Kinetic peculiarities in the low-temperature oxidation of H_2S over vanadium catalysts

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Abstract

H_2S oxidation by oxygen over V_2O_5/Al_2O_3, V_2O_5/TiO_2, V_2O_5/SiO_2, $V_2O_5/Al_2O_3/TiO_2$ catalysts was studied at the temperature below the sulfur dew-point. High activity and the oscillation nature of the oxidation process were demonstrated for the catalysts with low V_2O_5 contents (2–5 wt.%) supported on Al_2O_3, TiO_2 or a combination thereof. An increase in the V_2O_5 concentration up to 10–20 wt.% resulted in lowering of the catalytic activity and oscillation ability. The oscillations were not determined using V_2O_5/SiO_2 and pure V_2O_5 catalysts. Difference between pure V_2O_5, catalysts with high- and low-loaded V_2O_5 catalysts was accounted for by the structure of V^{5+} species formed in catalysts. The high activity of the catalysts with the low vanadium content supported on Al_2O_3, TiO_2 or combinations thereof was attributed to vanadium species bound directly to the surface. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic oxidation of H_2S is an important stage of processes of gas purification from hydrogen sulfide and preparation of sulfur. A number of papers [1–3] report the highest activity of vanadium catalysts at 200–300 °C in this reaction.

The investigation of low-temperature H_2S oxidation with oxygen (below the sulfur dew-point) over a vanadium catalyst [4] revealed periodic changes in the reaction rate at $O_2/H_2S > 2$, which entailed changes in the product composition and temperature in the catalyst bed. The discovered oscillation processes are directly related to the adsorption of sulfur and sulfur-containing intermediates on the catalyst surface. Periodic regeneration of the catalyst surface due to oxidation and sulfur removal takes place during the oscillations.

The present study is devoted to the elucidation of the forms of vanadium species accounting for the high activity and kinetic peculiarities in the H_2S oxidation at temperatures below the sulfur dew-point.

[51]V solid state NMR spectroscopy is known as the most suitable technique for characterization of the local environment of vanadium sites in different supported vanadium catalysts [5]. In this paper we used solid state [51]V MAS NMR technique for characterization of vanadium sites formed in titania, alumina and alumina/titania supported catalysts for oxidation of H_2S.

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2. Experimental

2.1. Catalyst characterization

The studies were carried out using different vanadium-containing catalysts supported on γ-Al_2O_3, SiO_2 and TiO_2 (anatase) or a combination of them. These were:

- V_2O_5 ("high purity" grade);
- Industrial catalyst IC-27-40 with the composition 4.5% V_2O_5/30% Al_2O_3/65% TiO_2;
- Industrial catalyst AVK-10 with the composition 10.8% V_2O_5/Al_2O_3.

Catalysts 5.5% V_2O_5/Al_2O_3, 2% V_2O_5/TiO_2, 3.5% V_2O_5/TiO_2, 10.5% V_2O_5/TiO_2, 20% V_2O_5/TiO_2 and 3.25% V_2O_5/SiO_2 were prepared by impregnation of the support with an aqueous solution of vanadyl oxalate followed by drying and calcination at 450 °C. BET specific surface areas (S_{BET}) of samples were determined from thermal desorption of argon. Characteristics of the catalysts are summarized in Table 1.

2.2. Apparatus and procedural details

Catalytic oxidation of H_2S was studied in a flow installation at atmospheric pressure and the temperature ranging from 100 to 200 °C using model gas mixtures containing 2.0 vol.% H_2S, oxygen and nitrogen. The gas flow rate was 60 l/h, catalyst weight 3 g, the catalyst grain size 0.4–0.6 mm. The catalyst temperature was measured using a thermocouple mounted at the bottom of the catalyst bed. A quartz reactor was 15×1 cm was in size, with the maximal volume of the catalyst loaded into the reactor equal to 8 cm. Components were analyzed using a procedure described elsewhere [4].

