

Further studies of the active phase in Cs-doped Fe–V–oxide catalysts

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The addition of Cs to an Fe–V–O material leads to the formation of an amorphous phase containing oxide vacancies, which is an excellent catalyst for the selective oxidation of polyaromatics due to its ability to activate O₂ to oxide ions suitable for nucleophilic insertion into the hydrocarbon molecule.

The selective oxidation of polyaromatics (*e.g.* anthracene, fluorene) to produce ketones and anhydrides is of considerable industrial and academic interest. For example, in the case of fluorene, it is important to achieve the maximum selectivity to 9-fluorenone while inhibiting the production of maleic anhydride which, although a valuable product in itself, is a major precursor to carbon oxides. Previous publications by Baerns and co-workers¹ have shown that the addition of caesium to an unsupported Fe–V–oxide catalyst results in a large increase in the selectivity to fluorenone production from 60% for an undoped material to >95% for the Cs doped material. This improvement in the selectivity was explained by changes in the acid–base properties of the catalyst surface on the addition of alkali metal. However, Brückner *et al.*² have studied the catalysts using electron paramagnetic resonance spectroscopy (EPR) and found that those catalysts doped with Cs exhibit an EPR signal at very low resonant field ($g' = 18$) which does not appear in the undoped samples. This signal was attributed to Fe³⁺–V_o(e⁻) species, and it was proposed that these centres are also responsible for the improved selectivities observed.

Despite this earlier work, the nature of the catalytically active sites is still not clear. The aim of this communication is to give further evidence for the formation of a new amorphous phase, which is important in the catalytic reactions using scanning electron microscopy.

Materials with atomic ratios of V : Fe of 1 : 0.13 to 1 : 2.0 have been prepared by co-precipitation from ammonium metavanadate (NH₄VO₃) and iron chloride (FeCl₃·6H₂O). Cs₂SO₄ was added before precipitation (by the addition of conc. NH₃) and then the samples were dried (rotary evaporation) and calcined (18 h at 623 K). The crystalline components of the materials were identified by X-ray diffraction (XRD) with Cu-K α radiation. Electron paramagnetic resonance spectroscopy (EPR) was performed on an ERS 300 cw-spectrometer (Zentrum für Wissenschaftlichen Gerätebau, Berlin). Scanning electron microscopy was carried out using a Zeiss DSM 962 microscope and EDX analysis on a Noran Voyager using Proza software for ZAF correction.

The XRD data obtained for the various materials are presented in Table 1. This data shows that, as the Fe content is increased, the most important phase observed changes from Fe₂V₄O₁₃ to FeVO₄, and finally α -Fe₂O₃ when the Fe is in excess. In the sample with the lowest Fe content, some unreacted V₂O₅ and an unidentified phase were observed. No significant differences in the XRD could be seen between the Cs-doped and undoped samples of the same V : Fe ratio.

The EPR spectrum of the undoped catalyst showed only a broad signal at around $g' = 2$, caused by dipolar and exchange-coupled Fe³⁺ ions, as are present in FeVO₄. No peak was observed at $g' = 18$ (see Table 1). However, in all the cases where Cs was used as a dopant, a low-field peak at $g' = 18$ was

observed. Table 1 shows that an increase in the Fe content, while keeping the Cs content constant, is accompanied by an increase in the size of the low-field EPR peak, up to a maximum for the 1 : 0.74 : 0.06 sample and slowly decreasing again. It is important to note that Baerns *et al.* found that the most selective catalysts were the caesium doped samples with V : Fe ratios between 1 : 0.75 and 1 : 1.4, *i.e.* those with a high amount of the new phase and FeVO₄ as the main crystalline phase. From the results of previous experiments, it was suggested that this low-field signal is due to Fe³⁺ ions in close proximity to oxide vacancies occupied by an electron, *i.e.* Fe³⁺–V_o(e⁻).^{2a,b}

Fig. 1 shows a scanning electron micrograph of a typical area of the Cs doped V : Fe = 1 : 0.74 sample. The presence of three different materials can be observed in this micrograph: (i) long needle-like crystals; (ii) large rectangular crystals; and (iii) an amorphous material. An EDX spectrum of the needle-like crystals confirmed that this was FeVO₄ and showed that no caesium was associated with this material. The large rectangular crystals were identified as Fe₂V₄O₁₃ and again no caesium was observed. However, in the spectrum obtained for the amorphous material, and shown in Fig. 2, the Fe : V ratio is *ca.* 1 : 1, and

