

Calorimetric study of the acidic character of V_2O_5 - TiO_2/SO_4^{2-} catalysts used in methanol oxidation to dimethoxymethane

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Abstract The surface acidic properties of sulfated vanadia–titania catalysts prepared by various methods were investigated by adsorption microcalorimetry, using ammonia as probe molecule. The acidic characteristics of the samples were shown to be strongly affected by the preparation method, calcination temperature, and sulfur content. The samples prepared by sol–gel and mechanical grinding exhibited higher acidity than co-precipitated samples. Moreover, increasing the calcination temperature of co-precipitated samples resulted in a decrease in surface area from 402 to 57 m² g⁻¹ and sulfur content from around 4 to 0.2 mass%, but up to a certain point generated a stronger acidity. The optimal calcination temperature appeared to be around 673 K.

Keywords Acidity · Calorimetry · Dimethoxymethane · Methanol selective oxidation · V_2O_5 - TiO_2/SO_4^{2-}

Introduction

Vanadia–titania catalysts can be found in wide applications, such as the methanol selective oxidation to formaldehyde [1] and methyl formate [2], and the selective oxidation of ethanol to acetaldehyde [3]. In addition,

sulfated vanadia–titania catalysts are starting to have new applications in the partial oxidation of methanol to dimethoxymethane (DMM) [4, 5], which can undergo further steam reforming to produce hydrogen.

The knowledge of the number and strength of the sites existing at the surface of a catalyst is of paramount interest, as the first step in any catalytic reaction is the adsorption and the subsequent activation of the reactant molecules. Adsorption microcalorimetry [6, 7] is a useful technique to describe, in detail, the quantitative and energetic features of surface sites. It allows, if properly arranged, the simultaneous determination of the adsorbed amounts of a suitable probe molecule and of the heat evolved at increasing surface coverage.

Although, we have previously reported the influence of the preparation method on the surface properties of some sulfated vanadia–titania catalysts calcined at a given temperature of 723 K [4, 8], the purpose of this article is to study in detail the influence of the calcination temperature and washing with deionized water on the surface acidity of V_2O_5 - TiO_2/SO_4^{2-} catalysts prepared by different methods. Results about the physicochemical characteristics of the samples and their acidity as studied by ammonia adsorption microcalorimetry are presented.

Experimental

Samples with the same theoretical amount of vanadia loading (25 mass%) were prepared using different procedures, namely co-precipitation (samples named VTiS-CP), co-precipitation with 1-mass% polyethylene glycol (VTiS-CPEG), sol-gel (VTiS-SG), and mechanical grinding (VTiS-MG). The precursors were $VOSO_4$ and $TiOSO_4$ for VTiS-CP and VTiS-CPEG, respectively, vanadyl

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acetylacetonate and titanium isopropoxide plus sulfuric acid for VTiS-SG, TiO₂ and VOSO₄ for VTiS-MG.

In this study, the samples VTiS-CP-723, VTiS-CPEG-723, and VTiS-MG-723 were prepared by the corresponding procedures cited above and calcined at 723 K in air for 5 h, except sample VTiS-SG-723 for which the calcination time was increased up to 12 h for a better decomposition of the organic precursors.

The VTiS-CP-573, VTiS-CP-623, VTiS-CP-673, and VTiS-CP-773 samples were prepared by co-precipitation and calcined in air for 5 h at 573, 623, 673, and 773 K, respectively. Moreover, the samples VTiSw50-CP-673 and VTiSw300-CP-673 were prepared by co-precipitation, washed, respectively, with 50 and 300 mL deionized water and then calcined at 673 K in air for 5 h.

The details of the preparation methods have been previously described in [4].

Elemental analysis was performed using ICP atomic emission spectroscopy (AES-ICP) with a flame PerkinElmer M1100 spectrometer. The BET surface areas were measured using nitrogen adsorption at 77 K on a Micromeritics 2010 apparatus.

