aromatic molecules was obtained only after the material had been "aged" at the measurement temperature for *ca.* 20 h.

Kolasnitsyna and Petrova⁸ described similar gas chromatographic behaviour for rutile, and ascribed it to the presence of water in the carrier gas. After dehydration at high temperature, and then cooling to the measurement temperature, rutile adsorbs water from the carrier gas until equilibrium is reached. After this treatment, the

retention times for aromatic compounds remain constant. Scott⁹ has reported similar behaviour for alumina.

On the other hand, it is known that, after dehydration *in vacuo* at high temperature, α -Fe₂O₃, like many other oxides⁸⁻¹¹, adsorbs water by chemisorption¹⁰, even at room temperature, via a dissociative process. This has been formulated by Morimoto *et al.*¹² by the reaction:



This step is then followed by physical adsorption of other water molecules, as has been demonstrated by McCafferty and Zettlemoyer¹⁰.

Accepting the model of the surface described by McCafferty and Zettlemoyer¹⁰, it may be suggested that conditioning the adsorbent at 200° in a stream of helium frees the surface of a certain amount of water. Decreasing the temperature of the surface then causes it again to adsorb water from the carrier gas. In fact, even the use of dehydrating agents is not sufficient to give a gas that is completely free from water¹³.

This suggestion was tested by following the adsorption of benzene on α -Fe₂O₃ under different pre-conditioning treatments. Fig. 1 shows the isotherms of benzene obtained using the peak elution profile method¹⁴. The choice of aromatic hydrocarbon is conditioned by the fact that saturated hydrocarbons give very similar retention parameters, even when the oxide is pre-conditioned differently.

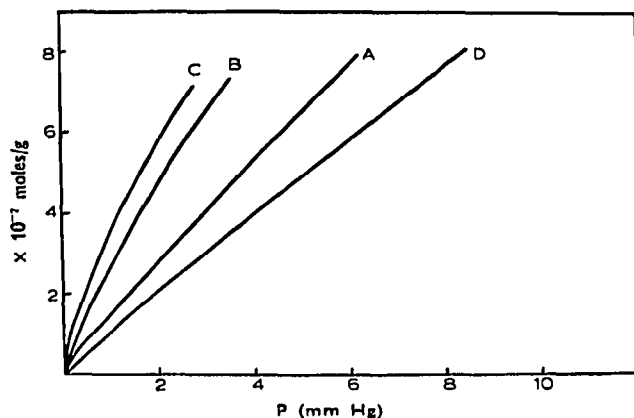


Fig. 1. Adsorption isotherms of benzene at 120° on α -Fe₂O₃. (A) 200° for 10 h and 120° for 24 h; (B) 200° for 10 h and 120° for 1 h; (C) 300° for 10 h and 120° for 1 h; (D) 200° for 10 h and 120° in the presence of water in the carrier gas.

Isotherm A was obtained by pre-conditioning the material for 10 h at 200° and then for 24 h at 120°, at which latter temperature the adsorption measurements were carried out. The reproducibility is poor under these conditions, the isotherms determined after 2 h, 5 h, etc., showing slowly decreasing adsorption values. Measurements carried out within 10–50 h after pre-conditioning are reproducible and identical with those of isotherm A. Curve C is the isotherm for benzene obtained by heating the adsorbent for 10 h at 300° and then for 1 h at 120°. In this case also the adsorption values decrease with time, until the values of system A are reached (*ca.* 20 h). The same results can be obtained by introducing some water into the column, immediately after conditioning at the higher temperature. The benzene isotherm, measured immediately after this, lies under curve A. After a certain time, depending on the amount of water introduced into the column, the adsorption values become stabilized and the benzene isotherm remains that of curve A.

One might ask whether the stabilization of the column might not be achieved more easily by more prolonged heating at the measurement temperature. Repeated measurements carried out with an oxide conditioned only at the measurement temperature gave adsorption values that were not reproducible, and in any event were lower than those of isotherm A.

