



	Experiment title: Operando XAS study of biomass-based glucose transformation catalyzed by tungstate and molybdate homogenous oxyanions	Experiment number: 30-02-1150
Beamline: BM30	Date of experiment: from: 29/06/2021 to: 04/07/2021	Date of report: 10/10/2021
Shifts: 18	Local contact(s): Antonio AGUILAR	<i>Received at ESRF:</i>
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Report:

The production of chemicals from biomass-based sugars has emerged an important research topic in the last decades. A key reaction, known as Retro-Aldol Condensation (RAC), allowing the synthesis of short-chain oxygenated compounds has been extensively investigated.¹ The main product of this reaction is ethylene glycol, a C₂ molecule, obtained through the hydrogenation of glycolaldehyde intermediate. Homogenous tungsten- and molybdenum-based monooxyanions and polyoxyanions such as (WO₄²⁻, MoO₄²⁻, W₁₂O₄₀⁸⁻, Mo₇O₂₄⁶⁻, ...) are efficiently selective catalysts for this reaction. Tungstate precursors are still more selective than molybdenum ones despite the similarity of the chemical properties of both metals. However, tungstate and molybdate do not show, strictly, the same behavior in aqueous solution. Tungstate tends to form more easily polyanions than molybdate.^{2,3} Therefore, a deeper investigation at a molecular scale was required to comprehend this dissimilarity. An *operando* study of the activity of both metals for the conversion of glucose to glycolaldehyde was undertaken on the FAME beamline in ESRF using a dedicated cell for liquid samples developed by the team members⁴ (experimental report n° 30-02-1150). A follow up of the existing W/Mo species in the presence of sugar under relevant conditions for RAC during the course of the reaction was carried out using High Energy resolved Fluorescence detection XANES at L₃-edge for tungsten and K-edge for molybdenum.

Samples prepared at standard conditions consist of aqueous solutions of 5 mmol/L of glucose and 1.32 mmol/L of W or Mo. The experiments occurred conventionally at 150°C and 40 bars of He inert atmosphere. The influence of a set of various parameters on the activity of W and Mo oxyanions was investigated (Temperature, pH of the reaction medium, metal concentration). XANES spectra were recorded during the reaction each 8 min at an interval of time of 1 to 2 hours depending on the temperature of the experiment. *Ex situ* analysis were performed for 3 tungstate and 2 molybdate solid precursors for which the geometry and the oxidation state of the metallic center are well known. The EXAFS spectra of these reference catalysts were recorded in a transmission mode (**Fig. 1 and 2**). For tungstate precursor (**Fig. 1**) the white line is either splitted or not depending on the structure of WO_x unit. Sodium tungstate (Na₂WO₄) consisting of four-fold coordinate tungsten sites exhibit one peak while tungsten (six-fold coordinated tungsten sites) centers of ammonium metatungstate (AMT) catalyst display a white line clearly consisting of two peaks. The splitting of the white line into two peaks is attributed to the existence of distorted octahedral structure that has an Oh symmetry. The largest difference between the spectra of the 3 catalysts is the shift of the L₃-edge maximum by 1.2 eV to higher energies when going from WO₂, for which the tungsten atom is of 4+ oxidation state, to AMT and Na₂WO₄ catalysts whose tungsten centers are of 6+ oxidation state. As for molybdenum-based precursors (**Fig. 2**), the spectrum exhibited by sodium molybdate (Na₂MoO₄) represents an intense pre-edge while ammonium heptamolybdate (HMA) catalyst displays a signal with a blurry pre-edge. Molybdenum can be either located in four-fold coordinated sites as in the case of Na₂MoO₄ or in six-fold coordinated sites as in the case of HMA. The less the environment is centrosymmetric, the more intense is the pre-edge peak, as it is seen by comparing the pre-edge feature of the tetrahedrally coordinated Na₂MoO₄ and the octahedral molybdenum center of HMA (**Fig. 2**).

