

The Structure of Vanadium Oxide on γ -Alumina; An *in-situ* X-ray Absorption Study during Catalytic Oxidation*

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In-situ X-ray Absorption Fine Structure (XAFS) experiments with a 17.5 wt% V_2O_5 on Al_2O_3 catalyst showed that the supported V_2O_5 phase mainly consists of monomeric tetrahedral $(Al-O)_3-V=O$ units after dehydration in air at 623 K. The vanadium oxide phase was reduced in CO/He at 723 K. It was found that the reduced species migrate into the γ - Al_2O_3 lattice, where the V^{3+} species are positioned at an Al^{3+} octahedral position. This migration process appears to be reversible, *i.e.* the $(Al-O)_3-V=O$ units are thus restored by re-oxidation.

1. INTRODUCTION

Supported vanadium oxide catalysts are widely used for catalytic partial oxidation of hydrocarbons [1,2], photo-oxidation [3,4], selective catalytic reduction of NO_x [5] and the oxidation of benzene to phenol with N_2O [6]. The molecular structures of surface vanadia species have been extensively investigated in the past few years with many different spectroscopic methods [7]. The local structure of V_2O_5 supported on silica and γ -alumina has been most intensively studied. In general, ESR and UV/VIS results are consistent with each other, although ESR results are restricted to paramagnetic V^{4+} containing species. On silica, vanadium atoms are generally stabilised in an oxygen tetrahedron in the dehydrated state. Hydrated silica-supported V_2O_5 mostly exists in an octahedral configuration. On alumina, both ESR and UV/VIS studies demonstrated that vanadium is five- or six-fold co-ordinated by oxygen. However, Raman studies revealed the formation of different types of vanadium oxide species: polymeric arrays of octahedral VO_6 units as the main phase and tetrahedral VO_4 species as a minor constituent on both, silica and alumina [8]. Unfortunately, the dynamic nature of the surface vanadia species has resulted in confusion in the published literature, since many studies have compared measurements taken under different experimental conditions (ambient *vs.* *in-situ*, hydrated *vs.* dehydrated) [7,9]. Most of the early studies were performed with samples exposed to atmospheric air. There is considerable evidence that under these conditions monolayer species react with atmospheric moisture and therefore, hydrated structures are assumed [10,11]. Under hydrous conditions, the VO_x species may be properly formulated as structure B or C in Figure 1. On heating in a dry atmosphere, dehydration may

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take place to structure A and/or to an octahedral polyvanadate species, such as structure D [12,13], or to isolated vanadyl species like structure E [14]. *In-situ* Raman experiments generally show a shift of the Raman bands due to dehydration of monolayer species [7,15]. In a recent review, Wachs *et al.* stated that dehydrated surface vanadia species on Al_2O_3 , TiO_2 , ZrO_2 , Nb_2O_5 and CeO_2 all possess identical molecular structures [9]. On these oxidic supports mainly isolated VO_4 units would be present (structure E in Figure 1) [16,17]. Furthermore, a small amount of polymerised species are present, which consist of a terminal $\text{V}=\text{O}$ bond with one bridging V-O-support bond and two bridging V-O-V bonds [7], which resembles structure

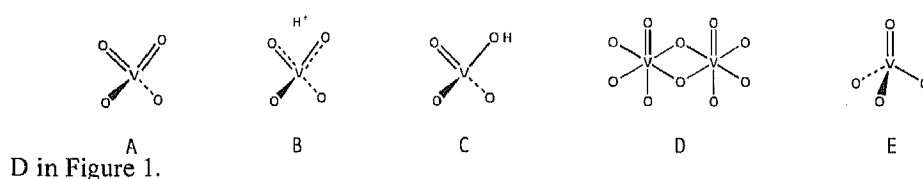


Figure 1 Possible structures for VO_x species in the monolayer phase.

X-ray Absorption Fine Structure (XAFS) has long been known to be rich in chemical and structural information. Various other authors have described the application of XAFS to study supported V_2O_5 catalysts, but the results are depending on the type of support and the applied preparation procedure [18,19,20,21,22,23]. We have applied *in-situ* X-ray absorption spectroscopy to reveal the structure of a 17.5 wt% V_2O_5 on Al_2O_3 catalyst, *i.e.* at reaction temperatures and in the presence of reactants. In the present paper we will deal with the structure of the dehydrated catalyst and the structure of the vanadium oxide phase after reduction with CO at 723 K. It will be shown that reduction brings about severe structural changes of the vanadium oxide phase, and that these changes are reversible, *i.e.* the V_2O_5 monolayer is restored after re-oxidation of the sample. The nature of the reduced vanadium oxide species is still unclear [9].

