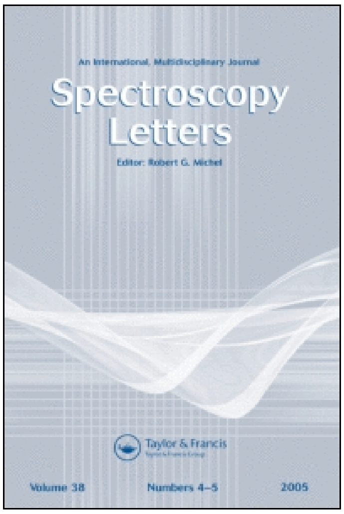

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FORMATION AND EVOLUTION OF CARBONATE SPECIES IN Na-DOPED Al_2O_3 AND V_2O_5-Al_2O_3

Key words: IR spectra, carbonate species, alumina-vanadia catalysts

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ABSTRACT

A study is carried out by FT-IR spectroscopy of the carbonate species formed upon interaction of CO_2 with alumina and vanadia-alumina catalysts doped with sodium. It is found that the presence of sodium enhances the ability of the catalyst surface to adsorb CO_2, yielding to carbonate formation. The species formed changes in the presence of vanadium, shifting the υ_{COO} stretching bands towards higher wavenumbers than those recorded in Na-Al_2O_3 systems.

INTRODUCTION

Vanadium-containing catalysts are widely used in partial oxidation processes[1,2] and reduction of nitrogen oxides with ammonia[3,4], reaction where V_2O_5/Al_2O_3 have proved to be well suited. The surface acid-base properties of these catalysts can be modified by adding species such as alkaline metals, sulfate, fluoride, phosphates, etc., species that, on the other hand, usually turn up being contaminants in industrial catalysts. Several authors[5,6] have claimed that addition of alkaline metals to alumina leads to deep changes in the physicochemical properties of the solid, that depend as well on the calcination temperature to which it has been submitted after impregnation. Parera and Figoli[7] and Ratnasany[8] have suggested that addition of sodium to alumina decreases its surface acidity, and Chuang et al.[9] have reported, from IR spectroscopy studies, that sodium reacts with the most acidic surface sites.

In the present paper, a study is carried out on the effect of contamination with carbon dioxide on the surface properties of alumina doped with sodium, used as a support for vanadia catalysts. It has been found that the surface carbonate species formed when sodium is present differ when vanadium exists in the catalysts, and that CO_2 seems to react with exposed V=O species.

EXPERIMENTAL

Alumina from Degussa (Aluminium Oxid C, batch RV0005) was calcined at 770 K to eliminate adsorbed organic contaminants. The solid was then doped with sodium (0, 1, 3 and 6% weight, samples A0, A1, A3, and A6, respectively) by impregnation with aqueous solutions of NaOH (Panreac, p.a.) in a rotary vacuum evaporator (Heidolph VV-60), and finally calcined (Heraeus ROK 3/60 furnace) up to 770 K at a heating rate of 10 K/min (RAX P-C 8601 temperature programmer). Incorporation of vanadium was performed by impregnation with aqueous solutions of NH_4VO_3 (Panreac, p.a.) containing a small amount of oxalic acid (Panreac, p.a.) to easy its dissolution. After stirring at room temperature for 6 h, the solvent was evaporated at 380 K and the solid then calcined at 773 K or 973 K in temperature programming conditions as above. The amount of vanadium was calculated to yield a monolayer of vanadia, from the specific surface area of alumina (ca. 100 m^2/g) and the surface occupied by a "molecule" of $VO_{2.5}$.

The IR spectra were recorded in a FT-IR 1730 Perkin-Elmer instrument, using KBr pellets. The resulting spectrum was the sum of 40 spectral scans, and KBr was used to substract the background.

