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MICROCALORIMETRIC STUDY OF THE ACID-BASE PROPERTIES OF BULK AND SILICA OR γ-ALUMINA-SUPPORTED VANADIUM OXIDES

J. Le Bars and A. Auroux

INSTITUT DE RECHERCHES SUR LA CATALYSE, 2 AVENUE ALBERT EINSTEIN, F–69626
VILLEURBANE, CÉDEX, FRANCE

The acid-base character of vanadium pentoxide, V_2O_5/SiO_2 and $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts has been investigated by adsorption of ammonia and sulphur dioxide using microcalorimetry. By depositing vanadium oxide on silica, new surface sites are formed which present more acid strength than bulk vanadium pentoxide and pure silica. Alumina-supported vanadium catalysts can be regarded as acidic monolayers VO_x. Sulphur dioxide was found to be selective for uncovered alumina.

Keywords: adsorption microcalorimetry, catalyst surface, vanadium oxides

Introduction

The dispersion of vanadium pentoxide over an other oxide of large specific area may produce modifications in the surface topology of the active sites, the acid-base properties and metal-oxygen bonds. A number of studies has dealt with the acid-base properties of these systems using infrared spectroscopy [1–3] and temperature-programmed desorption of probe molecules [4, 5]. Adsorption of acid or base probes in the gas phase using microcalorimetry is a suitable tool to effect these studies, and allows determination of populations and strengths of surface acid sites. In this investigation we have compared the acid-base character of bulk vanadium pentoxide, silica and γ-alumina-supported vanadium catalysts using adsorption microcalorimetry of probe molecules. Ammonia (pK_a $NH_3/NH_4^+ = 9.2$) was used as basic probe for the titration of acidic sites. Sulphur dioxide (pK_a $SO_2/HSO_3^- = 1.8$) adsorptions were used to investigate the basic character of the catalyst surfaces.

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Experimental

Materials

Bulk vanadium pentoxide V_2O_5 was prepared by stirring vanadyl oxalate VOC_2H_4 in methanol up to complete dissolution. Hydrolysis of the vanadyl complex was performed by addition of water. The solvent was then evacuated under hypercritical conditions of temperature and pressure of methanol, (553 K, 2×10^4 kPa), for one hour. Silica and γ-alumina-supported vanadium oxide were prepared by the wet aqueous impregnation method. Fixed amounts of ammonium metavanadate, NH_4VO_3, corresponding to vanadium pentoxide loadings from 1 to 20 wt%, were added to an aqueous suspension silica (Degussa, 380 $m^2\cdot g^{-1}$) or γ-alumina (Degussa, 138 $m^2\cdot g^{-1}$). Each suspension was stirred for 2 h at room temperature. The solvent was then slowly removed by rotavapor at 373 K. The catalyst powders were further dried overnight at 393 K.

All samples were heated finally under air flow at 833 K for 15 h.

Methods

The vanadium content of the supported samples was determined by atomic absorption spectroscopy (flame N_2O/C_2H_2, $\lambda = 318$ nm). Specific surface areas were measured by the BET method using nitrogen adsorption at 77 K. Prior to measurements, the samples were outgassed at 673 K for 3 h.

Calorimetric experiments were performed in a differential heat flow microcalorimeter of the Tian-Calvet type (Setaram) connected to a volumetric vacuum line equipped with a Barocel gauge [6]. Adsorption of probe molecules was performed by introducing successive doses of known amounts of the adsorbate onto the sample placed in the microcalorimeter cell. The microcalorimeter cell was maintained at 353 K for ammonia and sulphur dioxide adsorptions to avoid excessive physisorption. Differential and integral enthalpies of adsorption were plotted against the amount of adsorbed probe molecule. Before microcalorimetric measurement, the catalysts (100 mg) were pretreated overnight at 673 K under oxygen atmosphere and further desorbed at the same temperature under 1.33 mPa.

