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A FT-IR assessment of iso-C_4H_8 reactivity with V_2O_5/TiO_2 catalysts

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Low-loaded vanadia–titania catalysts have been prepared by impregnation of titania P-25 (Degussa). The catalysts were characterized by X-ray diffraction, specific surface area and porosity assessment by nitrogen adsorption at 77 K. For very low vanadia contents the absence of surface acid Brønsted sites leads to dimerization on surface acid Lewis sites, whereas the presence of surface acid Brønsted sites when the vanadia content is increased leads to oxidation to carbonyl and carboxylate species.

Keywords: Isobutene oxidation; isobutene oligomerization; vanadia–titania catalysts; FT-IR spectroscopy; surface processes

1. Introduction

Supported vanadia is one of the most widely used catalysts for partial oxidation processes [1–3]. The activity and selectivity shown by this catalyst in different reactions is one of the most peculiar examples on the effect of the nature of the support on the properties of supported heterogeneous catalysts. It has been shown [4,5] that these vanadia–titania catalysts perform best when there is only a monolayer of vanadia on the titania surface; for higher contents large crystallites are formed

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that no longer interact with the support, while for low loadings the exposed titania surface may lead to side-reactions.

Interaction of isobutene with pure titania and with vanadia–titania catalysts has been reported previously [6,7]. Reaction of isobutene with the surface of titania at room temperature leads to formation of oligomers, while for vanadia–titania systems containing about 9.6% weight, tert-butoxy species are formed, then are oxidized to acetone and to carboxylate species as the temperature is increased. Isobutene oligomers and tert-butoxy species are formed on both surface Lewis or Brønsted acidic sites, through the intermediate formation of a carbonium ion that acting as an electrophilic agent reacts with the double CC bond in the alkene molecule (oligomer formation) or with surface oxygen atoms (tert-butoxy formation).

We here report the interaction of isobutene with very low loaded vanadia–titania catalysts. Our aim is to investigate the catalytic behaviour of these systems for isobutene reactivity which can proceed through three different routes [8]; hydration yielding tert-butoxy species, oligomerization to form 2,4,4-trimethylpentene, and polymerization to poly-isobutene.

2. Experimental

2.1. SAMPLE PREPARATION

The support was TiO_2 P-25 from Degussa (Germany). Before incorporation of vanadium species, it had been calcined at 770 K overnight in air in order to remove adsorbed contaminants. 5 g of the support was impregnated with boiling aqueous solutions of NH_4VO_3 (from Merck) in amounts corresponding to final solids containing 1% (sample VT1) or 0.1% (sample VT0.1) of V_2O_5 (w/w). The suspensions were stirred at room temperature for 2 h, then dried and finally calcined at 770 K in dry oxygen flow for 3 h. Isobutene for adsorption measurements was from Societá Italiane de Ossigeno (Milan, Italy).

2.2. APPARATUS

X-ray diffraction (XRD) patterns were recorded in a Siemens D-500 instrument, using Cu Kα radiation ($\lambda = 154.050$ pm) and a graphite monochromator. Specific surface area and porosity properties were assessed from nitrogen (99.995%, from Sociedad Castellana del Oxígeno, Spain) adsorption isotherms at 77 K on the solids previously outgassed (residual pressure $\sim 10^{-4}\,\mathrm{N\,m^{-2}}$) in situ for 2 h at 420 K; the adsorption–desorption isotherms were recorded in a conventional high vacuum pyrex apparatus, with grease-free joints, silicon oil diffusion pump and a MKS baratron pressure transducer. The FT-IR spectra have been recorded at room temperature on a Nicolet MX1 Fourier transform instrument, equipped with a conventional evacuation/gas manipulation ramp ($10^{-4}\,\mathrm{N\,m^{-2}}$) and IR cells with NaCl windows. The solids were pressed in self-supported disks and were activated by heating at 673 K in air for 30 min, followed by evacuation at the same temperature for 1 h. The spectra of the adsorbed species are presented in this paper after subtraction of the spectrum of the activated catalyst disk (outgassing in situ at 770 K for 2 h) from that recorded after adsorption.

3. Results and discussion

The XRD profiles are similar in all cases; that for sample VT1 is shown in fig. 1. Diffraction lines due only to anatase and rutile were detected. From the equation of Criado and Real [9], the anatase content can be estimated as ~ 50%, as in the unloaded support. No diffraction peak due to vanadia or ternary V–Ti–O compounds was detected, probably due to good dispersion of the low amounts of vanadium-containing species existing in these samples.