2. EXPERIMENTAL

17.5 wt% V_2O_5 -on-alumina (Harshaw, $\sim 180 \text{ m}^2/\text{g}$) was prepared by incipient-wetness impregnation of vanadium(III) *iso*-propoxide (Alfa, 95-99% purity) in methanol (Fisher, 99.9% purity) as described elsewhere [24].

V K-edge absorption spectra were taken at station 8.1 of the SRS in Daresbury (UK), using a Si (111) double crystal monochromator. XAFS spectra were collected after dehydration in air at 623 K and after reduction in CO/He at 723 K. Experimental details have been reported in another paper [24]. Data reduction and data analysis were performed with the XDAP code developed by Vaarkamp *et al.* [25]. Standard procedures were used to extract the EXAFS data from the measured absorption spectra [24]. Phase shifts and backscattering amplitudes from reference compounds were used to calculate the EXAFS contributions: Na_3VO_4 for the V-O contribution and Ti-foil for the V-V contribution [24]. The fit parameters were determined by multiple shell fitting in R-space [24]. The inaccuracies in the fit parameters were estimated to

be 20% in co-ordination number (N), 1% in distance (R), 5% in Debye-Waller Factor ($\Delta\sigma^2$), and 10% in inner potential correction (ΔE_0).

3. RESULTS AND DISCUSSION

Figure 2 represents the raw XAFS data of the 17.5 wt% V_2O_5 on Al_2O_3 catalyst. The accompanying data analysis results are represented in Table 1. In Figure 3 the Fourier transforms of the raw EXAFS data as well as the best fit for the two treatments are represented.

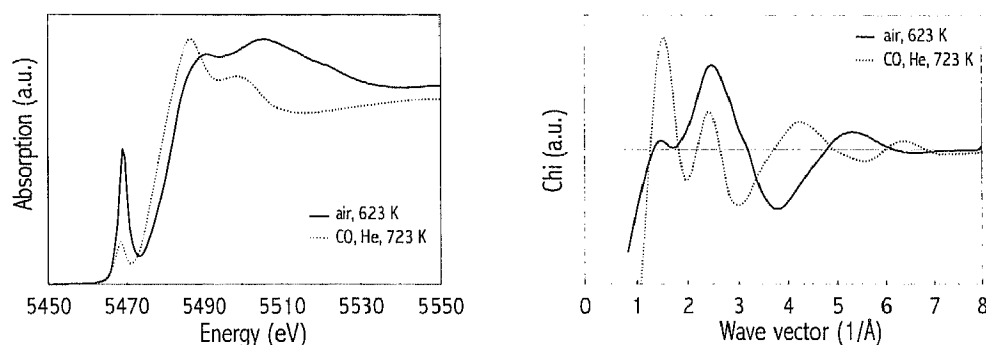


Figure 2 XANES and EXAFS spectra of the 17.5 wt% V_2O_5/Al_2O_3 catalyst before and during CO oxidation at 723 K.

The dehydrated state shows the characteristic XANES of a vanadium compound with tetrahedral (VO_4) configuration, which is in agreement with the EXAFS data analysis results, *i.e.* one short V=O contribution at 1.62 Å, and three bridging oxygen neighbours (V-O-Al) at 1.82 Å. After reduction with CO at 723 K, a dramatic change of the catalyst structure is observed. This structural change is the result of reduction of the vanadium species in the catalyst. As far as we know, no characterisation of a reduced vanadium oxide phase has been reported in the literature [9]. Therefore, analysis of the EXAFS data of the reduced phase will provide useful new information.

Haber has suggested that the reduced VO_x phase exists as bulk V_2O_3 on the surface of the support [26]. The structure of V_2O_3 is isomorphous with corundum $\alpha-Al_2O_3$, in which the oxygen positions are hexagonal close-packed (hcp), with the trivalent cations occupying the octahedral interstices [27]. This results in three vanadium-oxygen bonds of 1.96 Å, and three vanadium-oxygen bonds of 2.06 Å [27]. The pre-edge feature in the XANES spectra of the reduced samples makes this structure to be a possible candidate for the analysis of the EXAFS data. However, vanadium neighbours should also be taken into account and we were not able to fit the data with a V_2O_3 structure with V-V contributions. The other possibility of obtaining a six-fold co-ordination of V^{3+} is migration of the low-valent ions into the $\gamma-Al_2O_3$ lattice. Various authors have described processes in which low-valent cations have been incorporated in the (sub)surface layers of γ -alumina [28,29]. These ions might occupy the tetrahedral and octahedral sites of γ -alumina with the formation of a 'surface spinel' [28] or $AlVO_3$ type of compound [30]. We therefore suggest that the V^{3+} ions have migrated into the $\gamma-Al_2O_3$ lattice,

