ESRF	**Experiment title:** **XAS on V-Mo-(W) mixed oxide catalysts for the selective oxidation of acrolein to acrylic acid**	**Experiment number**: CH 2126
Beamline: BM 26 A	**Date of experiment**: from: 4.11.2005 to: 8.11.2005	**Date of report**: 20.02.06 *Received at ESRF:*
Shifts: 12	**Local contact(s)**: Serge Nikitenko	

Names and affiliations of applicants (* indicates experimentalists):

Lars Giebeler[a,*], Virginie Croze[b,*], Marian Mazurek[a,b,*], Emanuel Vollmar[a,*], Sergey Nikitenko[c,*], Christina Roth[b], Hartmut Fuess[a]

[a] Darmstadt University of Technology, Institute for Materials Science, Structure Research, Petersenstr. 23, D-64287 Darmstadt, Germany
[b] Darmstadt University of Technology, Institute for Materials Science, Renewable Energies, Petersenstr. 23, D-64287 Darmstadt, Germany
[c] ESRF, DUBBLE-CRG, BP 220, F-38043 Grenoble, France

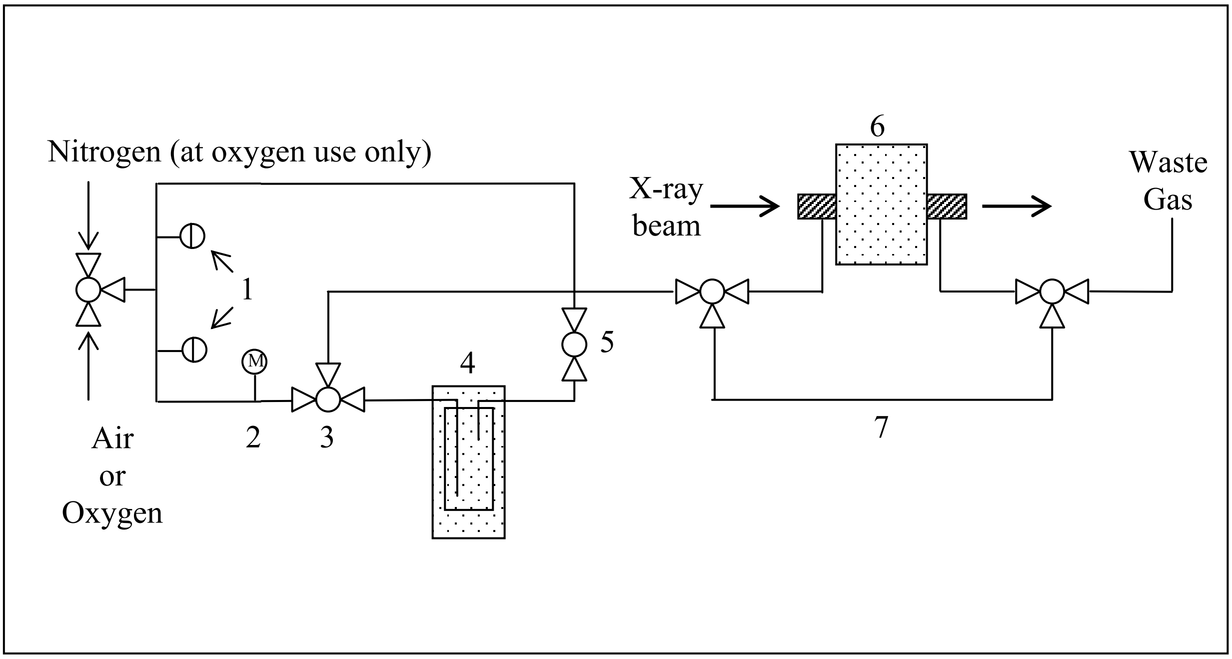
Report:

Aim of the experiment CH2126

The aim of the study is to elucidate the role of the transition metal ions in V-Mo-(W) mixed oxide catalysts. Therefore systematic changes in their properties, in particular valence states and local environment have to be investigated. These changes depend on sample composition and preparation and on the reaction temperature in the gas atmosphere. *In situ* XAS experiments on the proposed model systems will result in further details on the reduction-reoxidation cycle of the catalyst. Furthermore the influence of this treatment will be investigated systematically.

Experimental set-up

The reaction under investigation is the selective oxidation of acrolein to acrylic acid. For the production of a feed stream air is divided into two currents. The higher volume current displays the main feed. The second is connected to the acrolein vapour saturator. The feed is cooled with ice to 0 °C to obtain reproducible acrolein concentrations. The two gas currents are merged to the reaction gas current. Afterwards the reaction gas stream passes the reactor with the catalyst powder fixed between two quartz fiber filters (Fig. 1).



1	Mass flow controller	5	Two-way valve
2	Manometer	6	Reactor with tube furnace
3	Three-way valve	7	Bypass line
4	Acrolein vapour saturator with dewar for ice cooling		

Figure 1. Scheme of the acrolein experimental set-up

The reactor is equipped with the sample fixed in its centre between two filters. It is heated by a tube furnace to 400 °C in air only for the activation of the catalyst. After cooling to 380 °C, the reactor is switched from air to the reaction gas stream. Next step after the reaction is the re-oxidation of the catalyst. The reactor is switched back to air again and heated up again to 400 °C. Same procedure is applied at 400 °C and 450 °C as reaction temperature. The measurement is performed after every ramp when the temperature was held for 30 minutes until an equilibrium has been established.

Preliminary results

The measurements were performed at several spray-dried and crystallised samples of the stoichiometry $V_2Mo_8W_xO_y$ with tungsten contents in the range of $0 \leq x \leq 5$. For the investigation of the behaviour of the catalyst before (*ex situ*) and during the reaction (*in situ*) the V *K*- (5.465 keV) and the W L_{III}-edges (10.207 keV) were measured in fluorescence detection mode. For XANES analyses the single vanadium and tungsten oxides were also measured as references under *ex situ* conditions.

Vanadium was investigated but caused some problems which will be discussed in more detail in the next chapter. For tungsten most of the spray-dried and some crystallised single and mixed oxides were measured *ex situ* and the mixed oxide also under *in situ* conditions. Spectra were obtained in very good quality and resolution. At reaction temperatures of 380 °C and 400 °C, the tungsten environment seems to change slightly.

The origin has to be analysed and interpreted carefully. At 450 °C a significant change can be observed in the EXAFS part of the spectrum. The analysis of the spectra will focus mainly on the structural changes in the first and/or higher coordination shells.

Obstacles during measurements

The system has been investigated as an *in situ* experiment with this set up for fluorescence investigations for the first time. Severe problems have been encountered for the vanadium measurements in the mixed oxide samples. The content is low with respect to the content of molybdenum and tungsten. During the measurements in transmission only spectra with very low intensities could be obtained. Their analysis will not give reasonable results. The increase of the amount of the sample for a measurement leads to high absorption effects induced by the heavy atoms of molybdenum and tungsten. Consequently, fluorescence measurements were necessary. However, an additional problem was caused by the beryllium windows of the reactor. The aluminium layer on one side of the beryllium window was too thick and led to high absorption effects. Therefore *in situ* experiments at the V *K*-edge were not feasible with this set-up.

For further *in situ* and *ex situ* experiments the beryllium windows will be replaced by more suitable ones without an aluminium layer.

Another problem was the furnace which has worked under laboratory conditions only and not in a real experiment at an ESRF beamline before. Many problems were caused by the temperature-dependent deformation of the materials used in the furnace which had never been observed before. Several hours were needed to obtain and stabilise the working conditions of the furnace which also led to a time delay within our working schedule.