Specific surface areas [10] were almost coincident with those for the original support ($S_{BET} = 46–48$ m^2 g^{-1}). All isotherms correspond to type II of the IUPAC classification [11], with no hysteresis nor indication of micropores.

Adsorption at room temperature of isobutene on the samples was followed by FT-IR spectroscopy. The main differences are observed in the 1250–1150 cm^{-1} range, these differences being larger as the vanadium content increases.

The spectrum recorded upon adsorption of isobutene at room temperature on sample VT0.1 is shown in fig. 2a. This spectrum does not correspond to molecularly adsorbed isobutene nor gaseous isobutene [6], but important changes in the positions and intensities of the bands are detected. Bands at 1397 and 1378 (strong) cm^{-1} are due to symmetric deformation mode of methyl groups (1430 and 1381 cm^{-1} for iso-$C_4H_{8(g)}$), and together with the bands at 1240 and 1203 (weak) cm^{-1},

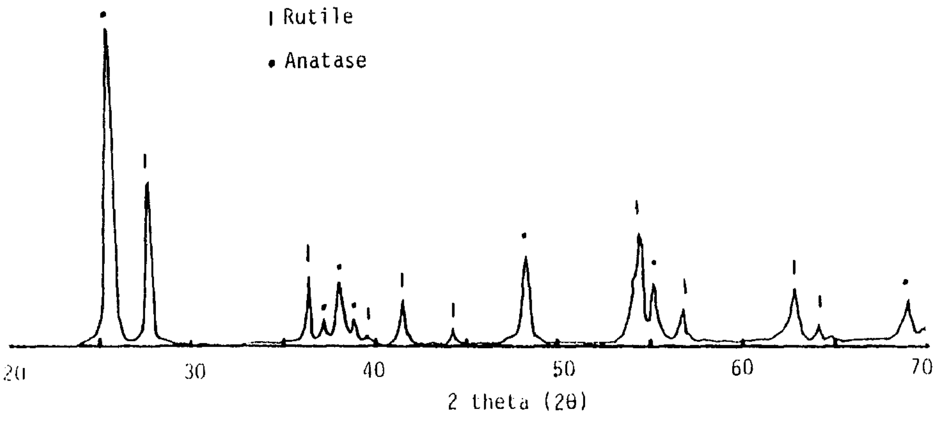


Fig. 1. XRD patterns of sample VT1.

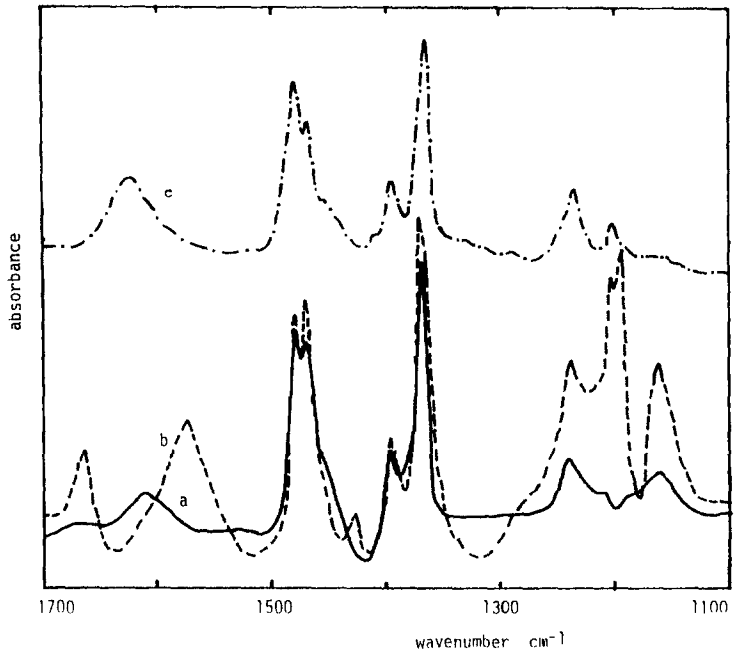


Fig. 2. FT-IR spectra of adsorbed species arising from isobutene adsorption at room temperature on samples (a) VT0.1 and (b) VT1, and (c) pure TiO_2 (taken from ref. [6]).