Results and discussion

Vanadium contents, expressed as weight percent of vanadium pentoxide, specific surface areas and theoretical vanadium oxide monolayers of the catalysts are listed in Table 1. The decrease in surface area of the V_2O_5/SiO_2 catalysts with increasing vanadium content can be attributed to mesopore plugging or sintering of silica particles during calcination at 833 K. Large amounts of vanadium oxide and the use of water as solvent in the preparation may favour this trend [7].

Mesopore plugging of γ-alumina particles may also occur on $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts, but leads to a minor decrease of specific surface. Theoretical vanadium oxide monolayers have been calculated assuming a cross-sectional area of 0.201 nm^2 for vanadium pentoxide on the surface [8].

Table 1 Physico-chemical characterizations of vanadium oxide catalysts

Catalysts	V_2O_5 / wt%	BET area / m^2g^{-1}	Monolayer / %	Probe molecules
V_2O_5	–	12.8	–	NH_3, 80°C
V_2O_5/SiO_2	1.1	305	2	
	4.8	270	12	NH_3, 80°C
	10.0	256	26	
	19.1	173	73	
V_2O_5/Al_2O_3	1.0	138	5	NH_3, SO_2
	2.9	135	15	80°C
	5.2	130	27	
	9.8	111	64	
	20.8	128	109	

Figure 1 shows the differential enthalpy of ammonia adsorption at 353 K over bulk vanadium pentoxide. Ammonia is adsorbed with an initial enthalpy of 67 $kJ \cdot mol^{-1}$. The surface sites which present an enthalpy of ammonia absorption above 50 $kg \cdot mol^{-1}$ represent 12 % of the total titrated acid sites (for a final ammonia pressure of 66 Pa). According to the cross-sectional area occupied by a single ammonia molecule (1.412 nm^2)[9], 42% of the overall surface has been recovered at the end of chemisorption. Thus, the surface of vanadium pentoxide only shows a weak acidic character.

Figure 2 shows in a three-dimensional diagram the differential enthalpy of ammonia adsorption at 353 K as a function of ammonia uptake and of vanadium content on the V_2O_5/SiO_2 catalysts. It is appears from this diagram that both number and strength of acidic sites increase with vanadium content. The lack of strong acidity of silica after outgassing at 673 K has already been reported [6], and the V_2O_5/SiO_2 catalysts display higher initial enthalpies of ammonia adsorption (78 to 124 $kJ \cdot mol^{-1}$) than bulk vanadium pentoxide (67 $kJ \cdot mol^{-1}$), except the 1.1 wt% V_2O_5/SiO_2 sample which shows weak acidity. The acidic properties of silica-supported catalysts are different from those of pure vanadium pentoxide. By depositing vanadium oxide on silica, new surface sites are formed which present more acid strength than pure silica and bulk vanadium pentoxide. The absence of strong acidity of silica allows direct measurement of the acidity created by the deposition of vanadium oxide (Fig. 3).

Alumina is not an ideal host oxide to study the acid-base properties of a supported phase because this support presents by itself an acid-base character [10].