resulting in the formation of a (surface) ABO_3 -type of compound. In literature, only a few examples of such materials are known [31]. Reid and Sabine reported the formation of $AlVO_3$ as the result of the H_2 -reduction of a physical mixture of V_2O_5 and Al_2O_3 [30]. In this metal-deficient spinel, V^{3+} cations are positioned preferentially in the octahedral Al^{3+} positions of the Al_2O_3 lattice, forcing the Al^{3+} ions into tetrahedral positions [30]. Although in our 17.5 wt% V_2O_5 -on- Al_2O_3 catalyst much less vanadium is present, we think that the process is similar. Therefore, we have used the structural parameters of $AlVO_3$ to fit the EXAFS spectrum of the reduced VO_x . The EXAFS data nicely correlate with this model, showing both V-O and V-Al contributions in the spectra. Analysis of the data is complicated, because the V-O and V-Al contributions in the Fourier transforms are strongly interfering and correlated [24].

We have fitted the structure of the reduced vanadium oxide phase with three oxygen neighbours at 1.97 Å and three oxygen neighbours at 2.10 Å (distorted octahedral geometry). Furthermore, two vanadium-aluminium contributions were included in the fit, *i.e.* at 2.73 Å (CN=3) and at 3.79 Å (CN=1). This distorted octahedral geometry is in agreement with the XANES data of this treatment (Figure 2).

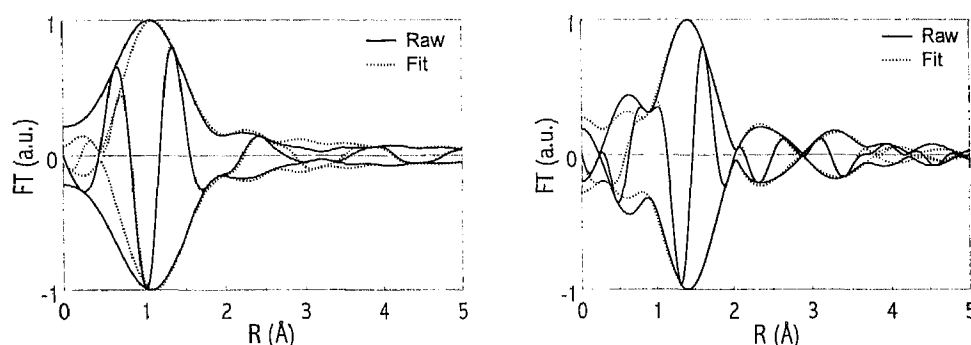


Figure 3 Fourier transforms (k^2 , $\Delta k=2.5-8.0 \text{ \AA}^{-1}$, $\Delta R=1.0-3.5 \text{ \AA}$) of the EXAFS spectrum (solid line) and the best fit (dotted line) of the sample before and after reduction in CO at 723 K.

Table 1 Structural parameters of the 17.5 wt% V_2O_5/Al_2O_3 sample after dehydration and after reduction with CO at 723 K. R = distance, CN = co-ordination number, $\Delta\sigma^2$ = Debye-Waller factor, E_0 = Inner-potential correction.

Conditions	Scatterer	R (Å)	CN	$\Delta\sigma^2$	E_0
Air, 623 K	O ₁	1.62	1.0	-0.00989	0.49
	O ₂	1.82	3.0	0.01463	0.84
CO, He, 723 K	O ₁	1.97	3.0	-0.00100	-4.85
	O ₂	2.10	3.1	0.00138	5.46
	Al ₁	2.73	2.9	0.02300	5.71
	Al ₂	3.79	1.0	0.00361	1.22

To show that the EXAFS data analysis results of the reduced vanadium oxide phase are very good, we have represented the four different contributions (two V-O and two V-Al) in the Fourier transforms in Figure 4.

