In situ Raman Spectroscopic Study of Supported Molten Salt Catalysts During SO_2 Oxidation

I. Giakoumelou,[1] R. M. Caraba,[2] V. Parvulescu[2] and
S. Boghosian[1]
[1]Department of Chemical Engineering, Univeristy of
Patras and Institute of Chemical Engineering and High
Temperature Chemical Processes (FORTH/ICE-HT), GR-
26500 Patras GREECE
[2]University of Bucharest, Department of Chemical
Technology and Catalysis, Bucharest 70346, ROMANIA

The catalytic oxidation of SO_2 to SO_3 plays a key role in a number of industrial processes, which due to the associated sulfur oxide emissions have significant environmental impact. Although the main source of SO_2 emissions to the atmosphere is the coal-fired power generation, large amounts of SO_2 are also emitted from sulfuric acid manufacturers and smelters of non-ferrous metals. Production of sulfuric acid is currently performed not only from traditional sulfuric acid manufacturers but also from NO_x and SO_x removal stations, combined with SCR technology like e.g. in the so-called Haldor-Topsoe SNOX process. The catalyst used for sulfuric acid production catalyzing the reaction $SO_2 + ½O_2 \rightarrow SO_3$ contains its active phase in a molten salt, which is distributed in the pores of an inert silica support and is the most important supported-liquid-phase (SLP) catalyst. During SO_2 oxidation, large amounts of SO_3 are taken up by the catalyst, of which the active phase is best simulated by vanadium oxide dissolved in alkali pyrosulfate thereby giving rise to formation of vanadium oxosulfato complexes (1). *In-situ* real-time spectroscopic characterization of catalytic active centers in vanadium oxide based SO_2 oxidation *supported molten salt catalysts* under gas and temperature conditions of practical importance has been a long-sought goal in catalysis (1).

In the present study, *in-situ* Raman spectroscopy at temperatures up to 500°C is used for the first time to identify vanadium species on the surface of a vanadium oxide based supported molten salt catalyst during SO_2 oxidation. Vanadia/silica catalysts impregnated with Cs_2SO_4 were exposed to various $SO_2/O_2/SO_3$ atmospheres and *in situ* Raman spectra were obtained and compared to Raman spectra of unsupported "model" V_2O_5-Cs_2SO_4 and V_2O_5-$Cs_2S_2O_7$ molten salts. Figure 1 compares a representative *in-situ* Raman spectrum of a supported molten salt catalyst with the Raman spectrum of a V_2O_5-Cs_2SO_4 molten salt. The data indicate that the V^V complex $V^VO_2(SO_4)_2^{3-}$ [bands a-e, of which the most characteristic at 1034 cm^{-1} (band b) due to ν(V=O) and 940 cm^{-1} (band c) due to sulfate] and Cs_2SO_4 (bands A,B) dominate the catalyst surface after calcination (2). Upon admission of SO_3/O_2 the excess sulfate is converted to pyrosulfate ($SO_4^{2-} + SO_3 \rightarrow S_2O_7^{2-}$) and the V^V dimer $(V^VO)_2O(SO_4)_4^{4-}$ [with characteristic bands at 1046 cm^{-1} due to ν(V=O), 830 cm^{-1} due to bridging S-O along S-O-V and 770 cm^{-1} due to V-O-V] is formed (3,4)

$$V_2O_5 + 2S_2O_7^{2-} \rightarrow (VO)_2O(SO_4)_4^{4-}$$

Admission of SO_2 causes reduction of V^V to V^{IV} and to V^{IV} precipitation below 420°C (4). Figure 2 shows the proposed structural models for the V species present in the liquid (molten) phase supported on the carrier.

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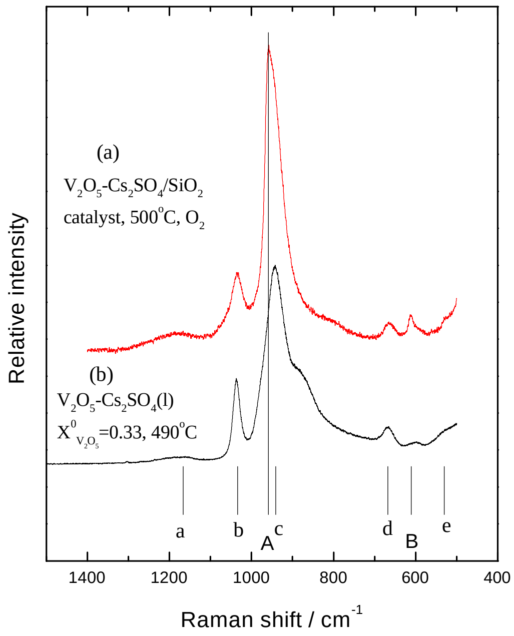

Figure 1. (a) *In situ* Raman spectrum of V_2O_5/SiO_2 (6.5 wt% V) impregnated with Cs_2SO_4 (Cs:V=3:1) at 500°C under O_2, calcined in the Raman furnace. Laser wavelength, λ_0 = 488.0 nm; laser power, w = 60 mW; spectral slit width, sww = 8 cm^{-1}; scan speed, ss = 0.2 cm^{-1} s^{-1}; time constant, τ = 1s. (b) Raman spectrum V_2O_5-Cs_2SO_4 molten mixture with $X^0(V_2O_5)$ =0.33 at 490°C.

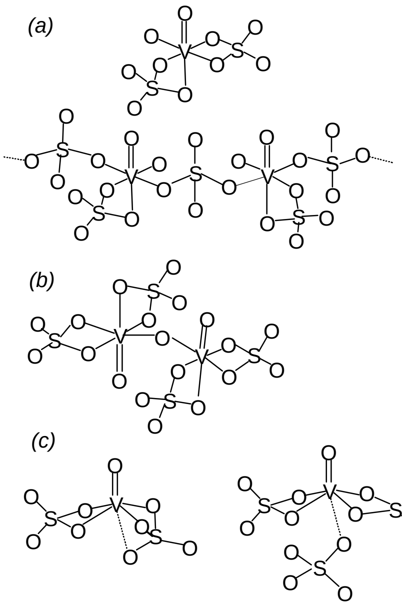

Figure 2. Possible molecular structural models for the V complexes present in the molten salt catalyst: (a) $V^VO_2(SO_4)_2^{3-}$ in monomeric and oligomeric form; (b); $(V^VO)_2O(SO_4)_4^{4-}$; and (c) $V^{IV}O(SO_4)_2^{2-}$ and $V^{IV}O(SO_4)_3^{4-}$.

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