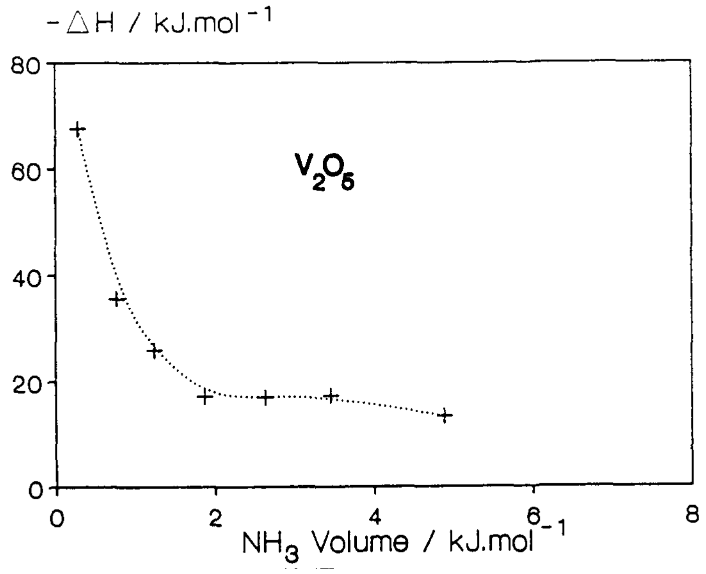

Fig. 1 Differential enthalpy of ammonia adsorption at 353 K (kJ per mole of adsorbed ammonia), *vs.* the ammonia coverage, over bulk vanadium pentoxide

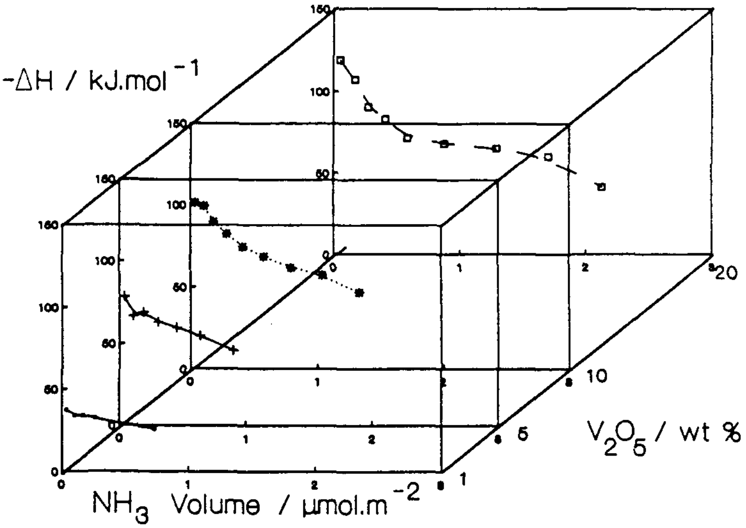

Fig. 2 Differential enthalpy of ammonia adsorption at 353 K as a function of the ammonia uptake and of the vanadium content on V_2O_5/SiO_2 catalysts

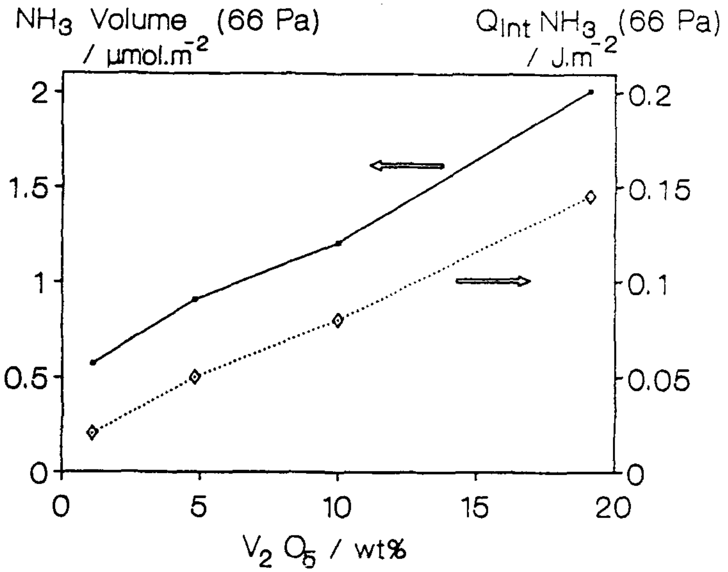

Fig. 3 Ammonia uptake irreversibly adsorbed (at $p(NH_3)$ = 66 Pa) and associated integral enthalpy of ammonia adsorption as a function of the vanadium content of V_2O_5/SiO_2. Adsorption at 353 K