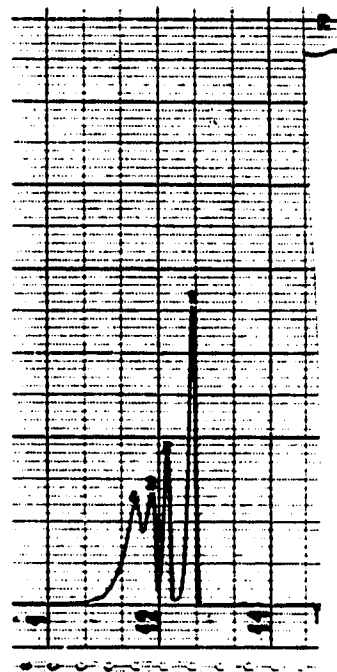
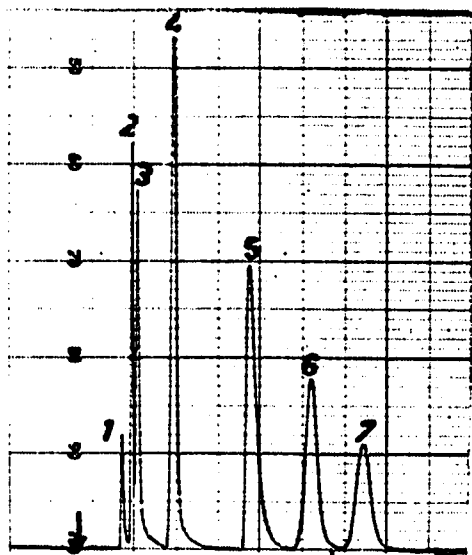


Fig. 2. Separation of (1) methane, (2) ethane, (3) ethylene, (4) propane, (5) propylene, (6) isobutane and (7) *n*-butane at 45°. Column: stainless steel, 95 cm long and 2 mm I.D. Packing: α -Fe₂O₃ (100–120 mesh), 200° for 24 h and 45° for 10 h. Carrier gas: helium PP (high purity), 0.4 ml/sec. Detector: FID, 250°; sensitivity, 10 × 16. Chart speed: 120 in./h.

Fig. 3. Separation of (1) 1-butene, (2) *trans*-2-butene, (3) isobutene and (4) *cis*-2-butene at 60°. Column and carrier gas as in Fig. 2. Detector: FID, 250°; sensitivity, 1 × 32. Chart speed: 60 in./h.

The above results lead to the following conclusions:

(1) Pre-conditioning at high temperature is necessary in order to eliminate materials adsorbed by the iron(III) oxide in contact with air during preparation of the column. The results are independent of the temperature chosen for pre-conditioning provided that it lies between 200 and 300°.

(2) A convenient period for conditioning the adsorbent at the measurement temperature is necessary in order to allow equilibration between the water contained in the carrier gas and that on the surface of the oxide.

In other words, the activity of iron(III) oxide as an adsorbent in gas chromatography, as is also the case with alumina⁹, depends on the operating temperature of the column and the amount of water adsorbed by the surface.

Examples of the surface activity of α -Fe₂O₃ when the material is conditioned at high temperature are shown in Figs. 2 and 3, the chromatograms in which show the separation of C₁-C₄ hydrocarbons and of the isomers of butene, respectively. These separations are not possible when water is allowed to enter the column before analysis. The variation in surface activity of the adsorbent with increase in the amount of surface water is illustrated in isotherm D (Fig. 1) for benzene, obtained by saturating the carrier gas with water (the saturator, at 16°, is inserted into the carrier gas line with a flow-rate of $4 \cdot 10^{-7}$ mole/sec of water).

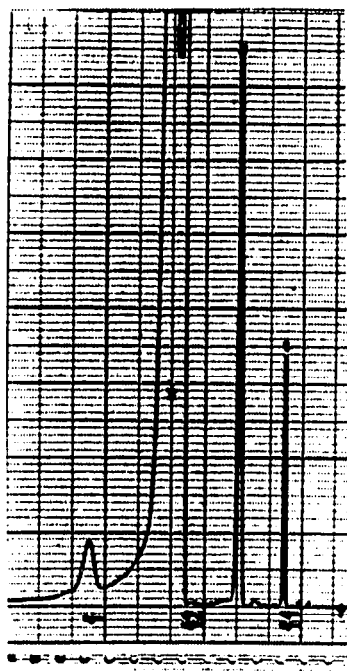


Fig. 4. Separation of (1) benzene and (2) toluene from (3) ethylbenzene in water at 175°. Column: as in Fig. 2. Packing: α -Fe₂O₃ (100-120 mesh), 200° for 10 h. Carrier gas: helium PP + water ($6 \cdot 10^{-7}$ mole/sec), 0.35 ml/sec. Detector: FID, 250°; sensitivity, 10×1 . Chart speed: 60 in./h.