We have performed force-field molecular modelling on the reduced vanadium oxide-on-alumina system. Preliminary results reveal that V^{3+} migrate to an Al^{3+} octahedral position after reduction. However, for most ions (Cr^{3+} , Ni^{2+}), this process is irreversible and re-oxidation of the sample is almost impossible [28,29]. Nevertheless, our TPR/TPO experiments show that it is possible to re-oxidise the reduced vanadium oxide catalyst [24].

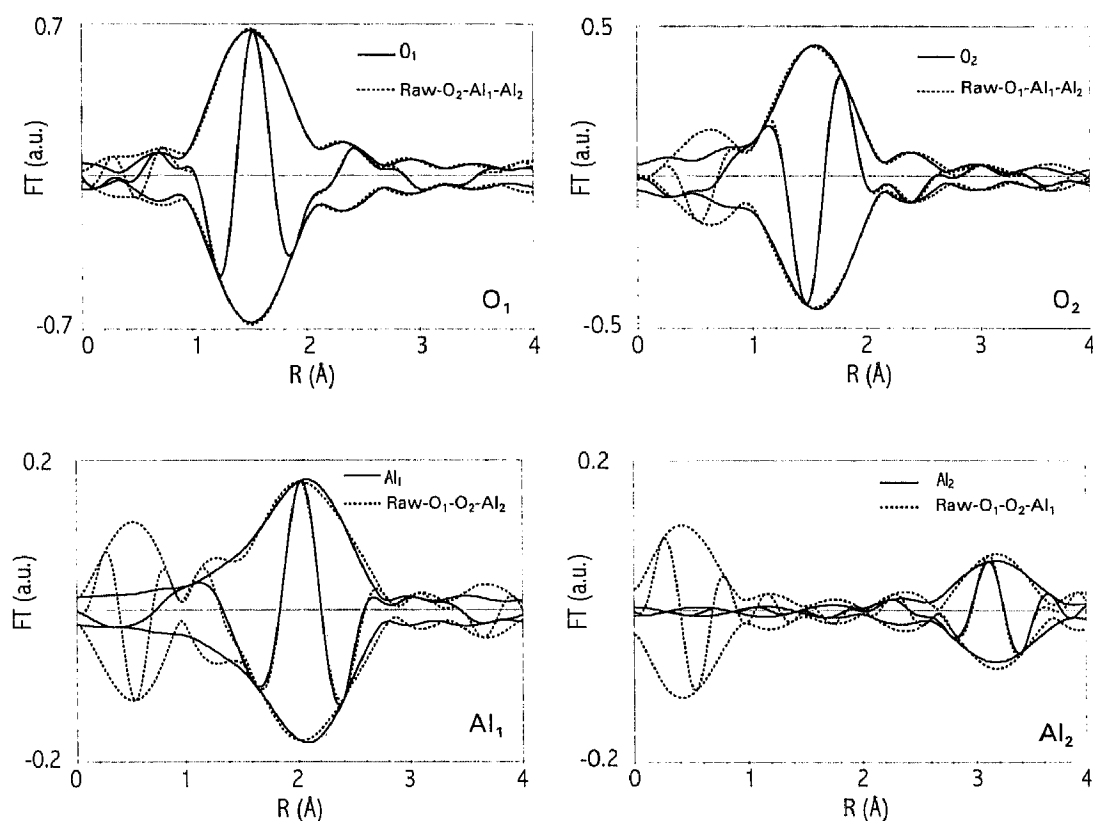


Figure 4 Fourier transforms (k^2 , $\Delta k=2.5-8.0 \text{ \AA}^{-1}$) of the fits of the various shells of the EXAFS spectrum (solid lines) and the raw data minus the fits of the other shells (dotted lines) of the sample after reduction in CO at 723 K.

4. CONCLUSIONS

We have performed *in-situ* X-ray absorption spectroscopy with a 17.5 wt% V_2O_5 -on- γ - Al_2O_3 catalyst. Experiments were performed *in-situ*, *i.e.* at reaction temperatures and in the presence of reactants. In agreement with the literature, the dehydrated species are tetrahedral

co-ordinated. The structure of this $(\text{Al-O})_3\text{-V=O}$ dramatically changed after reduction in CO/He at 723 K. EXAFS data analysis of the reduced species was complicated, but showed that the reduced vanadium ions migrate into the surface layers of $\gamma\text{-Al}_2\text{O}_3$. This process was confirmed by molecular modelling. We think that this process is reversible, and that the $(\text{Al-O})_3\text{-V=O}$ species are restored after re-oxidation. To our knowledge, this is the first time that the structure of the V^{3+} phase is confirmed by experimental data.

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