Conversion of hydrogen sulfide (X_{H_2S}), and selectivity to SO_2 (α_{SO_2}) were calculated according to formulas:

$$X_{H_2S} = \frac{C_{H_2S}^{in} - C_{H_2S}^{f}}{C_{H_2S}^{in}} 100\%$$

$$\alpha_{SO_2} = \frac{C_{SO_2}}{C_{H_2S}^{in} - C_{H_2S}^{f}} 100\%$$

where $C_{H_2S}^{in}$ is the inlet concentration of H_2S, $C_{H_2S}^{f}$ the final H_2S concentration calculated with account of changes in the gas volume during the reaction, and is the SO_2 outlet concentration of C_{SO_2}.

2.3. NMR measurements

NMR measurements were performed using a Bruker MSL-400 spectrometer at 105.25 MHz at room temperature. ^{51}V MAS spectra of powder samples were recorded at rotation frequencies of 10–15 kHz using a 5 mm rotor of Si_3N_4 and a NMR probe constructed by NMR Rotor Consulting ApS, Denmark. Repetition times from 0.1 to 2 s and the rf pulses with 1 μs duration were used in the experiments. All chemical shieldings are referenced to $VOCl_3$ as an external standard.

3. Results and discussion

Figs. 1–6 present dynamic curves of the reaction selectivity and temperature in the catalyst bed for the catalysts under study. A decrease in the catalytic activity with time accompanied by a decrease in the selectivity to SO_2 due to the accumulation of sulfur is seen (Figs. 1 and 3) for catalysts 20% V_2O_5/TiO_2, 10.8% V_2O_5/Al_2O_3. Microoscillations of the reaction selectivity and temperature in the catalyst bed ($\Delta T = 10$ °C, $\alpha_{SO_2} = 10$–15%) are observed over these catalysts. Low-loaded vanadium catalysts, 3.5% V_2O_5/TiO_2, 5.5% V_2O_5/Al_2O_3, 4.5% V_2O_5/Al_2O_3/TiO_2 (Figs. 2, 4, and 5) and 2%

Table 1
Compositions and characteristics of catalysts

Number of sample	Initial composition (wt.%)	S_{BET} (m²/g)
1	5.5 V_2O_5, 94.5 Al_2O_3	280
2	10.8 V_2O_5, 89 Al_2O_3	160
3	2 V_2O_5, 98 TiO_2	39
4	3.5 V_2O_5, 96.5 TiO_2	39
5	10.5 V_2O_5, 89.5 TiO_2	39
6	20 V_2O_5, 80 TiO_2[a]	33
7	4.5 V_2O_5, 30 Al_2O_3, 65 TiO_2	135
8	3.25 V_2O_5, 96.7 SiO_2	190
9	V_2O_5	6

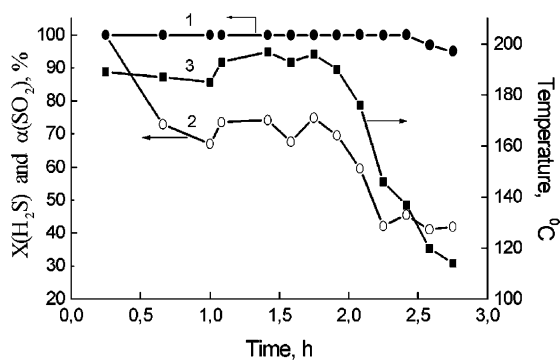[a] This catalyst was prepared by Dr. Zenkovets G.A. (BIC SB RAS).

