

NOTE

The Role of V=O Sites on the Oxidation of Methane to Formaldehyde over V/SiO₂

The direct conversion of methane to higher valued products has attracted the attention of many research groups in the last decade. One of the most studied routes has been the oxidation to formaldehyde, the best molar yield reported in the literature being about 5-6% (1). The object of this work is to characterize the surface species of V/SiO₂ catalysts and their relationship to the activity for this reaction. Catalysts containing different quantities of vanadium, with or without sodium, and catalysts based on sodium vanadate impregnated on silica, were characterized by XPS (X-ray photoelectron spectroscopy) and NARP (nitric oxide plus ammonia rectangular pulses).

A silica Cabot Aerosil, particle size 5-30 Nm, BET area 200 m² g⁻¹, was used as the carrier. This was impregnated with aqueous solutions to yield solids with 1-8 wt% of vanadium. The impregnated solids were calcined for 12 h at 873 K. Catalysts containing sodium as well were prepared by washing the support with 0.01 N sodium hydroxide and drying it prior to vanadium impregnation. This catalyst contains 5 wt% vanadium and 0.4 wt% sodium (5% V, Na/SiO₂). A catalyst was also prepared by impregnation with sodium vanadate so as to obtain 2.5 wt% of vanadium on silica (NaVO₃/SiO₂).

The XPS spectra were obtained at room temperature with an ESCA 750 computer-driven, Shimadzu instrument, using MgK α radiation. The V/Si, Na/Si, and V/O atomic ratios were calculated using the area under the Si2p, V2p_{3/2}, Na1s, and O1s peaks, the Scotfield photoionization cross sections, the mean free paths of the electrons, and the instrument function which was given by the ESCA manufacturer. The binding energies (BEs) were always referred to C1s at 284.6 eV on the surface. The surface of vanadium-silica and vanadium-sodium-silica catalysts was also characterized using the NARP technique, developed by Satsuma *et al.* (2), for bulk V₂O₅ which was used by Kartheuser and Hodnett (3) to measure vanadium oxide dispersions on V/SiO₂ catalysts. Oyama *et al.* (4) compared NARP results with oxygen chemisorption showing excellent agreement in V=O site density estimation. In the present work, NARP experiments were performed after calcination and degassing with He (100 cm³/min) at 400°C,

using 0.02 g catalyst and a 3-min-long rectangular pulse of NO (0.1%) + NH₃ (2%). Kinetic experiments were performed using a single-pass flow reactor made of fused silica with an inside diameter of 1.8 cm and a heated length of 15 cm. The reactor was loaded with 0.2 g catalyst, and the total flow rate (methane plus oxygen) was 17 cm³/min, with a CH₄/O₂ ratio of 9.

Table 1 shows XPS, NARP, and TOF (turnover frequencies based upon NARP estimations) data obtained with the V/SiO₂ series containing several vanadium loadings. At 5 and 8% loading a second O1s signal at 530.5 eV becomes visible which is assigned to V₂O₅ crystals, also detected in the XRD patterns. In solids containing sodium, the concentration of V=O abruptly decreases. When the V/Si ratio is plotted as a function of the vanadium content (Fig. 1a) a slope change occurs at about 2 wt%, which indicates the formation of multilayer structures above this loading. Also note that the V=O concentration calculated from NARP experiments follows a similar trend.

TOF data in Table 1 show that sodium has a deleterious effect on catalytic performance, thus the understanding of its interaction with both the support and vanadium helps to elucidate the nature of the active sites for the oxidation of methane. The first two rows of Table 2 show that Na/SiO₂ yields two Na1s peaks, 2 eV apart, the relative proportions of which are only slightly modified after calcination. To investigate the stability of these surface species the calcined Na/SiO₂ was washed with distilled water at room temperature for 1 h. This mild treatment produced a significant decrease in the 1070.9 eV peak and in the Na/Si ratio. These results may indicate that two Na surface species are present, one which interacts with the support, the most stable one (BE = 1072.7 eV), and another, more labile and soluble in water at room temperature. When vanadium is impregnated on the Na/SiO₂ (rows 4 and 5) the higher BE sodium species disappear. Compare the data in rows 5 and 9 and note that the V2p_{3/2} and Na1s BEs are the same as those recorded for NaVO₃. On the other hand, before calcination both 5% V, Na/SiO₂ and NaVO₃/SiO₂ show similar BEs for Na1s and V2p_{3/2}. This may indicate that the salt, upon dissociation in solution, interacts in the same way as when vanadium is impregnated on