indicate the presence of tert-butyl groups [12]. The complex feature formed by a doublet at 1482 and 1472 and the shoulder at 1455 cm^{-1} is ascribed to asymmetric deformation of methyl groups (1470, 1458, and 1444 cm^{-1} for iso-$C_4H_{8(g)}$). Bands at 2960, 2915 and 2875 cm^{-1} (fig. 3) are due to the stretching modes of methyl groups [6] (2981, 2946 and 2941 cm^{-1} for iso-$C_4H_{8(g)}$), and only a weak C–H band belonging to an olefin is recorded at 3075 cm^{-1} (3087 cm^{-1} for iso-$C_4H_{8(g)}$). The band at 1612 cm^{-1} (fig. 2a) is due to the C=C stretching mode, and is shifted towards lower wavenumbers with respect to the expected position (1660 cm^{-1} for iso-$C_4H_{8(g)}$) because of the interaction of the adsorbed molecule with surface cationic sites; this finding, together with that at 3075 cm^{-1}, indicates the presence of $CH_2{=}C{<}$groups. Taking into account these features, formation of the isobutene dimer, 2,4,4,-trimethyl-pent-1-ene can be assumed [7,13,14].

In addition to these bands due to hydrocarbon species, other bands indicate the presence of oxygenated species. The weak band at 1670 cm^{-1} is due to a C=O stretch. The band at 1160 cm^{-1}, with two shoulders at 1175 and 1190 cm^{-1}, has been also recorded upon adsorption of tert-butanol on vanadia–titania and on rutile [6,15], and is due to ν_{C-O}/ν_{C-C} coupling in small amounts of tert-butoxide species formed on the surface of the catalyst.

These results agree with the high reactivity of isobutene and its tendency to catio-

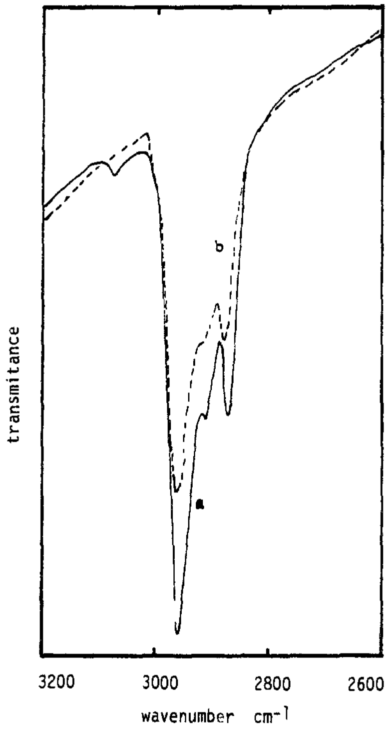
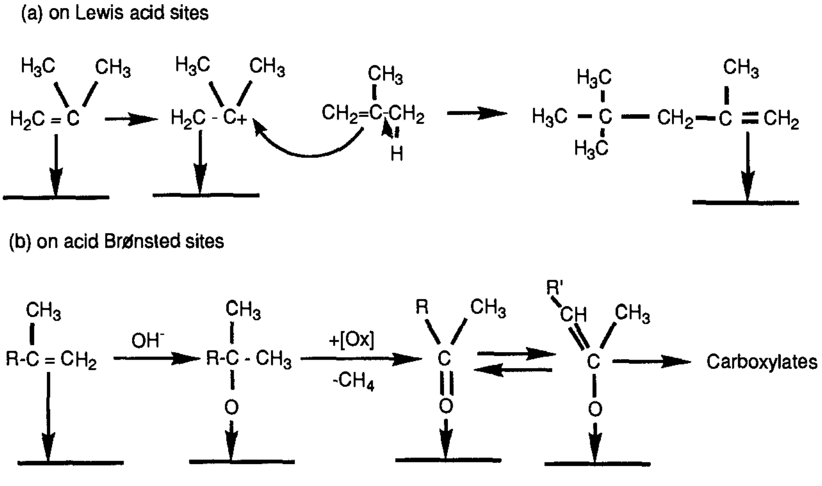


Fig. 3. FT-IR spectra of adsorbed species arising from isobuten adsorption at room temperature on samples (a) VT0.1, (b) VT1 (ν_{CH} region).

nic polymerisation, catalyzed by an active proton from surface acid Brønsted sites, or by Lewis acids [6–8].