Fig. 1. Time dependencies of X_{H_2S} (curve 1), α_{SO2} (curve 2) and temperature in the catalyst bed (curve 3) at $O_2/H_2S = 4.8$ on 20% V_2O_5/TiO_2 catalyst. Feed temperature is 95 °C.
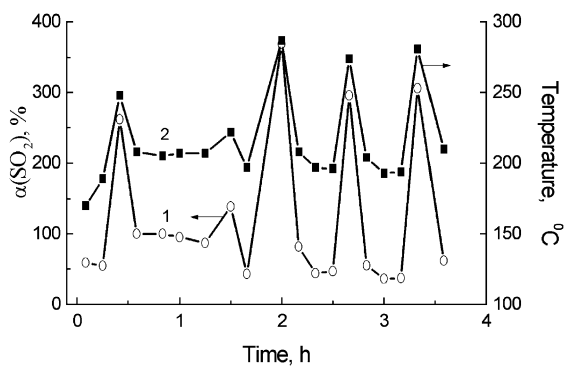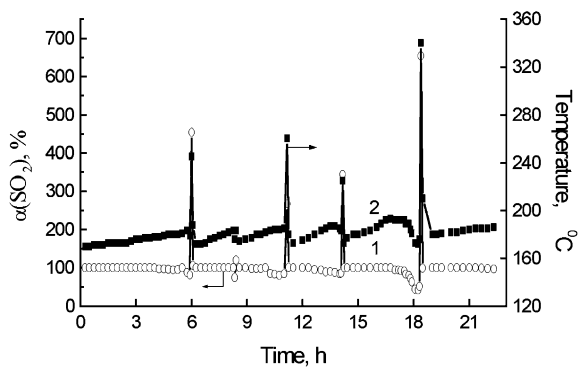

Fig. 2. Time dependencies of α_{SO2} (curve 1) and temperature in the catalyst bed (curve 2) at $O_2/H_2S = 4.9$ on 3.5% V_2O_5/TiO_2 catalyst. Feed temperature is 135 °C.
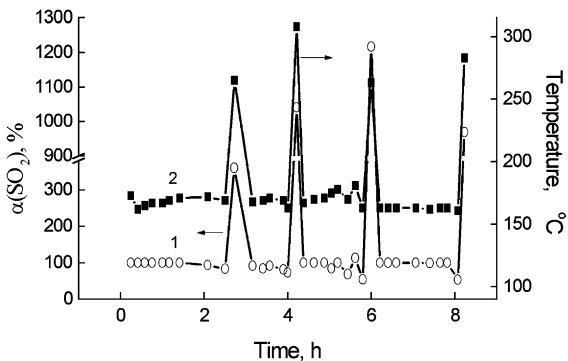

Fig. 3. Time dependencies of X_{H_2S} (curve 1), α_{SO2} (curve 2) and temperature in the catalyst bed (curve 3) at $O_2/H_2S = 5$ on 10.8% V_2O_5/Al_2O_3 catalyst. Feed temperature is 150 °C.

Fig. 4. Time dependencies of α_{SO2} (curve 1) and temperature in the catalyst bed (curve 2) at $O_2/H_2S = 4$ on 5.5% V_2O_5/Al_2O_3 catalyst. Feed temperature is 145 °C.

Fig. 5. Time dependencies of α_{SO2} (curve 1) and temperature in the catalyst bed (curve 2) at $O_2/H_2S = 5$ on 4.5% $V_2O_5/Al_2O_3/TiO_2$ catalyst. Feed temperature is 130 °C.
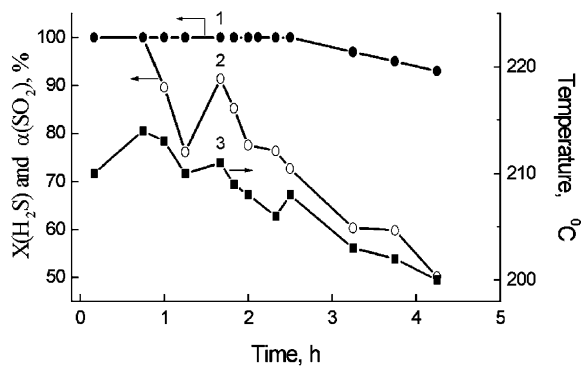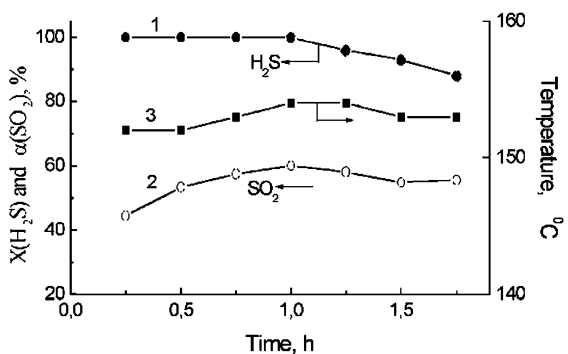

