



Combined application of XPS, XANES and mass-spectrometry to *in-situ* study of methanol oxidation over vanadium based catalysts

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Vanadium-based systems are widely applied as catalysts for selective oxidation of hydrocarbons, alcohols, etc. For example, V-P-O oxide catalysts convert n-butane to maleic anhydride [1], V-Ti-O mixed oxides – beta-picoline to nicotinic acid [3]; V-P-O/TiO₂ catalysts are active in methylpyrazine ammoxidation [2]. Oxidation of methanol to formaldehyde (or to methyl formate) and formaldehyde to formic acid over V₂O₅/TiO₂ catalysts attracts a special attention of researchers due to its practical importance [4-6]. Despite numerous reports, the exact mechanisms of these reactions are not clear yet.

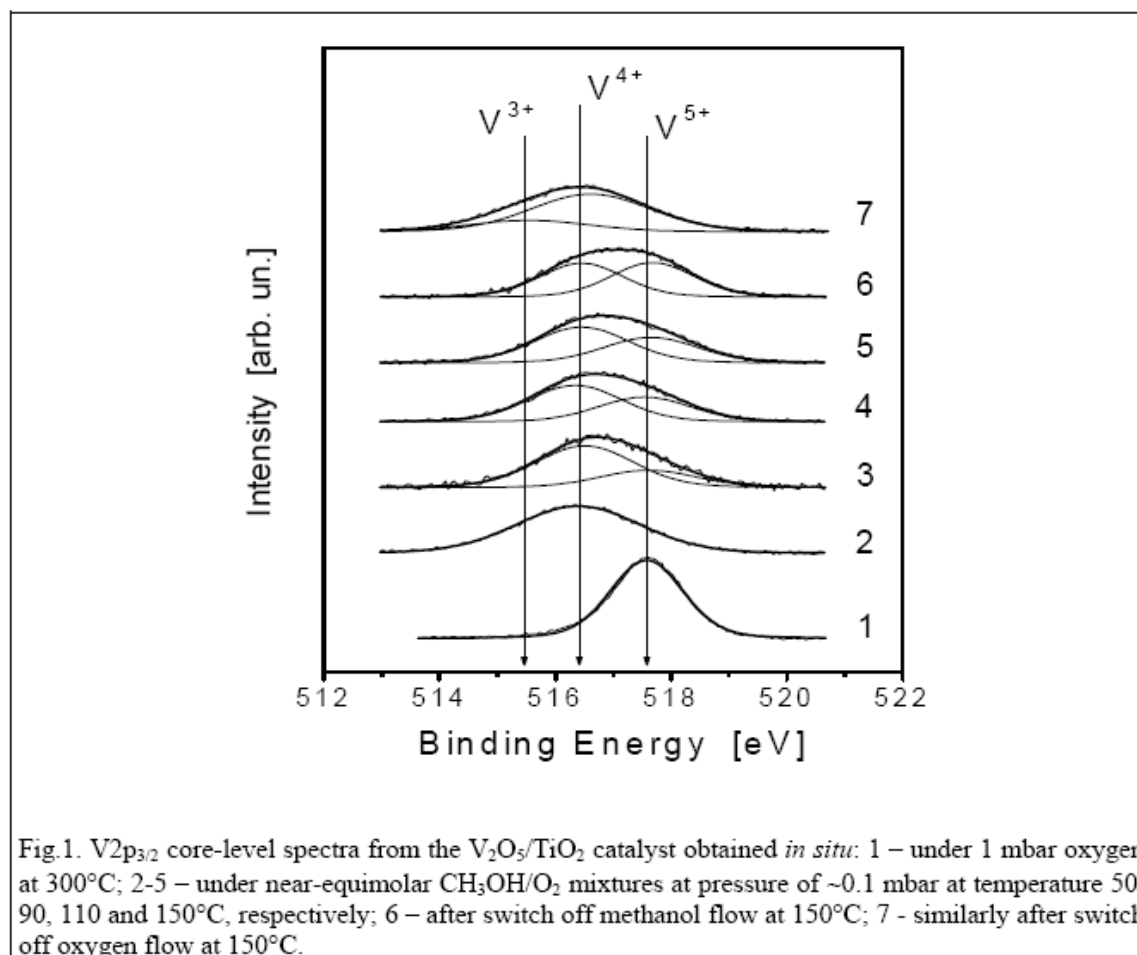
In this report we present the results of *in situ* study of methanol and propane oxidation over V₂O₅/TiO₂ catalysts performed with X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS). Catalytic properties of the catalysts studied were tested simultaneously using mass-spectrometry.

