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Catalysis Today 91–92 (2004) 33–37
CATALYSIS TODAY
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New vanadia-mesoporous catalysts for the oxidation of SO_2 in diluted gases

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Available online 18 May 2004

Abstract

Mesoporous SO_2 oxidation catalysts were prepared by impregnation of a sol–gel prepared vanadia-silica support with various amounts of cesium sulfate or mixtures of alkaline sulfate species (Na or K). The resulting catalysts were characterized by adsorption–desorption isotherms of nitrogen at 77 K, in situ evolution of crystallinity by X-ray diffraction, NH_3-DRIFT, XPS, transmission electron microscopy, dispersive X-ray analysis, and X-ray fluorescence spectrometry. Catalytic tests in oxidation of SO_2 in diluted gases (1 vol.%) showed that these systems were very active. A dependence on the alkaline metal loading was also evidenced.

Keywords: Mesoporous SO_2; Oxidation catalysts; XRD; NH_3-DRIFT; XPS; TEM; EDX; XRF

1. Introduction

The oxidation of SO_2 takes place at 713–873 K as a homogeneous reaction in the liquid phase of a molten salt mixture consisting of V_2O_5 dissolved in pyrosulfates (M = Na, K, Cs) and dispersed on an inert support. The process results in the melt located in the catalyst pores [1].

The performances of these catalysts as well as their stability are related to both their alkaline species nature and their molar ratio to vanadium. The increasing radius of the alkali metal ions in the sequence Li, Na, K, Rb, Cs leads to a stabilization of active vanadium compounds in the oxidation state (V) by stabilizing pyrosulfates and higher pyrosulfates [2–5]. Simonova et al. [6] showed, by quantitative analysis of EPR spectra, that the content of crystalline vanadium(IV) does not exceed 50% of the total vanadium amount at 693 K and 30% SO_2 conversion for cesium catalysts with a molar ratio M/V = 2. In the catalysts containing Na and K, all vanadium was found as inactive crystalline compounds. The commercial formulations contain all these alkaline species. Kinetic data collected for catalysts with a molar ratio K/Na/V = 3/0.8/1 and K/Cs/Na/V = 3/1/0.25/1 indicated that the breakpoint occurred at 652 K for the catalyst with Cs and at 692 K for the one with Na and K. The precipitation of V(IV) and/or V(III) compounds [1,2,7] takes place at the temperature where the catalysts deactivate. Most likely the support of the catalyst also has an effect on the deactivation process.

The aim of this study was to prepare alkaline-vanadia-silica catalysts with different alkaline/vanadia ratios using as support for impregnation a vanadia-silica prepared by the sol–gel procedure and to investigate these catalysts in SO_2 oxidation in diluted gases.

2. Experimental

V-SiO_2 support with 6.5 wt.% V was prepared by the sol–gel procedure. vanadylacetylacetonate (VAA) was dissolved in methanol with a molar ratio VAA-to-methanol of 0.013. TEOS was added drop-wise to this solution (molar ratios TEOS-to-VAA of 11.54 and TEOS-to-methanol of 0.15), maintaining the system under vigorous stirring. After the addition of water (water-to-TEOS ratio of 4), the

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0920-5861/$ – see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.cattod.2004.03.026

Table 1
Chemical composition, textural characteristics, XPS binding energies and Raman shift of the investigated catalysts