Table 1 XRD and EPR data for the various V : Fe : Cs materials

Sample V : Fe : Cs	Crystalline phases		
	major	minor	$I_{g'=18}^a$
1 : 1.0 : 0	FeVO ₄	α -Fe ₂ O ₃ ^b	0.0
1 : 0.13 : 0.06	Fe ₂ V ₄ O ₁₃ , V ₂ O ₅	unknown	3.3
1 : 0.30 : 0.06	Fe ₂ V ₄ O ₁₃	unknown	11.7
1 : 0.60 : 0.06	Fe ₂ V ₄ O ₁₃	FeVO ₄	284.4
1 : 0.74 : 0.06	FeVO ₄ , Fe ₂ V ₄ O ₁₃		1001.0
1 : 1.0 : 0.06	FeVO ₄	α -Fe ₂ O ₃ ^b	827.6
1 : 1.4 : 0.06	FeVO ₄	α -Fe ₂ O ₃	627.4
1 : 2.0 : 0.06	FeVO ₄ , α -Fe ₂ O ₃		455.2

^a Relative intensity of the $g' \approx 18$ EPR peak. ^b Small amount.

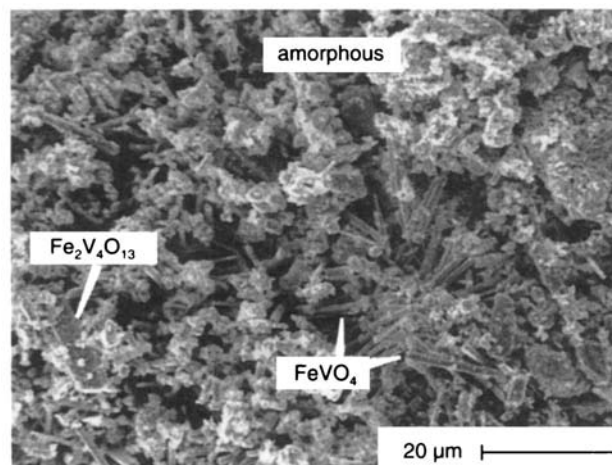


Fig. 1 Scanning electron micrograph of a Cs doped Fe–V–O material (V : Fe : Cs = 1 : 0.74 : 0.06)

caesium is present in high concentration ($\approx 10\%$). Since the caesium can only be seen in the amorphous material, and the addition of caesium leads to improved catalytic performance,¹ it can be assumed that it is indeed the amorphous part of the samples which is the active catalytic phase. Using ICP for further characterization, the approximate empirical formula, based on iron and vanadium, was calculated as $\text{Fe}_{0.65}\text{VO}_{3.4}$. The difference in the Fe:V ratio from the EDX and ICP analyses may be due to errors in the EDX measurement caused by localized differences in the sample stoichiometry.

We propose that caesium reacts with the Fe–V–O lattice and is incorporated in some of the cationic lattice positions. A greater amount of the new active phase is formed when the Fe:V stoichiometry is $< 1:1$, owing to the presence of holes in

the lattice, where Fe should be located, which can be filled by Cs. Replacement of Fe by Cs also leads to the formation of oxide vacancies due to the differences in the ionic charge, and these vacancies are involved in the activation of dioxygen to oxide ions, which then take part in the selective hydrocarbon oxidation reaction. This process is analogous to that which occurs when MgO is doped with Li for use as a methane oxidative coupling catalyst.⁴

In conclusion, the results presented here show that a new catalytically active amorphous phase is formed on the addition of caesium to a Fe–V–O material, and that the caesium probably has two effects: (i) modification of the surface acidity and (ii) formation/stabilization of oxide vacancies which are important for dioxygen activation.

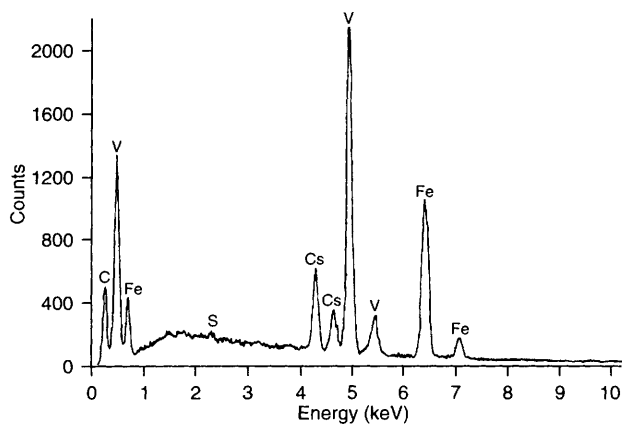


Fig. 2 Energy dispersive X-ray spectrum of the amorphous phase

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