The spectrum recorded upon adsorption of isobutene at room temperature on sample VT1 is shown in fig. 2b. Bands due to isobutene reaction products are also recorded in this case, their intensities being enhanced. The broad band recorded at 1160 cm^{-1} with shoulders at 1175 and 1190 cm^{-1} for catalyst VT0.1, is now clearly recorded as a doublet at 1197 and 1165 cm^{-1}. On the other hand, bands recorded for catalyst VT0.1 and ascribed to species with terminal double C=C bonds ($\nu_{C=C}$ at 1612 cm^{-1} and $\nu_{as(CH_2)}$ at 3075 cm^{-1}) have completely vanished (figs. 2b and 3b) for sample VT1; the band recorded at 1165 cm^{-1} is characteristic of isopropoxide species [7,15], formed through V–OH addition to the terminal C=C bond of 2,4,4,-trimethyl-pent-1-ene, the presence of monomeric tert-butoxide species being put into evidence by the band at 1197 cm^{-1} [15]. In addition, the bands at 1670 cm^{-1} ($\nu_{C=O}$) and 1580 and 1435 cm^{-1} (ν_{asym} and ν_{sym} for the –COO group) indicate that, even at room temperature, oxidation of isobutene proceeds to alkoxides, carbonyls, and finally carboxylate species.

Such a dimerization, but without formation of oxidized species, already takes



R = methyl; 2,2-dimethylpropyl; R' = tert-butyl or H

Fig. 4. Reaction schemes for isobutene dimerization and oxidation on Lewis or Brønsted acid sites.

place on parent TiO_2, as shown by the spectrum recorded upon adsorption of isobutene on TiO_2, fig. 2c.

From the above results we conclude that vanadia / titania systems catalyze cationic dimerization (or even oligomerization) of isobutene even at room temperature, probably through coordination of the olefin molecule to the vanadium cation through the π bond, thus forming a carbocation able to react with another isobutene moiety, leaving a free cation. This process is easily detected (together with small amounts of alkoxide species) on catalyst VT0.1. However, for larger vanadia contents (catalyst VT1), an oxidative dehydrogenation of isobutene takes place, thus mainly leading to formation of carbonyl species, probably through methane release [7], that undergo further oxidation to carboxylate. A reaction scheme for both processes is depicted in fig. 4. The presence of polymeric vanadyl species in the vanadium-rich sample would account for the larger oxidizing power of this catalyst.

On the other hand, from results in this and other [6,7,15] papers, we conclude that selectivity towards oligomerization is related to the absence of acid Brønsted sites; however, on increasing the vanadia content (and thus the concentration of acid Brønsted sites), oxidation processes are favoured.

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References

[1] M.S. Wainwright and N.R. Foster, Catal. Rev.-Sci. Eng. 19 (1979) 211.

[2] P.J. Gellings, in: *Catalysis*, Vol. 7, Specialist Periodical Report, eds. G.C. Bond and G. Webb (The Royal Society of Chemistry, London, 1985) p. 105.

[3] F. Cavani and F. Trifiro, Chim. Ind. (Milan) 70 (1988) 58.

[4] C. Martin, V. Rives, V. Sanchez-Escribano, G. Busca, V. Lorenzelli and G. Ramis, Surf. Sci. 251/252 (1991) 825.

[5] G.C. Bond and S.F. Tahir, Appl. Catal. 71 (1991) 1.

[6] G. Busca, G. Ramis and V. Lorenzelli, H. Chem. Soc. Faraday Trans. I 85 (1989) 137.

[7] V. Sanchez-Escribano, G. Busca and V. Lorenzelli, H. Phys. Chem. 95 (1991) 5541.

[8] K. Wessermel and H.J. Arpe, *Industrial Organic Chemistry* (Verlag Chemie, Weinheim, 1978).

[9] J.M. Criado and C. Real, J. Chem. Soc. Faraday Trans I 79 (1983) 2765.

[10] S. Lowell and J.E. Shields, *Powder Surface Area and Porosity*, 2nd Ed. (Chapman and Hall, London, 1984).

[11] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol and T. Sieminiewska, Pure Appl. Chem. 57 (1985) 603.

[12] L.J. Ballamy, *The Infrared Spectra of Complex Molecules*, Vol.2, 2nd. Ed. (Chapman and Hall, London, 1980).

[13] C.J. Pourchert, *The Aldrich Library of FT-IR Spectra* (Aldrich, 1985).

[14] N. Tokura, M. Matsuda and I. Shirai, Bull. Chem. Soc. Japan 38 (1962) 371.

[15] G. Ramis, G. Busca and V. Lorenzelli, J. Chem. Soc. Faraday Trans. I 83 (1987) 1591.