Catalyst	Chemical composition (%)				Surface area ($m^2\,g^{-1}$)	Binding energy (eV)		XPS Cs/V ratio	Raman shift (cm^{-1})		
	V	Cs	Na, Rb	K		V $2p_{3/2}$	Cs $3d_{5/2}$		V=O (mono-xo-vanadium)	V=O (dioxo-vanadium)	V–O–
V-1.5Cs-SiO_2	4.82	18.89	–	–	56	517.2	724.4	2.08	1033 wbr	943 wbr	720 sh, 694 sh, 528 m
V-2.0Cs-SiO_2	4.44	23.19	–	–	50	517.2	724.3	1.86	1036 mbr	910 mbr	760 m, 680 wbr 528 mbr
V-2.5Cs-SiO_2	4.12	26.86	–	–	44	517.0	724.5	2.61	1032 m	900 mbr	752 wbr, 688 m, 528 m
V-3.0Cs-SiO_2	3.81	29.19	–	–	38	517.0	724.5	3.36	1032 m	–	760 w, 684 mbr, 476 m
V-3.5Cs-SiO_2	3.59	32.81	–	–	34	516.9	724.5	4.63	1032 w	–	–
V-4.0Cs-SiO_2	3.37	35.28	–	–	34	516.5	724.1	8.19	1033 w	945 msh, br	
V-K-Cs-SiO_2	4.29	16.79	–	4.89	34	517.0	724.3	2.22	1038 wbr	948 mbr	744 wbr, 676 wbr, 536 mbr
V-Na-K-Cs-SiO_2	4.34	23.12	1.47	2.47	33	517.0	724.3	1.48	1035 wbr	950 mbr	764 m, 540 mbr, 492 mbr

br: broad; w: weak; m: medium; sh: shoulder.

pH was modified to 9, using a solution of NH_3 (17 wt.%). The mixture was then refluxed at 338 K for 5 h and, after cooling at room temperature, was mixed with a solution of 1 g $(CH_3)_3C_{14}H_{29}N^+Br^-$ in 2 ml methanol. The sol-polymerization and the aging of the gel were carried out at 373 K for 5 days in a teflon autoclave. V-SiO_2 was calcined at 823 K and then impregnated with alkaline sulfate species using the incipient wetness impregnation method. The samples were dried under vacuum and calcined at 773 K for 5 h with a ramp of 1 K min^{-1}. The chemical composition of the resulting catalysts is given in Table 1. This corresponds to Cs/V ratios of 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0, respectively. Samples containing two or three alkaline species were also prepared in the same way (Table 1).

The catalysts were characterized by adsorption–desorption isotherms of nitrogen at 77 K (by using a Micromeritics ASAP 2000), in situ evolution of crystallinity by X-ray diffraction (XRD, by using a Siemens D-5000 diffractometer), NH_3-DRIFT (by using a Bruker IFS88 infrared spectrometer), XPS (by using a SSX-100 Model 206 surface science instrument spectrometer), transmission electron microscopy (TEM, by using a Philips CM200 microscope with dispersive X-rays analysis (EDX), and X-ray fluorescence spectrometry (XRF, by using a Siemens SRS 3000 sequential spectrophotometer). Elemental analysis was performed by atomic emission spectroscopy with inductively coupled plasma atomization (ICP-AES). The catalytic tests were carried out in the temperature range 633–753 K in a flow microreactor using 55 mg catalyst and a feed composition of 1 vol.% SO_2, 19 vol.% O_2, 80 vol.% N_2, for a space velocity of 45 300 h^{-1}.

3. Results

3.1. Catalysts characterization

The resulted support exhibited typical mesoporous characteristics: the surface area was of 708 $m^2\,g^{-1}$ and the pore size distribution was centered at 4 nm in a very narrow range. The deposition of the alkaline sulfate species followed by calcination led to the extraction of vanadium from the vanadia-silica network. In situ XRD collected patterns during the activation of the catalysts confirmed this behavior. Fig. 1 corresponds to the sample with Cs/V of 2.5. The initial catalysts are amorphous, and at room temperature no reflexion lines of sulfate or other component species were evidenced. The increase of the temperature confirmed the solid state reaction and the structural changes. The patterns recorded beyond 673 K for Cs/V ratios smaller than 2.5, and 573 K for Cs/V ratios higher than this value, indicated the apparition of two reflexion lines at 2θ 26.73 and 28.14, respectively, which corresponds to the formation of active $VO_2(SO_4)_2^{3-}$ vanado-complexes species [8]. Actually, as it might be evaluated from the broadening of the XRD reflection lines using the Scherrer formula, the size of