All experiments were performed at beam line U49/2-PGM1 at BESSY. The spectrometer was equipped with a special gas cell which allowed increase in pressure for *in situ* XPS and NEXAFS measurements up to 2 mbar. The gas flows into the experimental cell were regulated using calibrated mass-flow controllers. Before experiments the catalyst powders were pressed to pellets and then mounted on a temperature-controlled heating stage. The sample temperature was measured using a chromel-alumel thermocouple pressed directly at the back of the sample. The overall spectral resolution was 0.1 eV at the Oxygen *K*-edge. All spectra were normalized by the incident photon flux, which was measured using a photodiode with known quantum efficiency. XPS spectra were calibrated against C1s line from adventitious carbon (284.8 eV). To extract the information about chemical states of the elements, the narrow regions of their core level spectra have been measured, original XPS spectra being decomposed on separate components. The latter procedure involved Shirley background subtraction and a curve fitting using Doniach-Sunjic functions.

Vanadia-titania catalysts 20V₂O₅ – 80TiO₂ (wt.%) were prepared by spraying titanium dioxide (anatase) suspension in an aqueous vanadyl oxalate solution followed by calcination of the obtained powder in air at 400°C [6]. The specific surface area of the catalyst was equal to 140 m²/g. In spite of the high content of V₂O₅, X-ray diffraction (XRD) analysis indicates that the catalysts contains only TiO₂ anatase phase. At the same time, transmission electron microscopy (TEM) shows the presence of

the V_2O_5 nanocrystals ($d = 1-2$ nm) located on the surface and inserted between small (3-8 nm) anatase particles, which are joined into aggregates with irregular shape. This sample exhibits high activity in methanol oxidation to formaldehyde and in formaldehyde oxidation to formic acid [6].

This sample was used as an object for our *in situ* experiments which include the step-wise heating of the sample from 50°C to 150°C under near-equimolar $\text{CH}_3\text{OH}/\text{O}_2$ mixtures at total pressure of ~ 0.1 mbar. MS, XPS and NEXAFS spectra were measured simultaneously at three different temperatures: 50, 90, 110 and 150°C . The corresponding XPS spectra are shown in Fig.1. Before *in situ* experiments were started, the catalyst was activated in 1 mbar of oxygen at 300°C for 30 min directly in the gas cell. This led to full oxidation of vanadia and removal of any carbon-contained impurities. Only sharp single feature at 517.6 eV, which corresponds to V^{5+} ions, is observed in the $V2p_{3/2}$ spectrum (fig.1). Under influence of the $\text{CH}_3\text{OH}/\text{O}_2$ mixtures, vanadium(V) ions are reduced to V^{4+} state that is identified on



appearance of wide $V2p_{3/2}$ peak at 516.4 eV. Increasing the temperature led to partial oxidation of vanadium(IV) ions and two features at 516.4 ± 0.1 eV (V^{4+}) and 517.6 ± 0.1 eV (V^{5+}) are observed in the $V2p_{3/2}$ spectra (fig.1). It should be noted, that the fraction of V^{5+} ions are increased constantly with temperature. Significant part of V^{4+} ions are remained on the catalyst surfaces even after removal of

methanol from the gas phase. On the other hand, removal of oxygen at 150°C results in further reduction of vanadium and two features at 515.6 and 516.6 eV, which can be attributed with V^{3+} and V^{4+} , respectively, are observed in the $V2p_{3/2}$ spectrum (fig.1). Thus, our data unambiguously show that lattice oxygen of vanadium oxide takes a part in the methanol oxidation via Mars-van Krevelen mechanism, which consists of reduction of the oxide catalyst surface by methanol and subsequent reoxidation by gas phase oxygen. The reduced V^{4+} ions are believed to be the active sites involved in the Mars-van Krevelen redox cycles.

It has been also found that surface composition of the V_2O_5/TiO_2 catalysts is changed as a function of the reaction atmosphere and temperature. At 150°C titanium signal disappears from the surface-sensitive spectra, but it is still detectable in the bulk-sensitive spectra. This result can be explained by the accumulation of carbonaceous species selectively on the low-active titania surface or by the redistribution of the elements so that the titania surface is covered with vanadium. The former concept seems to be more preferable, because recently some author observed agglomeration of the dispersed vanadia during methanol oxidation over V_2O_5/SiO_2 catalysts [7].

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References:

1. B.K. Hodnett, Heterogeneous Catalytic Oxidation, Wiley, New York, 2000, Chapter 5.
2. V.M. Bondareva, T.V. Andrushkevich, O.B. Lapina, A.A. Vlasov, L.S. Dovlitova, *Reac. Kinet. Catal. Lett.* 79 (2003) 165.
3. E.M. Al'kaeva, T.V. Andrushkevich, G.A. Zenkovets, G.N. Kryukova, S.V. Tsybulya, *Catal. Today* 61 (2000) 249.
4. P. Forzatti, E. Tronconi, A.S. Elmi, G. Busca, *Appl. Catal. A* 157 (1997) 387.
5. E. Santacesaria, A. Sorrentino, R. Tesser, M. Di Serio, A. Ruggiero, *J. Mol. Catal. A* 204-205 (2003) 617.
6. G. Popova, T.V. Andrushkevich, I. Zakharov, Yu. Chesalov, *Kinet. Catal.* 46 (2005) 217.
7. T. Feng, J.M. Vohs, *J. Phys. Chem. B* 109 (2005) 2120.