The microcalorimetric studies of ammonia adsorption were performed at 423 K in a heat-flow calorimeter (C80 from Setaram) linked to a conventional volumetric apparatus equipped with a Barocel capacitance manometer for pressure measurements. Before each experiment the samples were outgassed overnight at a temperature of 100 K lower than the calcination temperature. After a first adsorption, performed by repeatedly adding successive amounts of NH₃ onto the sample until an equilibrium pressure of

about 67 Pa was reached, the sample was evacuated for 30 min, to remove the weakly adsorbed NH₃, and a second adsorption was performed to determine the amount of ammonia irreversibly adsorbed.

Results and discussion

The results of bulk analysis (chemical analysis) as well as surface area for all the VTiS samples are given in Table 1. Depending on the preparation method and calcination temperature, the sulfur mass% varied greatly and remained difficult to control. The sulfur content was observed to be higher for samples prepared by sol-gel and mechanical grinding than by co-precipitation method. Meanwhile for co-precipitated samples, the sulfur concentration decreased with increasing the calcination temperature and by washing with deionized water, thus suggesting that the sulfur species did not seem to be tightly anchored to vanadia species or support surface. Additionally, the way the sulfur species anchored to the support surface was strongly affected by the preparation method, leading to different surface acidities. Furthermore, sample VTiS-CP-573 displayed a high surface area of 402 m² g⁻¹. With increasing the calcination temperature, the surface area decreased, down to the lowest value at 773 K (57 m² g⁻¹). Washing with deionized water did not significantly change the surface area of the same series samples. In addition, comparing samples prepared by different methods and calcined at 723 K, it was found that adding PEG did not influence the surface area of the co-precipitated samples and indeed no benefit was gained

Table 1 Chemical analysis, BET surface areas, ammonia adsorption data from microcalorimetry measurements at 423 K

Catalyst	CA/mass%			$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	$V_{\text{tot}}^{\text{a}}/\mu\text{mol g}^{-1}$	$V_{\text{tot}}^{\text{a}}/\mu\text{mol m}^{-2}$	$V_{\text{ir}}^{\text{b}}/\mu\text{mol g}^{-1}$	$V_{\text{ir}}^{\text{b}}/\mu\text{mol m}^{-2}$	$Q_{\text{int}}^{\text{c}}/\text{J g}^{-1}$
	V	Ti	S						
VTiS-CP-723	13.4	43.8	0.2	105	243	2.3	123	1.2	32
VTiS-CPEG-723	13.4	45.1	0.2	74	193	2.6	77	1.1	23
VTiS-SG-723	11.4	44.8	1.4	43	281	6.5	216	5.0	26
VTiS-MG-723	12.4	34.6	6.5	132	503	3.8	392	3.0	54
VTiS-CP-573	10.4	33.9	3.2	402	578	1.4	264	0.7	61
VTiS-CP-623	10.9	34.7	4.0	368	591	1.6	358	1.0	70
VTiS-CP-673	12.6	41.0	2.6	287	608	2.1	374	1.3	69
VTiS-CP-723	13.4	43.8	0.2	105	243	2.3	123	1.2	32
VTiS-CP-773	13.4	44.4	0.2	57	163	2.9	69	1.2	16
VTiSw50-CP-673	13.1	39.9	0.8	290	568	2.0	319	1.1	69
VTiSw300-CP-673	12.6	41.6	0.2	289	551	1.9	275	1.0	63

^a Total amount of NH₃ retained as determined at 27 Pa of equilibrium pressure

^b "Irreversible" amount of NH₃ retained as determined from the difference between the amounts adsorbed in the first and second adsorptions at 27 Pa

^c Total heat evolved at 27 Pa of NH₃ equilibrium pressure upon NH₃ adsorption

upon PEG addition. It was also found that sample VTiS-SG-723, prepared by sol-gel method, displayed the lowest surface area of $43 \text{ m}^2 \text{ g}^{-1}$.