Fig. 6. Time dependencies of X_{H_2S} (curve 1), α_{SO2} (curve 2) and temperature in the catalyst bed (curve 3) at $O_2/H_2S = 3.5$ on 3.25% V_2O_5/SiO_2 catalyst. Feed temperature is 150 °C.

V_2O_5/TiO_2, provide almost 100% conversion of H_2S, which do not decrease in the course of reaction. Periodic oscillations of the SO_2 concentration in the flue gas relative to the current concentration of converted H_2S (α_{SO_2}) and temperature in the catalyst bed are observed in this case. The temperature change during a flash can be as high as $300\,^{\circ}C$, while the SO_2 concentration can exceed that of the converted H_2S by a factor of 10–12 (Fig. 5). Hence, adsorbed sulfur compounds accumulated on the surface can undergo spontaneous oxidation to yield SO_2. The temperature elevation resulting from the sulfur oxidation favors the fast completion of this process and regeneration of the catalyst. Autooscillation phenomena are not observed with crystalline V_2O_5 and 3.25% V_2O_5/SiO_2 catalysts (Fig. 6). It was shown [5–7] that the catalytic behavior of vanadium catalysts is to a great extent determined by the structure and concentration of vanadium species.

^{51}V MAS NMR spectra of the samples supported on Al_2O_3 are shown in Figs. 7 and 8. At low vanadium content (5.5% V_2O_5) the spectrum represents the superposition of two lines (two sets of spinning sidebands in Fig. 7) from two unequivalent vanadium sites. SATRAS analysis of the satellite intensities allows chemical shielding parameters (see Table 2) to be estimated for these two lines. Small value of
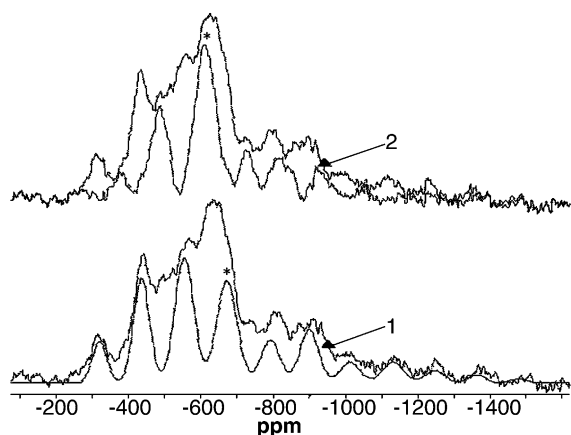

Fig. 8. ^{51}V MAS NMR spectra of 10.8% V_2O_5 supported on Al_2O_3. Spectrum represents the superposition of at least of four lines. MAS spectra of these lines with their relative intensities are shown: 1—MAS spectrum of V_2O_5, 2—spectrum of $AlVO_4$, 3—spectrum of distorted tetrahedral species II and 4—distorted tetrahedral species III, weakly bound to the surface.