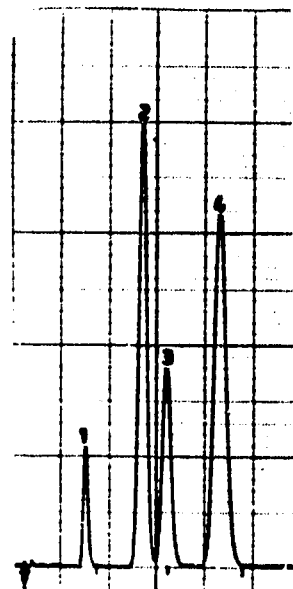


Fig. 5. Separation of (1) toluene; (2) ethylbenzene, (3) *o*-xylene and (4) cumene at 100°. Column: glass, 100 cm long and 4 mm I.D. Packing: α -Fe₂O₃ (80-100 mesh) + ca. 0.3% PEG 20M. Carrier gas: nitrogen UPP (very high purity), 1 ml/sec. Detector: FID, 250°; sensitivity 10×16 . Chart speed: 30 in./h.

The presence of water in the carrier gas and hence on the adsorbent surface may nevertheless be of use as in the elution of aromatic hydrocarbons, for which the symmetry of the peak increases and the retention time decreases. Fig. 4 shows the chromatogram obtained from a sample of $0.5 \mu\text{l}$ of water in contact with ethylbenzene containing benzene and toluene. The separation was found to be possible when the carrier gas was saturated with water.

The partial deactivation of very active surfaces by the use of polar solvents is common practice in gas chromatography. The deactivated substances can be deposited on the adsorbent surface from solution or in the gas phase. For alumina, deactivation by water⁹, silicone oil⁹ and inorganic salts¹⁵⁻¹⁷ has been obtained. Neumann and Hertl¹⁸ recently used alcohols and pyridine.

The results of Kiselev *et al.*¹⁹, describing the possibility of obtaining homogeneous surfaces with low adsorption energies by modifying porous and non-porous materials with monolayers of polymers or of large organic molecules, are of interest. Aue *et al.*²⁰ prepared monolayer polymer films deposited on silica-based materials.

In a manner similar to that of Aue *et al.*, we covered $\alpha\text{-Fe}_2\text{O}_3$ with polyethylene glycol 20M (PEG 20M) (4% solution in chloroform). After evaporation of the solvent, the material was heated in a stream of nitrogen at 250° for 15 h and then washed with chloroform for 8 h. PEG 20M was chosen on the basis of Aue *et al.*'s results

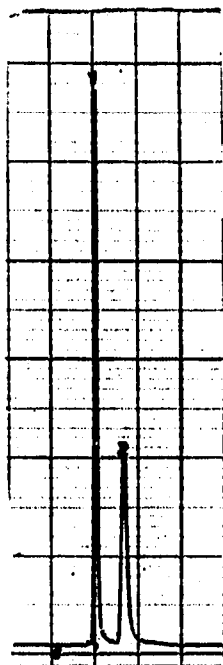


Fig. 6. Separation of (1) isopropanol from (2) *n*-propanol at 100° . Conditions as in Fig. 5.

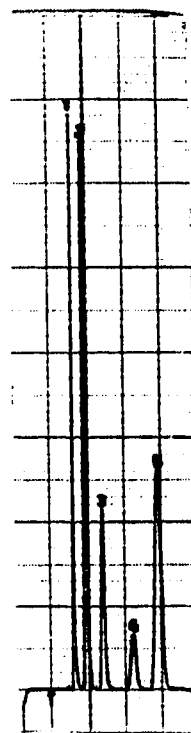


Fig. 7. Separation of (1) acetone, (2) ethyl acetate, (3) diethyl ketone, (4) methyl isobutyl ketone and (5) *n*-butyl acetate at 100° . Conditions as in Fig. 5.

and also because α -Fe₂O₃ adsorbs alcohols and ethers by chemisorption²¹. The amount of PEG 20M that remains on the oxide surface is estimated to be less than 0.3%.

The preliminary results obtained with iron(III) oxide modified in this way appear promising. Thus, the retention times of aromatic molecules are strongly reduced (Fig. 5) and it is then possible to elute oxygenated compounds with symmetrical peaks (Figs. 6 and 7).

The examples reported illustrate only a few of the possible uses of α -Fe₂O₃. They show how the range of use of an adsorbent can be increased by suitably varying and controlling the surface activity of the material by using carrier gases that are polar or contain polar compounds, or by using small amounts of common stationary phases.

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