For the conversion of glucose over AMT catalyst at 150°C we observed an unchanged signal (**Fig. 3**) during the reaction and all the spectra were coincident with the spectrum displayed by a reference aqueous solution of AMT at ambient temperature ([W] = 1.32 mmol/l). Although, in the case of the reaction over HMA catalyst, molybdenum sites have shown a change of structure during the course of the reaction. This evolution has been characterized by an increase and a decrease of the pre-edge intensity (**Fig. 4-A and B**) and the presence of isosbestic points indicating a change of molybdate species (**Fig. 4-A and C**). According to **Fig. 4**, before the beginning and after 8 min of reaction time, the spectra showed a blurred pre-edge similar to the pre-edge of HMA spectra in which molybdenum sites are octahedrally coordinated metal centers. At 16 min till the end of the reaction, the spectra have suddenly adopted the shape of a tetrahedrally coordinated metal site signal by showing the formation of an intense pre-edge. Then, when the reaction medium has been put back to the ambient temperature, the spectrum got back in a shape of an HMA spectrum. Such observation

means that the behavior of molybdate species is different at higher temperature than at ambient temperature which is contrary to the case of tungstate oxyanions that maintain an unchangeable structure when going from ambient to high temperature.

As a preliminary conclusion, under relevant conditions for RAC, tungstate species are probably octahedrally coordinated species, while molybdate anions are tetrahedral sites. The treatment of data is still ongoing, and it must be completed by further theoretical studies (DFT calculations) and experimental RAMAN measurements to clearly points the structural difference leading to the dissimilarity of the activity of both metals.

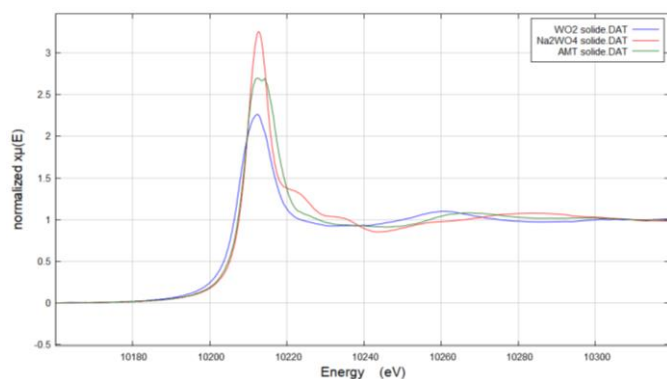


Fig. 1: W L₃-edge XANES spectra of solid WO₂, ammonium metatungstate (AMT) and sodium tungstate dihydrate (Na₂WO₄).

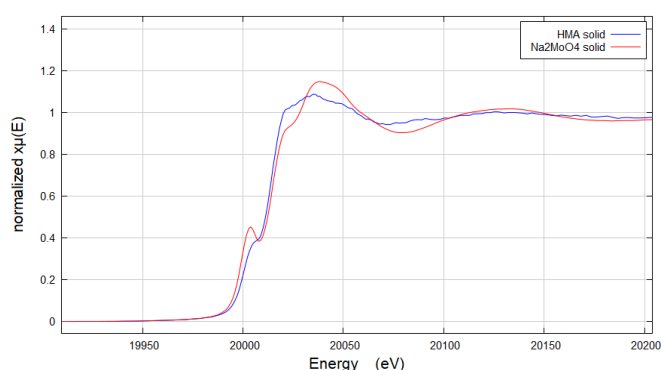


Fig. 2: Mo K-edge XANES spectra of solid ammonium heptamolybdate (HMA) and sodium molybdate (Na₂MoO₄).

