Short communication

Impact of the outermost layer of various solid metal vanadate catalysts on ammoxidation of 2-methyl pyrazine to 2-cyanopyrazine

Jörg Radnik [a,*], Naresh Dhachapally [a,1], Venkata Narayana Kalevaru [a], Ilya Sinev [b],
Wolfgang Grünert [b], Andreas Martin [a]

[a] Leibniz Institute for Catalysis at the University of Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany
[b] Laboratory of Industrial Chemistry, Ruhr-University Bochum, Universitätsstr. 150, 44801 Bochum, Germany

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ABSTRACT

Metal vanadates are promising catalysts for the ammoxidation of 2-methylpyrazine to 2-cyanopyrazine, an important intermediate in the production of pyrazinamide as an effective anti-tubercular drug. Low-Energy Ion Scattering (LEIS) investigations supplementing X-ray Photoelectron Spectroscopy (XPS) measurements showed the variation of the composition in the near-surface region. Only with this experimental approach it was possible to elucidate, how important are stable vanadium-enriched or pure vanadia outermost surface layers for a selective catalyst. In contrast, mixed oxide outermost layers are detrimental for the catalytic performance.

1. Introduction

Without any doubt, the composition of the outermost surface of a heterogeneous catalyst is critical for its performance, i.e. activity and selectivity. However, the analysis of this important layer is indeed a scientific challenge, in particular with respect to real catalysts. The most suitable method to deal with this question is Low-Energy Ion Scattering (LEIS, also referred to as Ion Scattering Spectroscopy, ISS) [e.g. [1–3]]. In LEIS, noble gas ions of a known energy between 1 and 10 keV are scattered at the atoms of the outermost layer of the solid sample. The backscattered ions are differentiated according to their kinetic energies, and provide information about the mass of their collision partners in the sample surface [4,5]. Such experiment enables the analysis of the composition of the outermost layer both qualitatively and also quantitatively, at an advanced level, i.e. elemental surface concentrations might be available. In addition, the sputtering effect due to the impact of the noble gas ions leads to the removal of surface atoms; therefore concentration depth-profiles for the near-surface region with a vertical resolution better than one monolayer can be obtained. Thus, it is possible to investigate the differences in the composition between the outermost layer and the layers below. Such experiments were used successfully for different kinds of catalysts, in particular for mixed oxides [6–11].

Vanadium oxide is well known as an effective oxidation catalyst, also employed in combination with various dopants as a catalyst for ammoxidation of methyl aromatics and hetero aromatics [12,13]. Recently, we used various metal vanadates ($AlVO_4$, $CrVO_4$, $FeVO_4$, $BiVO_4$, $LaVO_x$ and $NbVO_5$) as a solid catalysts for the gas-phase ammoxidation of 2-methylpyrazine (2MP) to 2-cyanopyrazine (2CP), an intermediate that is used to produce pyrazinamide as an effective anti-tubercular drug [14,15]. In the bulk of these catalysts, the V: Me atomic ratio is always 1: 1. In addition, a series of La-vanadates with different bulk composition (V: La = 0.1: 0.9 to 0.95: 0.05) was synthesized and applied for the above-mentioned reaction. The investigations revealed that $LaVO_x$ and $NbVO_5$ catalysts were very selective towards 2CP between 380 and 420 °C at 2MP conversions close to 100%. Some of the other catalysts were very active already at lower temperatures, but exhibited only poor nitrile selectivity below 50% ($AlVO_4$, $CrVO_4$, $FeVO_4$). Systematic studies of the parent samples using X-ray Photoelectron Spectroscopy (XPS) showed diverging V: Me (Al, Cr, Nb, La and Bi) ratios in the near-surface region. Surprisingly, an enrichment of vanadium in the near-surface region seemed to be beneficial for the selectivity, but led to smaller activity (mainly seen for La- and Bi-containing samples). In contrast, $AlVO_4$ with a low amount of V in the near-surface region revealed a high activity, but low desired product selectivity. Simultaneously, crystalline V_2O_5 as identified by X-ray Powder Diffraction (XRD) studies was detrimental for the selectivity, whereas amorphous

* Corresponding author.
   E-mail address: joerg.radnik@catalysis.de (J. Radnik).
[1] Present address: SABIC Research & Technology Pvt. Ltd., Bangalore — 562125, India.

non-stoichiometric VO_x phases were discussed to be beneficial. Valence states between $+V$ and $+IV$ were observed for vanadium by XPS, but no clear correlation between the valence states and the catalytic performance could be derived [14].

However, these observations obtained with XPS gave hints for the correlation between the near-surface composition and the catalytic performance, but have not resulted in consistent ideas about any correlation between surface structure and catalytic behavior yet. This may arise from the ignorance of the elemental composition of the outermost surface of these mixed oxides, which strongly affects catalysis. V: Me near-surface ratios as obtained by XPS (V/Me_{XPS}) may be important for the activity and selectivity of the catalysts, but due to the limited surface sensitivity of the method, it only provides averaged data for the sampling region of the outermost few nm if there are any compositional changes normal to the external surface. Therefore it remains unclear which species might be present at the outermost surface layer of the catalysts and probably determine catalytic properties. Another unanswered question is the stability of the surface region under the reaction conditions applied.

A recent study [11] showed impressively the differences between the compositions obtained for a number of mixed oxides including vanadates with methods of different surface sensitivity: from bulk methods (e.g. ICP-OES) via XPS and Energy-Resolved XPS employing synchrotron radiation, to LEIS, which analyzes only the outermost surface layer. Such results stress the importance of combining such methods to obtain more comprehensive relations between structural and catalytic properties.