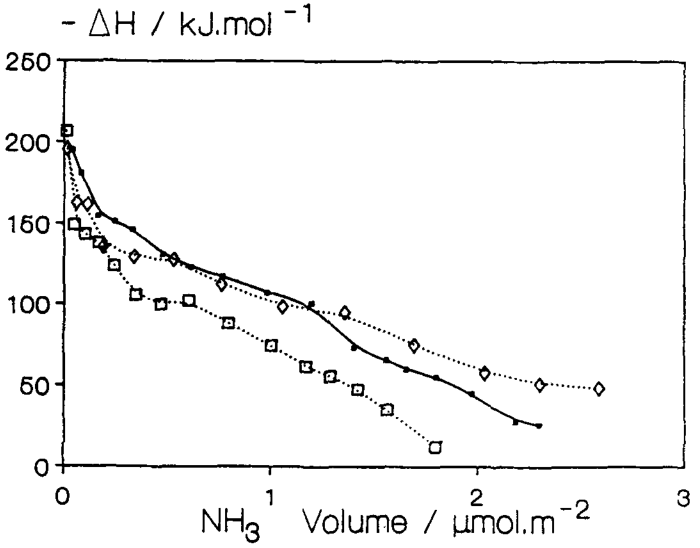

Fig. 4 Differential enthalpy of ammonia adsorption at 353 K as a function of the ammonia uptake on $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts: (□) 3 and (◇) 10 wt% V_2O_5 and on pure alumina (■)

Figure 4 shows the differential enthalpy of ammonia adsorption *vs.* ammonia uptake, at 353 K, on γ-alumina and on two V_2O_5/γ-Al_2O_3 catalysts (3 and 10 wt% V_2O_5). On the 3 wt% V_2O_5/γ-Al_2O_3 catalyst, the amount of vanadium oxide is sufficient to lower the acidic character of the host oxide. This argues for a high dispersion of the vanadium oxide over the surface of γ-alumina. This vanadium oxide layer presents by itself a lower acidic character than alumina.

Higher vanadium loadings (10 wt% V_2O_5) result in an increase in number of weak acid sites (see the curve in Fig. 4 above 1 μmol·m^{-2}). The alumina is probably almost fully recovered by a vanadium oxide layer. Multilayered vanadium structures may also be present for that vanadium loading. The number and strength of acid sites of the V_2O_5/γ-Al_2O_3 catalysts are depicted on Fig. 5 *vs.* the vanadium content of the catalysts. Variations of these acidic features obviously differ on V_2O_5/γ-Al_2O_3 and V_2O_5/SiO_2 catalysts (Fig. 3). This is mostly due to the different inner acidic features of alumina and silica.

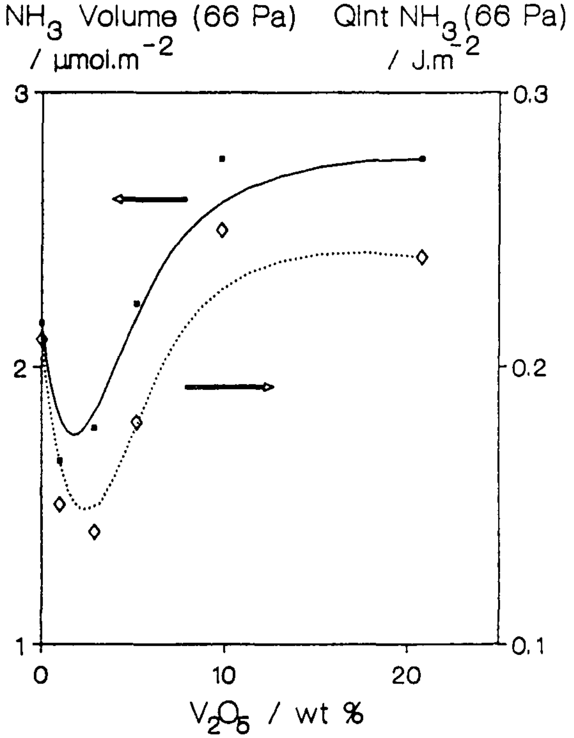

Fig. 5 Ammonia uptake irreversibly adsorbed (at $p(NH_3)$ = 66Pa) and associated integral enthalpy of ammonia adsorption as a function of the vanadium content of V_2O_5/γ-Al_2O_3 catalysts. Adsorption at 353 K