Ammonia adsorption microcalorimetry measurements were carried out to determine the number, strength, and strength distribution of the surface acid sites of catalysts [9, 10]. The surface acidity was thus determined in terms of number of acid sites and sites strength. The results are presented in Figs. 1 and 2 and Table 1. Figure 1a-c represents the differential heats of adsorption versus coverage

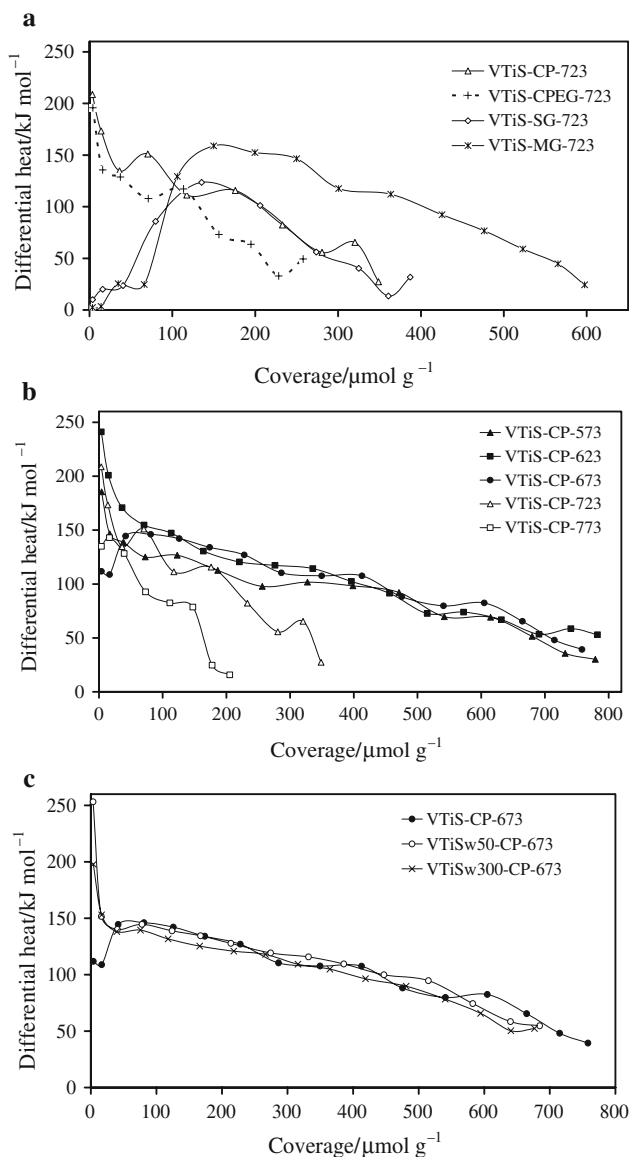


Fig. 1 Differential heat versus coverage (in $\mu\text{mol g}^{-1}$ of catalyst) for NH_3 adsorption at 423 K over VTiS catalysts **a** VTiS catalysts prepared by different methods and calcined at 723 K, **b** VTiS catalysts prepared by co-precipitation and calcined at various temperatures, **c** VTiS catalysts prepared by co-precipitation, washed with different amount of deionized water and then calcined at 673 K

of ammonia, while Fig. 2a-c gives the volumetric isotherms of NH_3 adsorption.

As shown in Fig. 1a, the initial heats of ammonia adsorption observed on co-precipitated VTiS samples doped or not with 1-mass% PEG-400 were similar, around 200 kJ mol^{-1} , which indicates that these two samples are quite acidic, in agreement with the results from Hammett titration [11]. However, very low initial heats of adsorption were observed for the VTiS-SG-723 and VTiS-MG-723 samples, containing high content of sulfur. The low heat