RESULTS AND DISCUSSION

The IR spectrum of parent alumina displays an absorption band at 1630 cm^{-1}, due to the δ_{H_2O} mode of surface water. When doped with sodium up to 3% weight, new bands develop, Fig. 1, at 1535-1528 and 1404-1405 cm^{-1}, the band at 1630 cm^{-1} remaining almost unchanged. If the sodium content is increased up to 6% (sample A6), the spectrum is dominated by an intense band at 1447 cm^{-1}, with a weak, sharp peak at 1404 cm^{-1}, a band close to 1020 cm^{-1}, due to de υ_1 mode of carbonate species, being also detected. The position of the strongest band coincides with that of sodium carbonate (1440 cm^{-1}) due to the υ_3 mode of free carbonate ions. Sodium carbonate displays also IR bands at 877 cm^{-1} (υ_2) and 700 cm^{-1} (υ_4), and the former band can even be recorded in the spectrum of sample A6. These results suggest that incorporation of sodium on the surface of alumina strongly favours formation of surface carbonate species, enhancing the surface basicity of the oxide. The bands at 1535-1528 and 1404-1405 cm^{-1} can be ascribed to the result of the splitting of the υ_3 mode of carbonate because of the interaction of CO_2 with the surface and thereof decreasing its local symmetry, similarly to the splitting observed in aragonite[10,11]. The positions of these bands do not coincide with those reported in the literature for systems similar to those here studied; Parkyns[12] has reported bands at, 1640, 1480, and 1233 cm^{-1} upon adsorption of CO_2 on alumina,

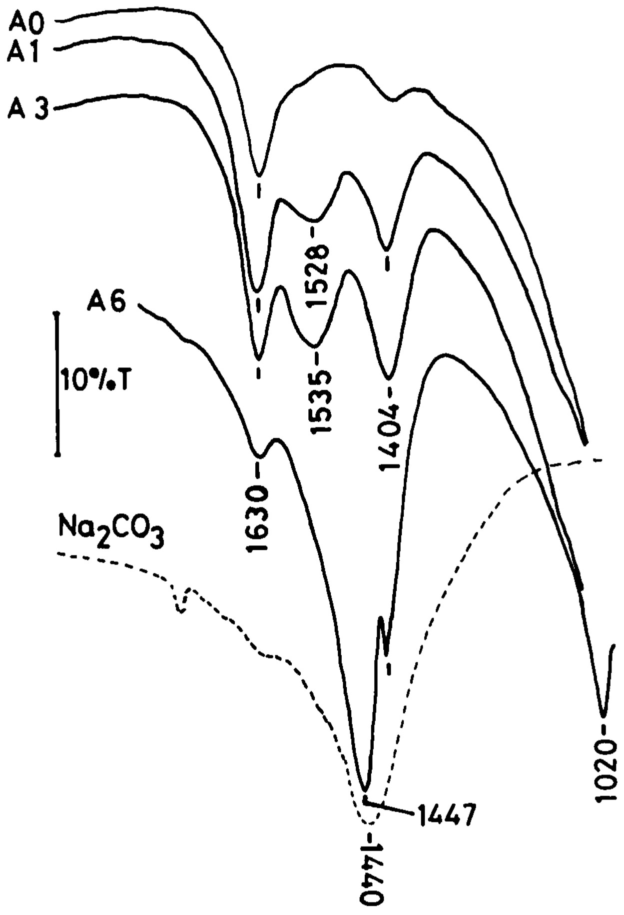

FIG. 1 Infrared spectra of alumina (A0), Na-doped alumina (A1, A3, and A6), and sodium carbonate.

that should correspond, according to Hair[13], to formation of bridged surface carbonate species (υ_{COO} modes at 1640 and 1232 cm^{-1}), although, according to Knözinger[14], they correspond to bicarbonate species. The presence of sodium in our samples and the modification of the surface basicity thereof should account for the shift in the bands originated by the symmetric and antisymmetric υ_{COO} modes. For low sodium content, carbonate should be adsorbed giving rise to bridge units between two surface metallic ions, while with the sodium-richest sample unidentate