Fig. 7. ^{51}V MAS NMR spectrum of 5.5% V_2O_5 supported on Al_2O_3. Spectrum represents the superposition of two lines (two sets of spinning sidebands, spectra 1 and 2, respectively) from two unequivalent vanadium sites in different tetrahedral coordination (species I and II). Isotropic shifts are indicated by asterisks.
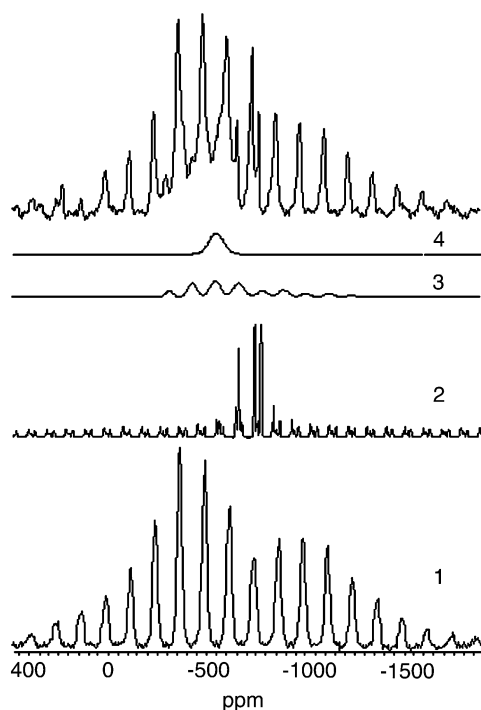
chemical shielding anisotropy and significant shift of σ_{iso} towards the high field indicates that species I may be assigned to isolated tetrahedral species strongly bound to alumina, while species II, due to a higher chemical shielding anisotropy, should be assigned to associated vanadium species in distorted octahedral or distorted tetrahedral coordination. The latter seems more probable due to a relatively high asymmetry parameter (0.5), although the parameter of chemical shielding anisotropy (375 ppm) argues the octahedral coordination of these species. Comparable intensities are seen for peaks of species I and II in the spectra at this vanadium concentration (5.5% of V_2O_5). An increase in the vanadium concentration (Fig. 8) leads to emergence of phases of vanadium compounds: V_2O_5 and $AlVO_4$ (spectra of these compounds are shown in Fig. 8 in accordance with their relative intensities, spectra 1 and 2; isotropic shifts of these compounds

Table 2
^{51}V NMR data of studied catalysts

No.	Sample	^{51}V site	σ_{iso} (ppm)	$\Delta\sigma$ (ppm)	η_σ	
1	5.5% V_2O_5/Al_2O_3	1	615 ± 10	250		Tetrahedral (species I)
		2	668 ± 5	375	0.5	(species II)
2	10.8% V_2O_5/Al_2O_3	1	668 ± 5	375	0.5	(species II)
		2	570	275 ± 25		Tetrahedral (species III)
		3	661	$\sim$100		$AlVO_4$
		4	740	$\sim$100		$AlVO_4$
		5	772	$\sim$100		$AlVO_4$
		6	610	640	0.1	V_2O_5
3	2% V_2O_5/TiO_2	1	610	650		Species 1
		2	650	670		Species 2
4	3.5% V_2O_5/TiO_2	1	610	650		Species 1
		2	650	670		Species 2
5	10.5% V_2O_5/TiO_2	1	500 ± 5			Weakly bound
		2	543 ± 5			Weakly bound
		3	605 ± 5			Strongly bound
		4	670 ± 5	520	0.4	Polymer octahedral species
6	20% V_2O_5/TiO_2		610	640	0.1	V_2O_5
7	IC-27-40	1	527			Tetrahedral species
		2	570	275 ± 25		Tetrahedral species