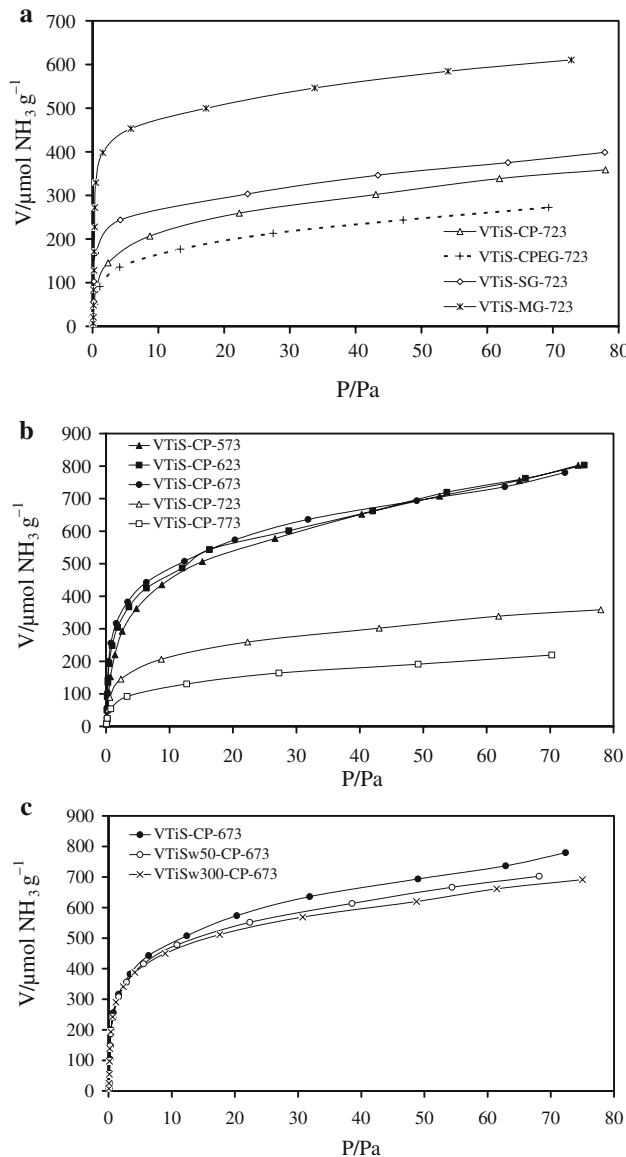


Fig. 2 Volumetric isotherms of NH_3 adsorption at 423 K for VTiS catalysts **a** VTiS catalysts prepared by different methods and calcined at 723 K, **b** VTiS catalysts prepared by co-precipitation and calcined at various temperatures, **c** VTiS catalysts prepared by co-precipitation, washed with different amount of deionized water and then calcined at 673 K

values recorded for the first four ammonia increments (which were totally consumed by the sample) were followed by an increase to higher heats of adsorption, corresponding to what is normally expected for a strong acid. This strange phenomenon can only be interpreted by the combination of two phenomena, endothermic and exothermic, thus inducing a lower initial heat. The very strong acid sites due to sulfate ions are supposed to create either a strong or a dissociative chemisorption. It has been reported in the literature [12] that the first doses of NH_3 could dissociate at the surface (endothermic phenomenon) with the formation of OH species, evidenced by NH_3 adsorption infrared spectroscopy [12]. The low heats of adsorption are then attributed to the contribution of NH_3 dissociation to the differential heat of adsorption. Another explanation could be probably the formation of ammonium sulfite [13]. This particular behavior observed for samples containing a relatively high amount of sulfur made it difficult to appreciate the initial heats of adsorption of the sulfated oxides. As this phenomenon was scarcely observed by adsorption calorimetry for sulfated zirconias it is supposed to imply a special type of sulfur species on the catalyst surface, which could involve the support type and/or the preparation method. For co-precipitated catalysts with or without 1-mass% PEG-400, which contain a much lower amount of sulfur species, the heats of NH_3 adsorption gradually decreased with NH_3 coverage, revealing the heterogeneous strength distribution of these catalysts. Figure 2a, which represents the ammonia adsorption isotherms, did not reflect the particular behavior of samples VTiS-SG-723 and VTiS-MG-723, thus confirming that these two samples chemisorbed more ammonia and were more acidic due to their higher sulfate species content.