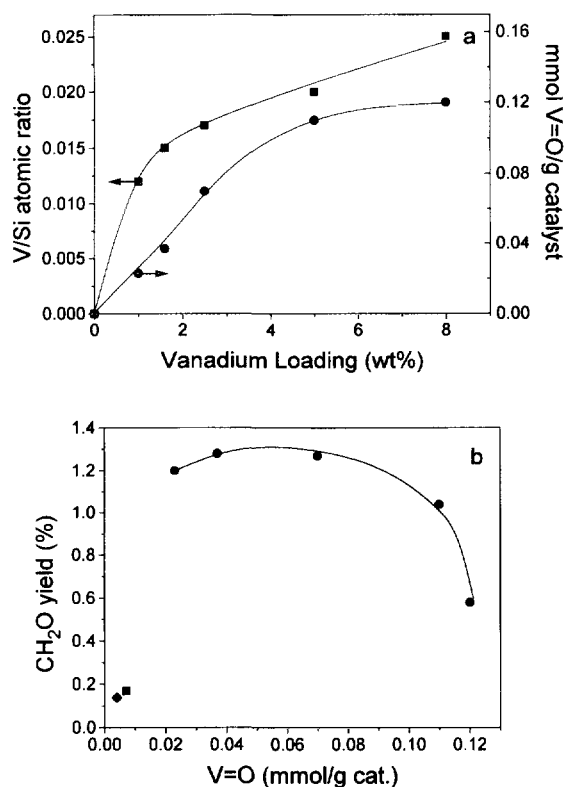


FIG. 1. (a) Surface V=O concentration (NARP data) and V/Si ratio (XPS data) on silica-supported vanadium containing solids. (b) Effect of surface V=O concentration on the catalytic behavior of V/SiO₂ formulations. Reaction conditions: 0.2 g catalyst, total flow rate 17 cm³/min. CH₄:O₂ = 9:1, reaction temperature 823 K. ●, V/SiO₂; ■, 5% V, Na/SiO₂; ◆, NaVO₃/SiO₂.

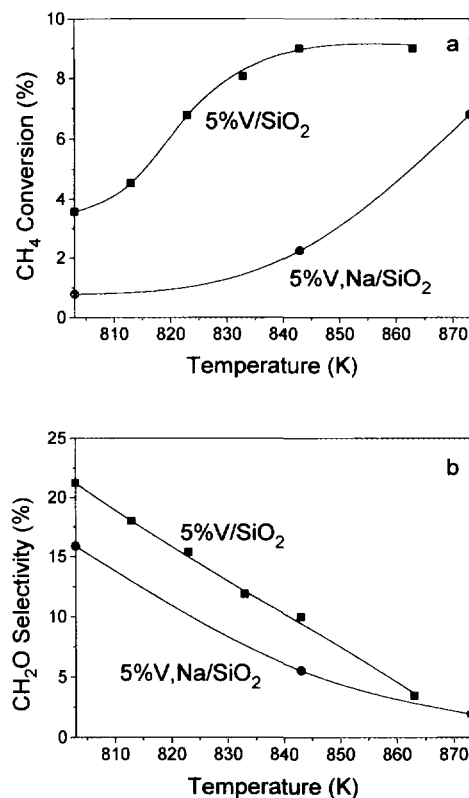


FIG. 2. Poisoning effect of sodium on 5% V, Na/SiO₂ catalyst. Reaction conditions are the same as in Fig. 1.

TABLE 1
XPS and NARP Data on Catalysts with Different Vanadium Loadings

Catalyst	S_g^a (m ² /g)	O1s ^b (eV)	V2p _{3/2} (eV)	V/Si _s ^d	V/O _s × 10 ^{3c}	V=O ^f (mmol/g)	TOF × 10 ^{2g} (s ⁻¹)
1% V/SiO ₂	177	533.0 (2.6)	515.3 (4.6) ^c	0.012	5.5	0.023	2.34
1.6% V/SiO ₂	177	533.1 (2.5)	515.6 (3.2)	0.015	6.6	0.037	1.68
2.5% V/SiO ₂	176	532.9 (2.6)	515.5 (2.0)	0.017	7.4	0.070	0.88
5% V/SiO ₂	132	532.9 (2.6)	515.9 (2.8)	0.020	9.4	0.110	0.46
		530.5 (2.2)					
8% V/SiO ₂	121	532.8 (2.6)	515.8 (2.7)	0.025	11	0.120	0.21
		530.5 (2.2)					
5% V, Na/SiO ₂	64	532.9 (2.3)	516.6 (2.6)	0.035	15	0.007	0.12
		530.1 (2.3)					
NaVO ₃ /SiO ₂	69	532.7 (2.2)	516.5 (2.8)	0.012	4	0.004	0.17
		530.3 (2.2)					

^a Surface area.

