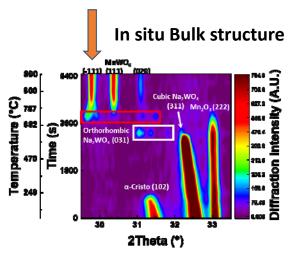
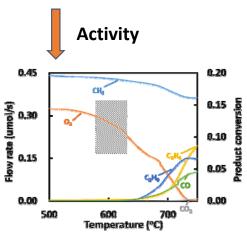
## Experimental *In situ* **XRD-MS**





## Online MS

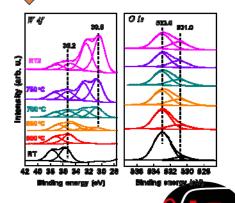




## In situ XPS







Yang, Y.; Zebang, L.; Li, J.P.H.; Evgeny, V. Reaction control and mass spectrometry workstation for coupling an X-ray spectroscopic characterization instrument with an in-situ reaction cell. 2022.

## Discussion Ti-NaWMnSi

XRD and XPS results of Mn and W at different temperatures and different atmosphere conditions

\* In situ treatment in HPGC, the spectrum is collected after cooling down to RT

		Species	Heating			Temperature	Cooling				
	Atmosphere		550 ~ 60	00 630	6:	50 I	680 690	700	730	252	RT
Sealed vacuum capillary	Oxidant exposure	Mn compound	Mn <sup>3+</sup>						•		
		Nu <sub>2</sub> WO <sub>4</sub>	Cubic		Ortho	orhombic			Molten		
Flowing Ar	Inert	Mn compound	Mn <sup>3+</sup>				Unknown species	~	Mn <sup>2+</sup>	Mn <sup>2+</sup>	Mn³·
		Na <sub>2</sub> WO <sub>4</sub>	Cubic		(W <sup>6+</sup> )	Orthorhombic (W <sup>6-\delta</sup> , W <sup>6+</sup> )			Molten	Ineversible	W6- W6-8
Flowing OCM reactants	Slightly reductive and oxidative	Mn compound	Mn <sup>3+</sup> (Mn <sup>2+</sup> )	Unknown species					Mn <sup>2+</sup> (Mn <sup>3+</sup> )	Mn <sup>2+</sup>	Mn³-
		Na <sub>2</sub> WO <sub>4</sub>	Cubic	Orthorhombic					Molten	Cubic	W6-
In situ XRD / XPS											XPS*

- ➤ The reduction from Mn³+ to Mn²+ is favored by inert or slightly reductive gas exposure while a high temperature (> 650 °C) is always required.
- ➤ It also shows that to inhibit Mn³+ reduction to Mn²+ at the same high temperature, or to reverse the reduced Mn²+ to Mn³+, slightly oxidative exposure other than inert gas must be provided.
- > The "unidentified species" should be related with the complex catalyst components and is a transition state which can only be observed at high temperature.
- W self reduction observed after melting under inert condition.