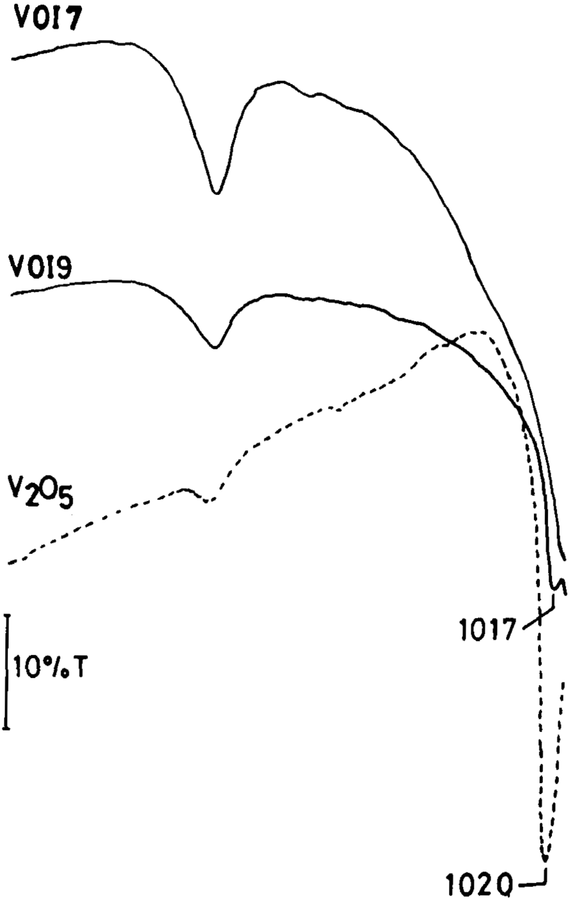

FIG. 2 Infrared spectra of Na-free, V-containing alumina, calcined at 773 (spectrum V0I7) or 973 K (spectrum V0I9), and of vanadia.

species should predominate, accounting for the strong band at 1447 cm^{-1} due to free $CO_3^{=}$ species.

Incorporation of vanadium oxide onto the surface of Na-free alumina, following the method described above, yields samples named V0I7 and V0I9. According to their X-ray diffraction diagrams, the former contains highly dispersed vanadia, while in the second both vanadia and $AlVO_4$ have been formed[15]. The IR

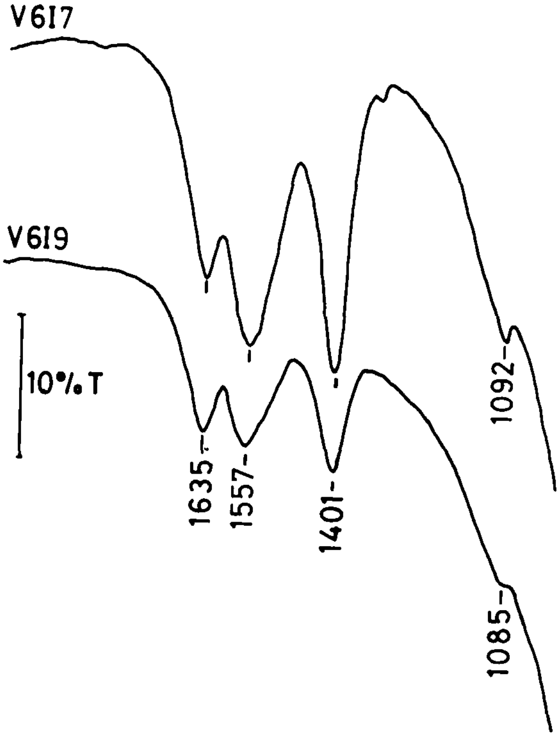

FIG. 3 Infrared spectra of Na-doped (6% weight), V-containing alumina, calcined at 773 (spectrum V6I7) or 973 K (spectrum V6I9).

spectrum of sample V0I9, Fig. 2, shows a peak at 1017 cm^{-1}, coinciding with that recorded in the spectrum of bulk V_2O_5 at 1020 cm^{-1}, due to the $\nu_{V=O}$ mode[16]; for sample V0I7 the band is only recorded as a weak shoulder. Bands due to carbonate species are absolutely absent.

The spectra displayed by samples where vanadium and sodium exist on the surface of alumina are very different from those above reported, Fig. 3. While the band due to surface water is recorded again at 1635-1633 cm^{-1}, the bands due to ν_{COO} modes (ν_3) are recorded at 1558-1557 and 1401-1400 cm^{-1}. In addition, the band at 1020 cm^{-1}, recorded in the spectra of V_2O_5 and the Na-free, V-containing alumina samples, due to the $\upsilon_{V=O}$ mode, is not recorded, while a new band at 1092-1085 cm^{-1} develops. Removal of the band at 1020 cm^{-1} clearly indicates that the CO_2 molecule interacts with exposed V=O units at the surface of V_2O_5 and/or $AlVO_4$ crystallites. On the other hand, the new band at 1092-1085 cm^{-1} can be ascribed to the υ_1 mode of carbonate that was IR-forbidden in the free carbonate ion, but becomes active upon adsorption on the surface (It is also IR-active in aragonite).

As, under similar conditions, the spectrum of bulk vanadia does not show any band that could be ascribed to formation of carbonate species, it could argued that the bands at 1558-1557, 1401-1400 and 1092-1085 cm^{-1} are not originated by CO_2 adsorption on vanadium sites; however, the absence of the band at 1020 cm^{-1} (due to $\upsilon_{V=O}$ mode) can be only explained assuming that interaction of CO_2 with the surface is via vanadium sites, i.e., the presence of sodium should enhance the basicity of the vanadium-containing surface, similarly to the role it plays when incorporated on the bare surface of alumina.