are indicated by asterisks, NMR parameters are given in Table 2). In addition to these compounds two types of tetrahedral species (species II, III) are detected at this vanadium concentration. Species III (spectrum 4), with a small value of isotropic shift and high value of the anisotropy characteristic of it, corresponds to associated tetrahedral species of metavanadate type (chain structure) weakly bound to alumina (all the lines and their relative intensities are shown in Fig. 8, NMR parameters are given in Table 2). As
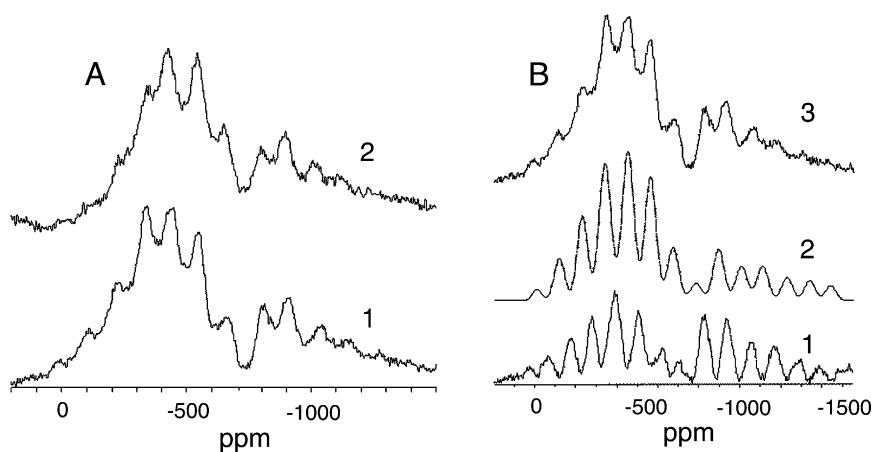

Fig. 9. (A) ^{51}V MAS NMR spectra of 2 and 3.5% V_2O_5 supported on TiO_2 (spectra 2, 1 respectively). Both spectra represent the superposition of two lines (two sets of spinning sidebands in each spectrum) from two unequivalent vanadium sites in distorted octahedral oxygen environment (as shown for example for 3.5% V_2O_5, (B)).

seen in the figure, this sample is mainly constituted by V_2O_5.

^{51}V MAS NMR spectra of TiO_2 supported catalysts are shown in Fig. 9. At low vanadium content (2, 3.5% V_2O_5) the spectra can be described by the superposition of two lines (two sets of spinning sidebans in Fig. 9B, spectra 1, 2) of vanadium in distorted octahedral oxygen environment (see Table 2 for the chemical shielding parameters). Close intensities of these lines, which depend on the vanadium content, are seen in both spectra. The further increase in the vanadium content up to 10.5 wt.% leads to formation of vanadium oxide species of another type (Fig. 10). From the value of the isotropic shifts, these are vanadium species strongly and weakly bound to titania (-605, -670 and -500, -543 ppm, respectively). The association of vanadium species may be responsible for appearance of weakly bound vanadium aggregates with strong internal V–O–V bonds (like metavanadate chains) and weak bonding to the titania surface. Spectrum 2 in Fig. 10 corresponds to this aggregates, while spectrum 1 in Fig. 10 to the superposition of at least of two lines of distorted octahedral species bound to titania. Only spectrum of V_2O_5 compound is observed in the ^{51}V MAS NMR spectrum of the catalyst containing 20% V_2O_5.

^{51}V MAS NMR spectrum of industrial catalyst IC-27-40 (vanadium supported on Al_2O_3/TiO_2) is shown in Fig. 11. Spectra of the catalysts with similar vanadium content supported on individual Al_2O_3 and TiO_2 are also shown for comparison. The influence of the mixed oxide support is clearly seen in these spectra. In the case of the mixed oxide support, these are the most symmetric and narrow lines. Similar to the individual oxides, the spectrum of IC-27-40 is superposition of two lines. The low anisotropy these lines allows them to be assigned to isolated tetrahedral species and to associates of the tetrahedra (types Q^0 and Q^1, respectively).