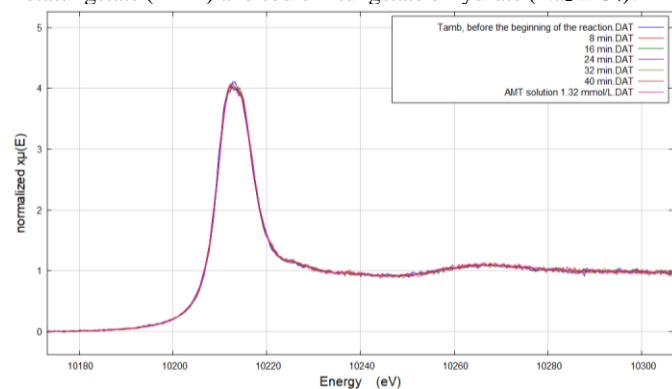


Fig. 3: W L₃-edge XANES spectra recorded during the reaction of glucose over AMT at 150°C under 40 bars of He and pH 4. [W] = 1.32 mmol/L, [glucose] = 5 mmol/L.

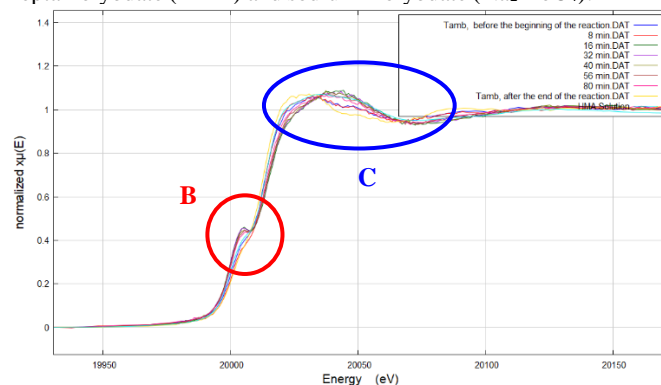


Fig. 4-A: Mo K-edge XANES spectra recorded during the reaction of glucose over HMA at 150°C, under 40 bars of He and pH 4. [Mo] = 1.32 mmol/L, [glucose] = 5 mmol/L.

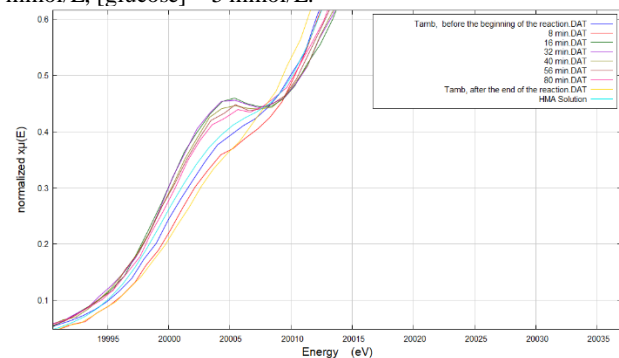


Fig. 4-B: Mo K-edge XANES spectra recorded during the reaction of glucose over HMA at 150°C, under 40 bars of He and pH 4. [Mo] = 1.32 mmol/L, [glucose] = 5 mmol/L.

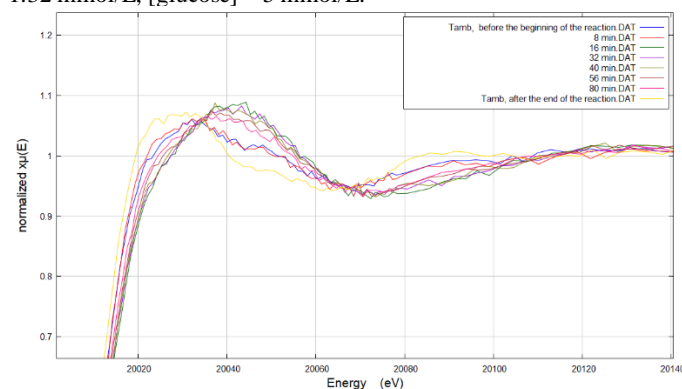


Fig. 4-C: Mo K-edge XANES spectra recorded during the reaction of glucose over HMA at 150°C, under 40 bars of He and pH 4. [Mo] = 1.32 mmol/L, [glucose] = 5 mmol/L.

References:

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