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REFERENCES

1 (a) Mori K., Miura M., Miyamoto A., Murakami Y. Catalytic Reactions on Well-Characterized Vanadium Oxide Catalysts. 3. Oxidation of Hydrogen; J. Phys. Chem. 1984; 88: 5232-5235. (b) Mori K., Miyamoto A., Murakami Y. Activity and Selectivity in Catalytic Reactions of Buta-1,3-diene and But-1-ene on Supported Vanadium Oxides; J. Chem Soc., Faraday Trans. I 1986; 82:13-24. (c) Mori K., Miyamoto A., Murakami Y. Activity and Selectivity in Toluene Oxidation on Well Characterized Vanadium Oxide Catalysts; J. Chem Soc., Faraday Trans. I 1987; 83:3303-3315.

2 (a) Martín C., Rives V. V_2O_5/TiO_2 Oxidation Catalysts. III. Oxidation of CO on Pure and Sodium-Doped Systems; React. Kinet. Catal. Lett. 1988; 36:401-406. (b) Martín C., Rives V. Selective Oxidation of Propene to Acrolein on VO_x/TiO_2 Systems containing Sodium; J. Molec. Catal. 1988; 48:381-391.

3 Jansen F. J. J. G., van der Kerkhoff F. M. G., Bosch H., Ross J. R. H. Mechanism of the Reaction of Nitric Oxide, Ammonia, and Oxygen over Vanadia Catalysts. 1. The Role of Oxygen studied by Way of Isotopic Transients under Dilute Conditions; J. Phys. Chem. 1987; 91:5921-5927.

4 Sobalik Z., Pour V., Sokolova L. A., Nevskaya O. V., Popova N. M. Determination of the Exposed Surface Area of V_2O_5 on a V_2O_5/Al_2O_3 Catalyst; React. Kinet. Catal. Lett. 1986; 30:179-184.

5 Marczewski M., Malinowski S. Free Radical Properties of Alumina Gel Surface treated with different amounts of Sodium Hydroxide; Bull. Acad. Pol. Sci., Ser. Sci. Chim. 1976; 187-191.

6 Hombek R., Kijenski J., Malinowski S. Methods of Saturation with Alkali Ions. Influence of the Properties of Oxides. In: Delmon B., Grange P., Jacobs P. and Poncelet G. eds. *Preparation of Catalysts II.* Amsterdam: Elsevier Scientific Publishers 1979: 595-603.

7 Figoli N. S., Hillar S. A., Parera M. Poisoning and Nature of the Alumina Surface in the Dehydration of Methanol; J. Catal. 1971; 20:230-237.

8 Ratnasany P., Sharma D. K., Scharme L. D. Surface Acidity of Co-Mo-Al_2O_3 Catalysts; J. Phys. Chem. 1974; 78:2069-2070.

9 Chuang T. T., Dalla Lona I. Catalytic Activity and Selectivity of Sodium Hydroxide-doped γ-aluminas. G. J. Chem. Soc. Faraday Trans I 1972; 68:773-784.

10 Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th. ed. New York: John Wiley & Sons, 1986.

11 Rives-Arnau V., Munuera G., Criado J. M. Raman Spectrum of the split υ_4 mode of $CO_3^=$ Ions in Aragonite. Spectroscopy Lett. 1979; 12:733-738.

12 Parkyns N. D. The influence of Thermal Pretreatment on the Infrared Spectrum of Carbon Dioxide Adsorbed on Alumina; J. Phys. Chem. 1971; 75:526-531.

13 Hair M. L. *Infrared Spectroscopy in Surface Chemistry.* New York: Marcel Dekker Inc., 1967.

14 Knözinger H. Specific Poisoning and Characterization of Catalytically Active Oxide Surfaces. In: Eley D. D., Pines H., Weisz P. B. eds. *Advances in Catalysis.* New York: Academic Press 1976; 25:184-271.

15 del Arco M., Holgado M. J., Martín C., Rives V. Reactivity of Vanadia with Silica, Aumina, and Titania Surfaces. Submitted for publication.

16 Nakagama Y., Ono T., Miyata H., Kubokawa Y. Infrared and X-ray Diffraction Investigations of Vanadium-Titanium Oxides for the Oxidation of Alcohol. J. Chem. Soc. Faraday Trans. I 1983; 79:2929-2936.

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