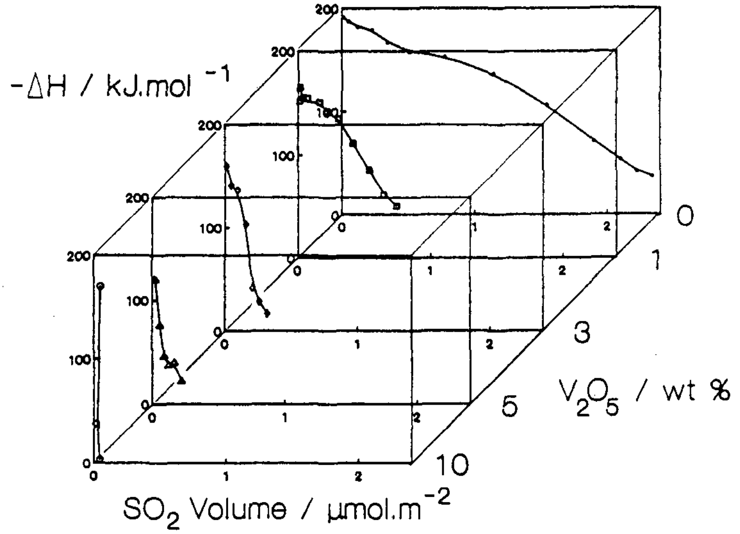

Fig. 6 Differential enthalpy of sulphur adsorption at 353 K as a function of the sulphur dioxide uptake and of the vanadium content of $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts

Sulphur dioxide was chosen as acid probe to investigate the basic character of the vanadium oxide catalysts. Figure 6 reports in a three-dimensional diagram the differential enthalpy of adsorption at 353 K as a function of the sulphur dioxide uptake and of the vanadium content of the $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts. Sulphur dioxide was not found to be adsorbed on bulk vanadium pentoxide and on V_2O_5/SiO_2 catalysts, and it is noteworthy that the population and strength of the basic sites titrated by sulphur dioxide on $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts decrease with the vanadium content. Thus, sulphur dioxide can be regarded as a selective probe for uncovered alumina. The uncovered alumina ratio can be estimated from the sulphur dioxide total uptake on $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts and on pure alumina. The acid-base character of the vanadium oxide layer and of uncovered alumina can be further distinguished.

Conclusion

Bulk vanadium pentoxide is a weak acidic metal oxide. Stronger acid sites are created by depositing vanadium oxide on silica or on γ-alumina. The lack of strong acidity of silica allows unequivocal measurement of the acidity created on the silica-supported vanadium oxide. On $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts, sulphur dioxide is found to be selective for uncovered alumina, and further allows the distinction between acid-base features of the vanadium oxide layer and uncovered alumina.

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Zusammenfassung — Durch Adsorption von Ammoniak und Schwefeldioxid wurde mittels Mikrokalorimetrie der Säure-Basen-Charakter von Vanadiumpentoxid-, V_2O_5/SiO_2- und V_2O_5/γ-Al_2O_3-Katalysatoren untersucht. Wird Vanadiumoxid auf Siliziumoxid aufgetragen, werden neue Oberflächenstellen gebildet, die eine größere Säurestärke darstellen als massives Vanadiumpentoxid oder reines Siliziumoxid. Aluminiumoxidgetragene Vanadiumkatalysatoren können als saure VO_x Monoschichten betrachtet werden. Schwefeldioxid erwies sich als selektiv für unbedecktes Aluminiumoxid.