It was the aim of the present work to determine the surface region properties (i.e. near-surface domain including outermost layer) of some metal vanadates used for the ammoxidation of 2MP to 2CP in order to identify beneficial surface relations using XPS and LEIS analyses methods and also to compare parent and spent samples.

2. Experimental

2.1. Catalysts and test conditions

The metal vanadates under study (Me = Al, Nb and La) were synthesized by a simple citric acid decomposition method described in detail elsewhere [15]. The catalysts revealed a V: Me molar ratio of 1: 1 in the bulk and they were denoted as $AlVO_4$, $NbVO_5$ and $LaVO_4$. In addition, a further sample with a V: La molar ratio of 9: 1, denoted as $La_{0.1}V_{0.9}O_x$, was included in the investigations. The samples were calcined in air at 500–600 °C for 4–48 h. The sample label was extended by appendix "−c" in such case. The catalytic tests were carried out in continuous mode using a tubular reactor and 1 g of catalyst at reaction temperatures of 320–460 °C, ambient pressure and a GHSV of 9500 h^{-1} (2MP: air: NH_3: water: $N_2 = 1$: 26: 7: 13: 22), in general [15]. Time-on-stream (tos) was set to 10 h for all the samples under study. Spent samples will be denoted by attachment "−s".

2.2. Characterization methods

2.2.1. Low-Energy Ion Scattering (LEIS)

LEIS was performed with a Leybold LH10 spectrometer equipped with an EA 10/100 multi-channel detector (Specs). The spectrometer is dedicated for XPS, but can be used for ISS by changing the polarity of the detector. For LEIS, 2000 eV He ions provided by an IQE 12/38 ion gun were employed. Samples were not pretreated before measurements except for gentle grinding in a mortar to crush particle aggregations. The powders were deposited on the sample holder from slurry in n-pentane. Spectra were taken at room temperature. After the stabilization of ion source operation, the sample was transferred into the measuring position and the acquisition of spectra was started. Sweeps of the selected kinetic energy region were repeated to generate a series of spectra reflecting the effect of the ions on the sample surface (sputter

series). During the measurements, surface charge was removed by a flood gun. Spectra were processed with the Casa software. Peak integration was performed on a linear background. As no reference samples (foils of V and of the secondary metals) were available, the data reported in this contribution are intensity ratios, no elemental ratios.

2.2.2. X-ray Photoelectron Spectroscopy (XPS)

Oxidation states and averaged compositions of the near-surface region were determined by XPS. The measurements were performed with an ESCALAB 220iXL (Thermo Fisher Scientific) with mononchromatic Al Kα radiation (E = 1486.6 eV). The samples were fixed on a stainless steel sample holder with double adhesive carbon tape. For charge compensation a flood gun was used, the spectra were referenced to the C1's peak at 284.8 eV. After background subtraction the peaks were fitted with Gaussian–Lorentzian curves to determine the peak positions and areas. The surface composition was calculated from the peak areas divided by the element-specific Scofield factor and the transmission function of the spectrometer.

3. Results and discussion

As already stated above, the catalytic performance depends on the surface composition [14,15]. In our recent papers it was proposed that the catalysts were stable under the reaction feed because no significant changes of the catalytic properties were observed during the first hours on-stream. Additionally to these data, the spent catalysts were now studied by XPS. Surprisingly, for all samples differences in the surface composition could be noticed between the calcined and spent samples (Fig. 1). This observation led to the conclusion that some dynamic changes occurred on-stream. Whereas for $NbVO_5$ these changes were moderate, the remaining vanadates showed more dramatic differences in the composition of the XPS sampling region. After the catalytic tests,
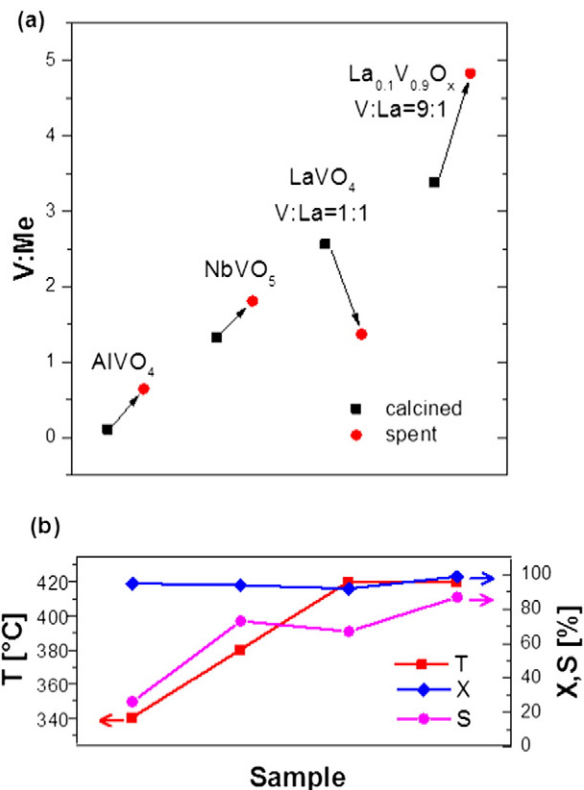

Fig. 1. V: Me ratio of various calcined and spent metal vanadate sample pairs in the near-surface region obtained by XPS: (a) correlated with the catalytic performance and (b) in terms of the reaction temperature needed for nearly complete conversion (T,■), conversion at this temperature (X, ◆) and 2CP selectivity (S,●).