

# Supported Rhenium catalysts for the methanol conversion to methylal – Water as unexpected ingredient for catalytic activity

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## Introduction

The direct conversion of alcohols over heterogeneous catalyst affords a most strategic entry to valuable chemicals from biomass. The direct conversion of methanol to methylal (dimethoxymethane, DMM) requires a bifunctional catalyst retaining at least one redox couple to oxidize the methanol to formaldehyde and one acidic function to mediate the condensation reaction:  $\text{CH}_2\text{O} + 2\text{CH}_3\text{OH} \rightarrow \text{CH}_2(\text{OCH}_3)_2 + \text{H}_2\text{O}$  [1]. Rhenium oxide based materials were reported as presenting the ideal balance to orientate the selectivity towards DMM [2]. Under dehydrated conditions, the structure of supported  $\text{ReO}_x$  ( $\text{ReO}_x/\text{S}$ ) catalysts is essentially depicted as isolated  $\text{ReO}_4$  moieties regardless the nature of the support and the preparation technique [3]. Concerning the catalytic performances of  $\text{ReO}_x/\text{S}$  materials prepared using conventional methods, high discrepancies were however reported which correlated different hydration level of the surface under reacting conditions. In the present paper, we propose an original investigation of the structure-activity implications by considering water as a building block of the active site. Both realistic catalysts and model oxides were investigated using operando spectroscopies (Raman and EXAFS) and refined using DFT modeling.

## Experimental

Raman and EXAFS data reported here were recorded under *in situ* and *operando* conditions using an appropriate reaction chamber. A series of catalysts ( $\text{ReO}_x/\text{S}$ ;  $\text{S} = \bullet\text{-Al}_2\text{O}_3, \bullet\text{-Al}_2\text{O}_3, \text{TiO}_2, \text{SiO}_2, \text{SBA-15}$ ) were synthesized by different techniques: IWI, CVD, one pot sol-gel preparation with or without template agent. Both the *operando* measurements and the catalytic tests were performed at 101 kPa with a typical methanol partial pressure of 5kPa.

## Results/Discussion

The compared catalytic activities of selected catalysts are presented in Table 1. Both anatase-supported materials exhibit comparable activities, regardless the preparation technique whereas outstanding differences are observed for silica-supported catalysts. The structure of the catalysts, probed using *operando* Raman spectroscopy reflects the same trends: only tiny differences are detected by comparing the two  $\text{ReO}_x/\text{TiO}_2$  solids while the Raman spectra of ReSi-C and ReSi-SG are totally different.

Table 1. Compared activities after 1 hour on stream of selected materials containing 10%<sub>wt</sub> Re

Material	Catalyst	Preparation route	Conv. (% <sub>mol</sub> ) at 260°C	Selectivities (% <sub>mol</sub> ) at 260°C				
				DMM	DME	MF	F	CO <sub>x</sub>
$\text{ReO}_x/\text{TiO}_2$	ReTi-C	CVD	44.3	76.7	12.1	7.8	1.8	2.0
	ReTi-IWI	IWI	45.1	79.0	12.1	5.0	1.9	2.1
$\text{ReO}_x/\text{SiO}_2$	ReSi-C	CVD	8.0	50.0	0	50.0	0	0
	ReSi-SG	Sol-Gel	31.8	91.6	3.5	2.4	0.3	2.2

As shown in Figure 1, the Raman spectrum of dehydrated ReSi-SG exhibits very original modes which were assigned to a specific coordination of rhenium with water featuring an unprecedented active site [4]. A further investigation of the interaction of both realistic catalysts and model Re oxides with water was required to depict this very particular site, which will be detailed along the presentation.

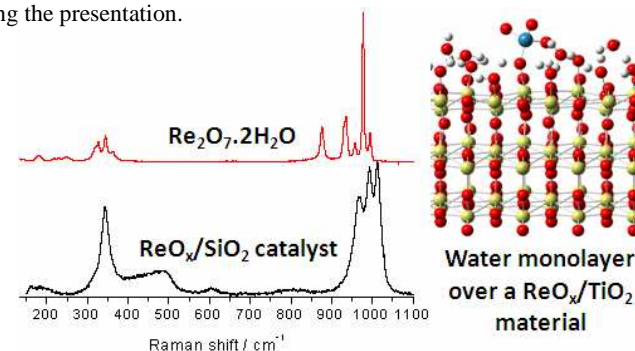


Figure 1. *in situ* Raman spectra of ReSi-SG catalyst after activation at 350°C under He (bottom),  $\text{Re}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  (top) and structure modeling of a water monolayer over ReTi-C

The ReSi-SG catalyst exhibits a very promising activity, accounting for a mild redox potential and a significant reduction of Re loss by volatilization. An original active site is proposed on the base of both theoretical and experimental data, opening the way to the design of a new class of highly selective materials. To this end, a review of practical key parameters will be presented.

## References

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