If summarize these data, we can conclude that at low vanadium concentrations (below 0.5 monolayer), complexes with a tetrahedral environment of oxygen atoms are formed on alumina and mixed alumina–titania support, while two types of significantly distorted octahedral species are formed on individual titania. The main common feature of these species is their direct bonding to the support. An increase in the concentration up to one monolayer gives rise to association
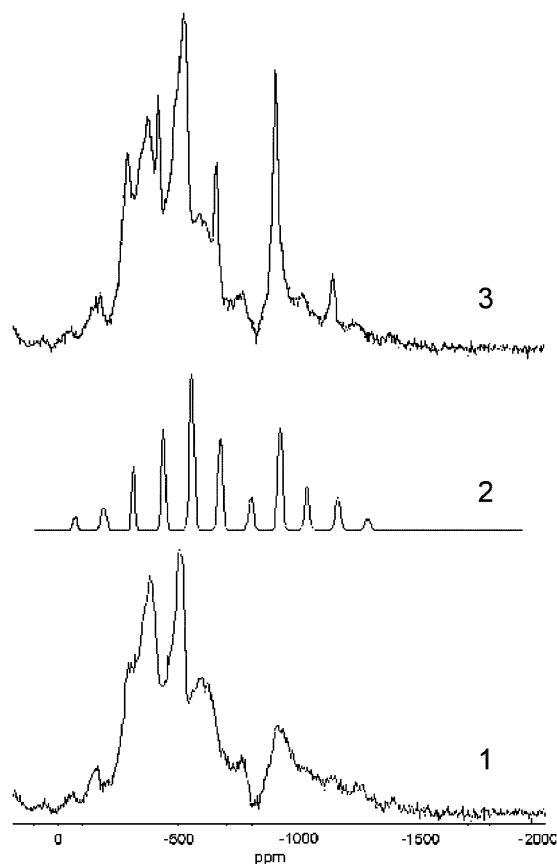

Fig. 10. ^{51}V MAS NMR spectra of 10.5% V_2O_5 supported on TiO_2 (spectrum 3). Spectrum represents the superposition of at least three lines. MAS spectra of these lines with their relative intensities are shown. Spectrum 2—corresponds to associated tetrahedral species weakly bound to titania, spectrum 1 corresponds to the superposition of at least two lines of distorted octahedral species.

of isolated species. In this case, there appear polymer octahedral species and associated tetrahedral species weakly bound to the support. The further increase in the vanadium concentration results in formation of V_2O_5 or $AlVO_4$ compounds. Studies of the activity of the catalysts to partial oxidation of hydrocarbons reveal the highest catalytic activity of vanadium bound directly to the support. The low catalytic activity of silica-supported samples with vanadium oxide species coagulating to form hydrated amorphous V_2O_5-like clusters, which are not connected to the support [8], confirms this suggestion.
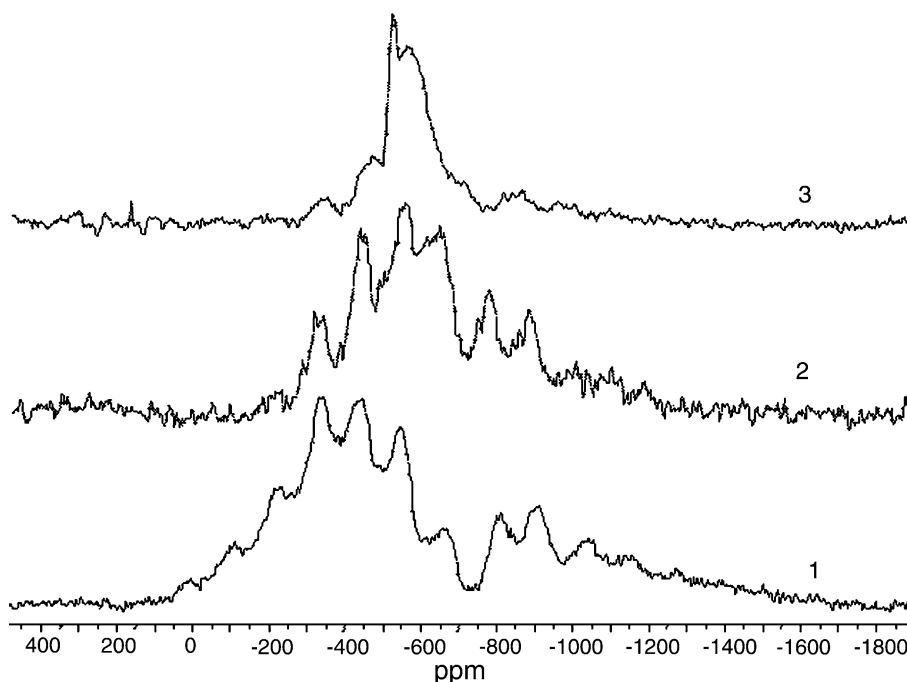
Fig. 11. ^{51}V MAS NMR spectra of 3.5–5.5 wt.% V_2O_5 supported on TiO_2 (3.5 wt.% V_2O_5), Al_2O_3 (5.5 wt.% V_2O_5) and Al_2O_3–TiO_2 (4.5 wt.% V_2O_5) (spectra 1–3, respectively).

