FeMo-based catalysts for acrolein production: An in situ X-ray Photoelectron Spectroscopy study

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Abstract: At present, the main acrolein production method is the petro-sourced propylene oxidation. Recently, it has been demonstrated that the **conversion of light alcohols to acrolein** can be performed over an iron molybdate catalyst. In this study, the activity of a **FeMo-based catalyst ($Fe_2(MoO_4)_3$ + MoO_3) in the selective oxidation reaction** of a methanol/ethanol mixture has been studied under near working conditions, using **time-resolved Near Ambient Pressure XPS (NAP-XPS)**.

Keywords: Near-Ambient Pressure XPS, Iron-Molybdate, Alcohol selective oxidation.

1. Introduction

Acrolein is the simplest unsaturated aldehyde which – due to its high reactivity - finds numerous applications as an intermediate in the chemical industry (e.g., for acrylic acid and methionine production). Until now, the main method of acrolein production is propylene oxidation. However, the increasing demand as well as environmental requirements cause the active research of alternative processes[1]. Recently, a new method of acrolein production was shown,[2,3] based on methanol and ethanol as raw materials. This reaction can be schematically described along two successive steps, namely the alcohols oxidation (1) followed by the aldol condensation to acrolein (2):

$$(1)\qquad CH_3OH + C_2H_5OH + O_2 \rightarrow HCHO + CH_3CHO + H_2O$$

$$(2)\qquad HCHO + CH_3CHO \rightarrow CH_2CHCHO + H_2O$$

This reaction has been achieved in the gas phase with the use of iron molybdate mixed oxides ($Fe_2(MoO_4)_3$ + MoO_3), a catalytic system already described elsewhere and industrially used to perform the methanol to formaldehyde oxidation.

Catalysts surface modifications can be monitored by in situ / operando surface spectroscopies such as NAP-XPS. This technique provides direct access to the oxidation state of the catalyst surface at millibar pressures[4]. We applied this approach to study the mechanism taking place at the catalyst surface during the alcohols selective oxidation reaction (1).

2. Experimental

The XPS spectra of the catalyst (Mo 3d, Fe 2p, C 1s and O 1s) were recorded on the SOLEIL synchrotron TEMPO B beamline. The whole redox processes involving the surface metal centers (Fe and Mo) have been monitored under mixtures of methanol, ethanol and/or oxygen at millibar pressures. The catalyst temperature during the analysis was controlled by laser (up to 593 K). XPS spectra were analyzed using a mathematical method first described by Baltrusaitis et al.[5] in 2015: the vectorial method.

3. Results and discussion

Thanks to the high flux of the synchrotron radiation, the evolution of Mo and Fe oxidation state was followed at different temperatures as a function of time during either reduction reaction under alcohol or oxidation reaction under oxygen.

The use of NAP-XPS enabled us to demonstrate that molybdenum sites of the catalyst appear to be the active sites responsible for the alcohols selective oxidation reaction. Indeed, during the reaction, the Mo initially present as Mo^{VI} at the catalyst surface undergoes changes in its oxidation state, whereas the Fe initially present as Fe^{III} is not modified.

The vectorial method applied to XPS data was used to study the changes in Mo oxidation state. During the reduction reaction, we evidenced clearly that the Mo^{VI} is reduced into Mo^{IV} through a 2 electrons transfer process; no trace of Mo^{V} was detected at the catalyst surface (Figure 1). Then, during the oxidation reaction, the Mo^{IV} species was reversibly oxidized into Mo^{VI}. Moreover, the monitoring of oxidation state evolutions as a function of time enabled us to determine the Mo oxidation and reduction reaction initial rates at different temperatures to finally calculate the Mo oxidation and reduction apparent activation energies.

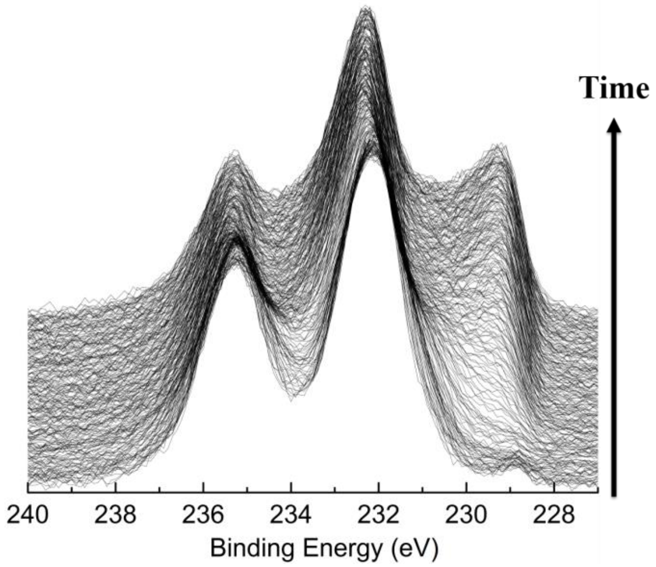

Figure 1. Mo 3d XPS spectra *in situ* monitoring during reduction under methanol and ethanol at 503 K and 1 mbar for 90 min.

4. Conclusions

Using NAP-XPS, the redox processes involved at the surface of an industrial FeMo-based catalyst were monitored *in situ* during the alcohols selective oxidation reaction under 1 mbar. A mathematical method applied to the XPS data has highlighted that this 2 electrons process does not involve Mo^{V} species: Mo^{VI} is reversibly reduced into Mo^{IV}. Finally, this study shows that NAP-XPS experiments can be used to enable the determination of catalytic reactions kinetic parameters.

References

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