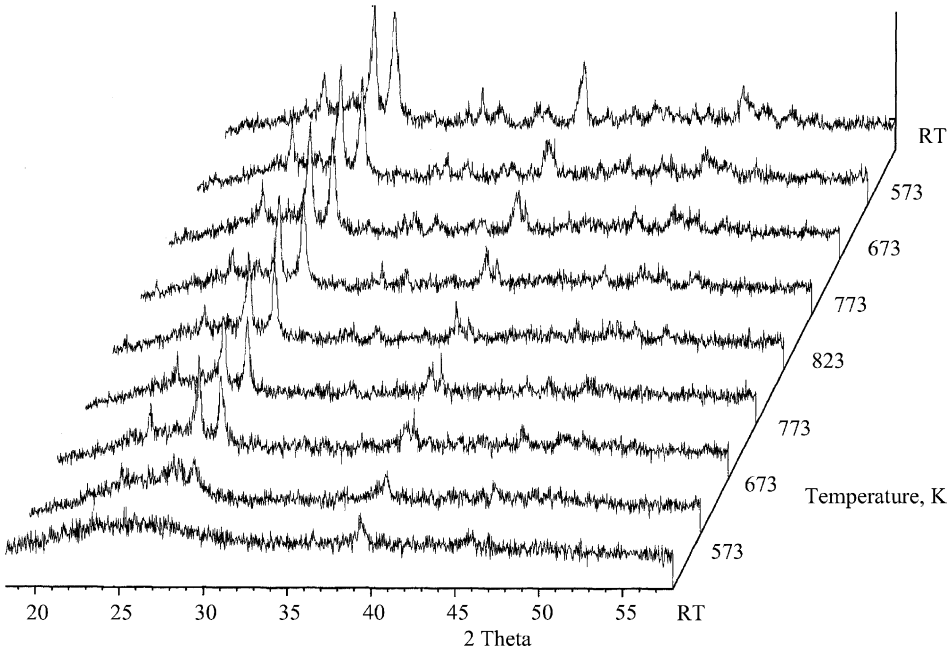

Fig. 1. In situ XRD patterns of V-2.5Cs-SiO_2.

these complexes are typically in the range of nano-structures (about 7 nm). Cooling of these samples at room temperature led to a change in the structure, new reflexion lines at 2θ 27.36 and 28.62 being detected. These lines correspond $(V^{V}O)_2O(SO_4)_4^{4-}$ structures [9]. In the same time, the intensity of the broadening of these lines decreased indicating a segregation process (about 9.5 nm). The intense reflexion lines at 2θ 39.5 and 46.0 correspond to the Pt holder.

Measuring the surface area of the samples after cooling resulted in a dramatic decrease of the surface area comparatively to V-SiO_2 support irrespective of the nature of the species and the loading (Table 1). Since the measurements were performed after the calcination of the catalysts this decrease is caused by the pore blockage with frozen vanadyl sulfate complexes resulted at activation temperature by extraction of vanadium from the V-SiO_2 network.

However, the silicon network remains almost intact hosting these complexes. A confirmation of the stability of the mesoporous silica host was supplied by TEM investigation coupled with EDX and XRF measurements. It results from these analyses that V-SiO_2 presents a texture that corresponds to a pre-organized mesoporous texture. Although some changes occurred, the deposition of cesium was not accomplished by dramatic changes as it resulted from the adsorption–desorption isotherms of N_2 at 77 K. EDX and XRF measurements carried out on these samples indicated that indeed impregnation with cesium produced no important changes in the dispersion of vanadium (Table 1). However, the correlation of these data with the XPS results indicated that vanadium exists in a rather agglomerated state. Table 1 also compiles binding energies of the V $2p_{3/2}$ and Cs $3d_{5/2}$ components. In all the catalysts the oxidation state corresponds to V^{5+} [10]. But the deposition of cesium led to a partial reduction of vanadium, which becomes more evident for Cs/V ratios of 3.5 and 4. This behavior was not accompanied by any change in the oxidation state of cesium which binding energies remained essentially the same. The changes in the oxidation state were accomplished or maybe even caused by changes in the surface distribution of vanadium. Calcination caused a superficial enrichment with cesium when Cs/V exceeded 3.5.

