

An EXAFS study of the metal-promotor interface of a vanadia promoted rhodium catalyst in the precursor state

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Vanadium oxides are widely used in carbon monoxide hydrogenation reactions as additives in Rh based catalyst, because they increase the selectivity for oxygenates [1]. Although several structural hypothesis have been given, there is no direct structural information of the type of interaction between the metal and the additive. Since no crystalline phases are formed, X-ray Absorption Spectroscopy is a unique tool to study the structure of the precursor $\text{VO}_x\text{-SiO}_2$ and the Rh-V interface.

In the present communication we report on an EXAFS study of the vanadium and rhodium edges of a freshly impregnated (4%)Rh/(16%) $\text{VO}_x\text{-SiO}_2$ catalyst. This system shows several properties which are very interesting both from the catalytic and preparative chemistry point of view: (i) full coverage of the surface of the silica by vanadium oxide, (ii) high metal dispersion after reduction and (iii) high activity and selectivity in CO/H₂ reaction. The reason of these interesting properties seems to be the interaction between the metal salt and the promotor during the impregnation step. Thus, the aim of this study is to obtain structural information about the interface between the metal ion and the promoting oxide in the precursor state.

The support $\text{VO}_x\text{-SiO}_2$ (16% V_2O_5) was prepared by homogeneous deposition/precipitation method [2], and the metal was deposited onto this support by incipient wetness from a $\text{Rh}(\text{NO})_3$ solution. XAS spectra were measured at the S.R.S at Daresbury Laboratory (V edge: Station 8.1, Rh edge: Station 9.2). Data analysis was carried out by fitting in k - and R - space using phase and amplitude corrected Fourier transforms to identify the different contributions [3].

Table 1 includes the parameters obtained from the fit of the isolated EXAFS data (FT: $\Delta k = 5.61 \text{ \AA}^{-1}$; FT^{-1} : $\Delta R = 3.25 \text{ \AA}$) of the vanadium edge. This Table includes as well the parameters obtained for the fit of the spectra of the bare support, $\text{VO}_x\text{-SiO}_2$, published elsewhere [4]. The first shell of oxygen atoms ($N = 1$, $R = 1.60 \text{ \AA}$) can be attributed to the terminal vanadyl oxygen. This value is slightly larger than in V_2O_5 (1.57 \AA) but smaller than in V_6O_{13} (1.65 \AA) and in the support $\text{VO}_x\text{-SiO}_2$ before the addition of the metal salt (see Table 1). Shells number 2 and 3 have similar distances to that obtained found for VO_x on silica and can therefore be assigned to a coordinating oxygen in the equatorial plane of the square pyramid, and to oxygen atoms from the surface of the SiO_2 respectively. The fourth shell shows the typical distances of V-V bonds pentoxides and tetroxides, and is again similar to that found in $\text{VO}_x\text{-SiO}_2$ sample.

Table 1. V-edge Coordination parameters for the samples dried at 120 C

Shell	4%Rh/16% $\text{VO}_x\text{-SiO}_2$			16% $\text{VO}_x\text{-SiO}_2$ (ref 4)		
	N	R(\AA)	$\Delta\sigma^2(\text{\AA}^2)$	N	R(\AA)	$\Delta\sigma^2(\text{\AA}^2)$
V-O ₁	1.0	1.60	0.0087	1.0	1.66	-0.0052
V-O ₂	1.9	1.97	0.0031	4.0	1.94	0.0016
V-O ₃	1.0	2.18	-0.0016	1.1	2.17	-0.0048
V-V	1.6	3.09	-0.0054	1.9	3.05	-0.0020

It was possible to describe the EXAFS data with 4 coordination shells (16 parameters), although they were statistically allowed only 12, by keeping some of the coordination parameters the same as found for the bare support, where all the parameters were allowed due to better data quality, resulting in larger Fourier Transform ranges [4]. The increase in the Debye-Waller factor of the first V-O shell in the Rh/ $\text{VO}_x\text{-SiO}_2$ catalyst compared to the same value in the bare support $\text{VO}_x\text{-SiO}_2$ may reflect the existence of two types of vanadyl bonds: one at 1.60 \AA appearing in the vanadium atoms affected by the Rh and the other at 1.66 \AA appearing in the V atoms unaffected by the rhodium atoms.

Table 2 includes the parameters obtained from the fit of the isolated EXAFS data (FT: $\Delta k = 11.8 \text{ \AA}^{-1}$; FT⁻¹: $\Delta R = 3.9 \text{ \AA}$) of the rhodium edge. The distance of the first shell is typical of $\text{Rh}^{\text{III}}-\text{O}^-$ bonds. They can be due oxide, but most probably to oxygen from OH^- groups or water molecules. The presence of this shell indicates that the interaction with the support and the drying treatment does not disrupt the Rh^{III} complex, since the first coordination sphere seems to be complete. The second shell can be due to coordination to the oxygen atoms from the support while the third shell was expected taking into account the direct interaction of the Rh salt with the support.

Table 2. Rh-edge Coordination parameters for the sample 4%Rh/16%VO_x-SiO₂ dried at 120 C

Shell	N	R(Å)	$\Delta\sigma^2(\text{Å}^2)$
Rh-O ₁	6.0	2.01	-0.0007
Rh-O ₂	0.9	2.50	0.0002
Rh-V	1.9	3.03	0.0000

Considering the results from the V and Rh edges, a tentative model for the interaction between Rhodium ions and Vanadium oxides is displayed in Figure 1. This model ensures the maximum number of vanadium atoms affected by the presence of Rh and explains the decrease of the oxygen atoms in the equatorial plane of the VO₅ square pyramids, and the coordination number for the bond Rh-V seen from the Rh edge. The lack of the Rh shell in the V-edge is not surprising since a maximum of 50% V atoms would "see" rhodium, the coordination number of the resulting shell would be one, and the shell at 3.09 Å due to V-V bonds could mask the bonds at 3.03 Å due to Rh-V.

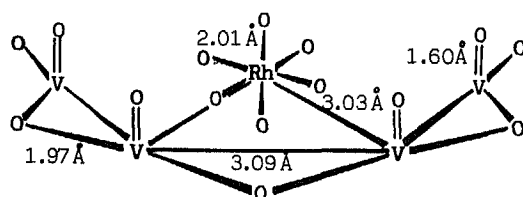


Figure 1. Tentative model for the interactions between Rh ions and vanadium oxide.

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