The strength of interaction of V_2O_5 with the support may be accounted for by the participation of the bridging oxygen (V–O) in redox transformations. This effect may be also used for explaining the results on oxidation of hydrogen sulfide over vanadium catalysts.

At low V_2O_5 concentrations (IC-27-40, 2–3.5% V_2O_5/TiO_2, 5.5% V_2O_5/Al_2O_3) vanadium species are attached directly to the surface to form tetrahedral or distorted octahedral vanadium sites. The reaction selectivity at excess oxygen is shifted to the formation of SO_2; autooscillation phenomena can be observed in this case.

At a higher concentration of V_2O_5 (AVK-10, 20% V_2O_5/TiO_2), polymeric vanadium species is the octahedral or tetrahedral coordination, as well as and V_2O_5 or $AlVO_4$ compounds less active to complete oxidation are formed. The selectivity to SO_2 decreases in time due to blocking of remained vanadium species bound directly to the surface. Adsorbed sulfur lowers the exposed surface area, and the catalyst activity goes down. In this case, minor oscillations can occur at a steady decrease in the activity. Autooscillation phenomena are not observed with crystalline V_2O_5 and $3.25V_2O_5/SiO_2$ catalysts.

4. Conclusions

The content of vanadium is found to determine the nature of the H_2S oxidation over vanadium catalysts under the conditions of sulfur condensation at excess oxygen. A higher catalytic activity is observed at the concentration of V_2O_5 ranging between 2 and 5% against the 10–20% range. The oscillation mode is characteristic of the reaction in the presence of low-loaded vanadium catalysts. Periodic changes in the reaction rate accompanied by changes in the products composition and catalyst bed temperature are observed. The high activity of the low-loaded vanadium catalysts is attributed to formation of vanadium species bound directly to the surface.

Acknowledgements

References

[1] V.I. Marshneva, V.V. Mokrinskii, Kinet. Katal. 29 (1988) 989.
[2] K.-T. Li, M.-Y. Huang, W.-D. Cheng, Ind. Eng. Chem. 35 (1996) 621.
[3] M.V. Batygina, N.M. Dobrynkin, O.A. Kirichenko, S.R. Khairulin, Z.R. Ismagilov, React. Kinet. Catal. Lett. 48 (1992) 55.
[4] O.N. Kovalenko, N.N. Kundo, V.M. Novopashina, V.M. Khanaev, React. Kinet. Catal. Lett. 64 (1998) 129.
[5] O.B. Lapina, V.M. Mastikhin, A.A. Shubin, V.N. Krasilnikov, K.I. Zamaraev, Prog. NMR Spectrosc. 24 (1992) 457.
[6] A. Khodakov, B. Olthof, A.T. Bell, J. Catal. 181 (1999) 205.
[7] I.E. Wachs, J. Catal. 124 (1990) 570.
[8] N. Das, H. Eckert, H. Hu, I. Wachs, J.F. Walzer, F.J. Feher, J. Phys. Chem. 97 (1993) 8240.