In Fig. 1b are shown the differential heats of adsorption versus ammonia coverage on samples prepared by co-precipitation and calcined at different temperatures (system VTiS-CP). Relatively, low initial heat of adsorption was obtained for sample VTiS-CP-673. However, it is noteworthy that no low initial heats were observed for VTiS-CP-573 and VTiS-CP-623 samples which contained a higher sulfur concentration than sample VTiS-CP-673 thus confirming the role played by the calcination temperature in the determination of the sulfate-type species on the catalyst surface. In order to determine how the sulfur concentration could influence the acidity of VTiS catalysts, NH_3 adsorption microcalorimetry experiments were also performed on the VTiSw catalysts, washed with deionized water and then calcined at 673 K. After washing with different amounts of deionized water, the content of sulfur (chemical analysis) drastically decreased from 2.58 mass% (VTiS-CP-673) to 0.75 mass% (VTiSw50-CP-673) and even to <0.1 mass% (VTiSw300-CP-673). As can be seen in Fig. 1c, the low initial heat of adsorption previously observed for sample

VTiS-CP-673 disappeared for the washed catalysts at low ammonia coverage (<40 $\mu\text{mol g}^{-1}$). Beyond this value, the profiles of the three curves are similar, characteristic of vanadia-titania mixed oxides. This phenomenon could suggest that only a high concentration of sulfur species can modify significantly the relatively strong acidity of VTi catalysts prepared by co-precipitation.

The quantitative results of NH_3 adsorption are summarized in Table 1. The total amount of adsorbed ammonia at an equilibrium pressure of 27 Pa (V_{tot}) and the amount irreversibly adsorbed at the same pressure (V_{irr}) are indicative of the total number of acid sites and amount of strong acid sites on the surface of the sample, respectively. For samples prepared by different methods and calcined at 723 K, both V_{tot} and V_{irr} , reported in $\mu\text{mol g}^{-1}$, varied in the order of VTiS-MG-723 > VTiS-SG-723 > VTiS-CP-723 > VTiS-CPEG-723, greatly influenced by the preparation method and consequently by the sulfur amount. In addition, the adsorption isotherms for these samples (Fig. 2a) varied in the same order with a maximum uptake of 360, 270, 400, and 610 $\mu\text{mol g}^{-1}$ for VTiS-CP-723, VTiS-CPEG-723, VTiS-SG-723, and VTiS-MG-723, respectively. For co-precipitated samples calcined at different temperatures, the maximum uptake values of V_{tot} and V_{irr} were obtained for sample VTiS-CP-673, calcined at 673 K. The maximal ammonia uptake was analogous for all the samples except for VTiS-CP-723 and VTiS-CP-773 samples (see Fig. 2b and c), due to their drastic decrease in surface area. Furthermore, the total and strong surface acid sites densities of co-precipitated samples (Table 1) increased with increasing calcination temperature up to a maximum at 673 K (sample VTiS-CP-673), despite a slight decrease in surface area and sulfur content when compared to samples VTiS-CP-573 and -623 respectively. Interestingly, it was the only co-precipitated sample displaying low initial heats of adsorption. Above 673 K a drastic decrease of the number of acid sites was observed. The data in Table 1 clearly indicate that most of the adsorbed ammonia is strongly chemisorbed on samples VTiS-SG-723 and VTiS-MG-723, while all the co-precipitated series samples display a large part of physisorption.

Conclusions

$\text{V}_2\text{O}_5\text{-TiO}_2/\text{SO}_4^{2-}$ catalysts were prepared by co-precipitation, co-precipitation with 1-mass% PEG-400, sol-gel, and mechanical grinding methods. The investigation has demonstrated the existence of differences in surface acidity between catalysts prepared by various methods, calcined at different temperature and more or less washed with deionized water. Co-precipitation method was by far the best preparation method in terms of maximizing the surface area

and 673 K was the optimal calcination temperature in terms of maximizing the total acidity. The ammonia adsorption calorimetric study showed the special behavior of NH_3 dissociation at the surface of samples VTiS-SG-723, VTiS-MG-723, and to a small extent VTiS-CP-673. Meanwhile, the data from calorimetric study performed on the washed catalysts (system VTiSw) indicated that a high concentration of sulfur affected only the very strong acidity of VTiS catalysts. For co-precipitated samples, the strongest acidity found for sample VTiS-CP-673 cannot be associated to the sulfur content which was smaller for this sample than for VTiS-CP-573 and VTiS-CP-623 samples, but to the sulfate-type species on the catalyst surface. To sum up, the acidic properties of VTiS samples were affected by the preparation method and calcination temperature as well as by the type of sulfur species present on the surface.

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