Table 1 also summarizes the Raman bands observed for the various vanadia-silica catalysts studied. A tentative assignment is given based on literature data [11,12]. These spectra indicated a sharp band in the 1032–1038 cm^{-1} range, assigned to terminal V=O stretching of monomeric vanadyl anchored to silica as O=V-$(OM)_3$ species and a broad band in the 920–935 cm^{-1} range, assigned to terminal V=O stretches of dioxo vanadium groups participating in polymeric units. Bands due to sulfate modes [$\upsilon_1(SO_4)$], 611 [$\upsilon_4(SO_4)$] and 443 [$\upsilon_2(SO_4)$] appeared near 968 cm^{-1}. The increase of the Cs content led to both a surface Cs coverage and a more advanced interaction with vanadia, which brings about the decrease of the intensity of the bands due to vanadium.

The deposition of Cs also changed the acid–base surface properties. The NH_3-DRIFT spectra recorded on V-SiO_2 support in the range 273–573 K indicated corresponding bands due to ammonia adsorbed on both Bronsted (1430 cm^{-1}) and Lewis (1610 cm^{-1}) acid sites. After the deposition of alkaline sulfates no adsorption of ammonia has been determined irrespective of the nature of the metal or loading.

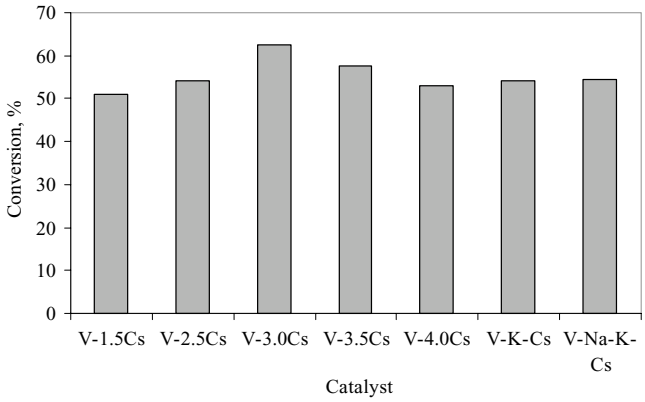

Fig. 2. Conversion of SO_2 for the investigated catalysts (713 K, 55 mg catalyst, 1 vol.% SO_2, 19 vol.% O_2, 80 vol.% N_2, for a space velocity of 45 300 h^{-1}).

3.2. Catalytic activity

Fig. 2 shows the variation in the conversion of SO_2 on the investigated catalysts. The increase of the Cs/V ratio led to an increase in the conversion till this reached 3, and it decreased for higher Cs/V ratios. The replacement of a part of Cs by K or Na/K led to catalytic performances very near to those of the catalysts with Cs/V of 2.5 and 4.0, respectively. Fig. 3 gives the variation of Arrhenius plots for the catalysts with Cs/V ratios of 2.5, 3.0 and 4.0. The breaking point corresponds to the deactivation temperature. This is well correlated with the activity of these catalysts. For the samples given in Fig. 3 it decreases from Cs/V = 2.5 to 3, and then slightly increases for Cs/V = 4. The values of the apparent activation energies indicate that in the temperature range in which the catalysts are active, the energies were smaller than 10 kcal mol^{-1}, which corresponds to a reaction occurring in mass transfer limited conditions. The apparent activation energies, in the region where the catalysts deactivate, have typical values for such temperatures.Discussion