^b Binding energies and full widths at half maximum (shown between brackets) are given in electron volts (eV).

^c Wide peak with uncertain binding energy (± 0.2 eV).

^d Surface vanadium/silicon ratio calculated from XPS data.

^e Surface vanadium/oxygen (532.9 ± 0.1 eV) ratio calculated from XPS data.

^f Concentration of surface V=O sites measured by NARP.

^g Turnover frequencies, defined as moles of formaldehyde formed, per second and per V=O site.

TABLE 2
XPS Data on Sodium-Containing Solids^a

Solid	Pretreatment ^b	V2p _{2/3}	Na1s	V/Na ^c	Na/Si ^d
Na/SiO ₂	a	—	1072.7 (58%) 1070.7 (42%)	—	0.22
Na/SiO ₂	b	—	1072.6 (46%) 1070.9 (53%)	—	0.21
Na/SiO ₂	b,c	—	1072.7 (72%) 1070.4 (28%)	—	0.11
5% V, Na/SiO ₂	a	516.1	1072.8 (23%) 1070.8 (77%)	0.16	0.11
5% V,Na/SiO ₂	b	516.6	1070.9 (100%)	0.16	0.22
5% V/SiO ₂	b	515.9	—	—	—
NaVO ₃ /SiO ₂	a	515.7	1072.3 (55%) 1070.9 (45%)	0.07	0.14
NaVO ₃ /SiO ₂	b	516.5	1072.7 (20%) 1070.9 (80%)	0.12	0.16
NaVO ₃	As received	516.6	1070.9 (100%)	0.75	—

^a Binding energies and full widths at half maximum (shown between brackets) are given in electron volts.

^b Pretreatment: (a) dried at 393 K, (b) calcined at 873 K, (c) washed with distilled water after calcination.

^c Surface vanadium/sodium atomic ratio.

^d Surface sodium/silicon atomic ratio.

Na/SiO₂. In the last two columns of Table 2 it is shown that both the V/Si and Na/Si ratios increase with calcination, the different proportions of the Na peaks being accounted for by the different V/Na bulk ratios.

In Fig. 1b, formaldehyde yields are presented as a function of the concentration of V=O sites. The maximum yield is obtained with vanadium loadings between 1.6 and 2.5%. In this interval the XPS data shows the onset of multilayer formation. This is further substantiated by the appearance of V₂O₅ crystallites detected through XRD on solids containing 5 and 8% vanadium. The decrease in formaldehyde yield observed in catalysts containing V₂O₅ multilayers or crystallites seems to indicate that the selective V=O sites are located on well-dispersed vanadium oxygen species which interacts with the silica support. Figure 2 shows methane conversions and formaldehyde selectivities for 5% V/SiO₂ and 5% V, Na/SiO₂, showing that the presence of Na results in a decrease of formaldehyde yield in the whole range of temperature under study.

The XPS data reported in Table 2 might indicate that a NaVO₃-like compound is formed on the surface of 5% V,Na/SiO₂ calcined at 873 K for 12 h. The strong interaction of sodium with the vanadium oxygen moieties on silica is further supported by the increased vanadium dispersion measured by higher V/Si and V/O ratios. Note that vanadium reacts with the Na that is more strongly held on the silica surface and very likely also with the weakly held alkali metal. However, it can be seen in Table 2, that the Na/V surface ratios for sodium-vanadium-silica catalysts

are higher than those observed for the model compound NaVO₃, suggesting that the poisoning effect of sodium may not be due to NaVO₃ formation only but also to sodium surface enrichment.

In short, the catalytic results together with the XPS and NARP data indicate that surface V=O sites play a key role in defining the catalytic performance for methane oxidation of V/SiO₂ solids. Although these sites are needed to convert methane to formaldehyde, increasing their surface concentration above ca. 0.07 mmol/g negatively affects the formaldehyde yield, probably due to the subsequent oxidation of this product over V₂O₅ crystallites (Fig. 1b). The role of V=O in this reaction is further substantiated by the effect of small additions of sodium, which sharply reduces its concentration and consequently diminishes the formaldehyde yield.

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