The achievement of the active catalysts is the contribution of both the alkaline metal loading and the activation conditions. The alkaline species extract vanadium from the vanadia-silica support leading to sulfato–vanado complexes. XRD and Raman characterization indicated these complexes are of the same type as those identified in industrial catalysts [13]. They are hosted in the silica mesopores. TEM investigation of these catalysts coupled with EDX and XRF measurements showed that no important changes occurred in the texture of the silica host, which may lead to the conclusion that the decrease of the surface area is due to the solidification of the melt resulting from the solid reaction of cesium sulfate with vanadium oxide. However, the advantage of using mesoporous hosts is the relatively high dispersion of the nano-complexes. For the industrial catalysts prepared by simple impregnation which are able to oxidize only concentrated SO_2 gases the size of these nano-complexes is higher than 40 nm [14], while in this case was around 7 nm.

Such a high dispersion is provided by the way in which these catalysts were prepared. The vanadyl sulfate nano-complexes resulted via the extraction of vanadium from the V-SiO_2 network by the alkaline sulfate species. The existence of the solid–solid reaction was confirmed by the in situ XRD measurements, which indicated the formation of the vanadyl complexes after 573 K. The same data confirmed the solidification of the species formed during the activation. However, as XRD, XPS, and Raman spectra indicated, the interaction between vanadia and cesium is controlled by the amount of supported Cs. For Cs/V ratios higher than 3.5, part of cesium did not interacted with V, and covered the catalysts surface with cesium sulfate species.

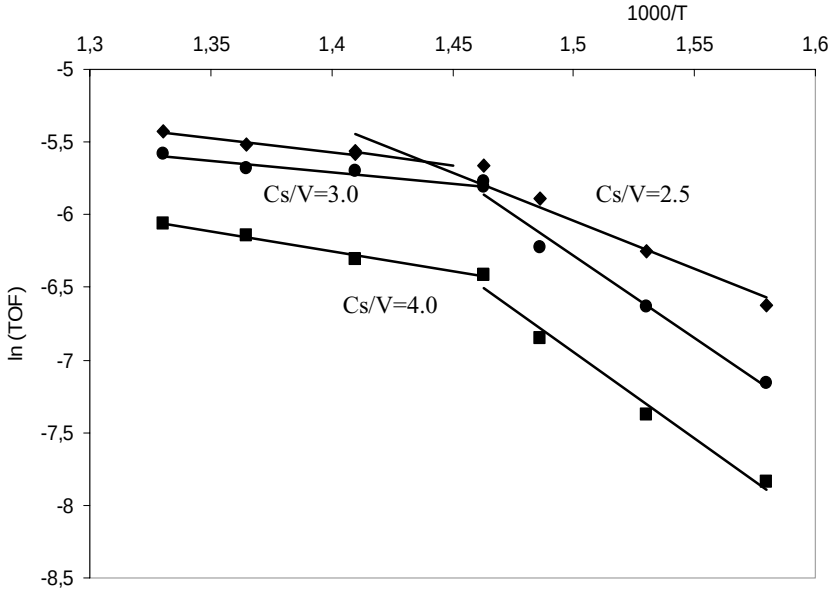

Fig. 3. Arrhenius plots.

Catalytic data are a consequence of these characteristics. A Cs/V of 3 corresponds to the maximum extraction of vanadium with formation of sulfato complexes. In accordance, this catalyst showed the highest activity. It is important to note that a conversion of ca. 60% for a space velocity of 45 300 h^{-1} with gases containing 1 vol.% SO_2 is indeed very high. Such a behavior results from the dispersion of the molten vanadia–alkaline complexes inside the large surface area mesopores support. It is worth to note that the comparison of these catalysts with typical oxidation catalysts indicated an almost four times more active catalyst.

In conclusion, the impregnation of large surface area vanadia-silica supports with alkaline sulfate species may provide active catalysts for the oxidation of SO_2 contained in very diluted gases.

Acknowledgements

The authors kindly acknowledge NATO Science for Peace project Sfp971984, and Profs. R. Fehrmann for very helpful discussions.

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