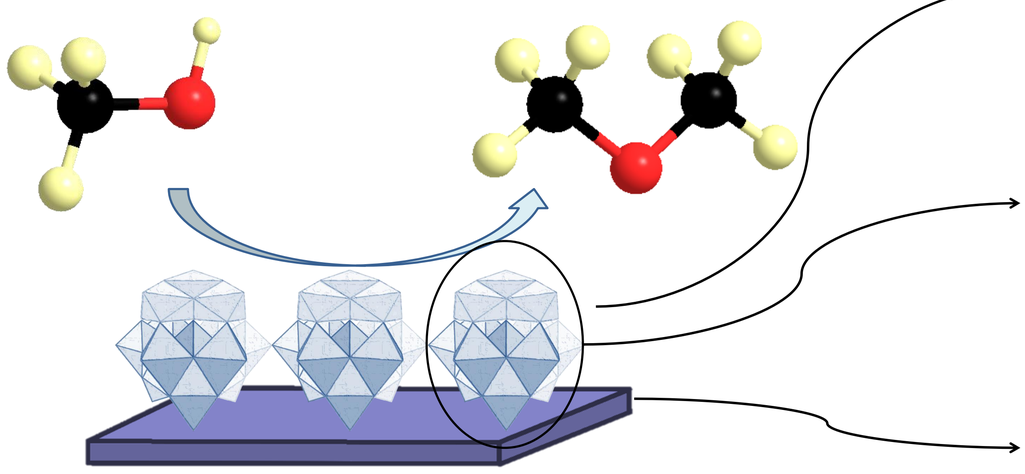
Support and **reaction conditions** effects on the catalytic activity of supported **tungstosilicic acid** for the **dimethyl ether** production

C. Peinado; D. Liuzzi; M. Retuerto; R.M. Ladera; M. A. Peña; J. L. G. Fierro; S. Rojas. Institute of Catalysis and Petrochemistry (CSIC), Marie Curie street, 2, 28049, Madrid, Spain

Introduction



Tungstosilicic acid (HSiW): heteropoly acid known to be highly active and selective for DME production via methanol dehydration at low T (180 ºC) and P (1 bar) [1].

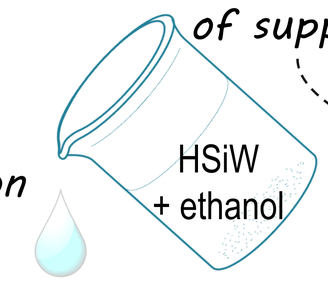
Keggin structure: most common structure of heteropoly acids, confers them strong BrØnsted acidity. Responsible for the pseudo-liquid catalysis (within the bulk) which takes part in addition to the surface catalysis process.

Support: TiO_2, SiO_2 or BN have been reported to be suitable for these catalysts and reaction [1, 2].

Experimental

Synthesis: Incipient wetness impregnation

4.5 Keggin units/m^2 of support



TiO_2 | SiO_2 | ZrO_2 | Al_2O_3 | CeO_2 | BN

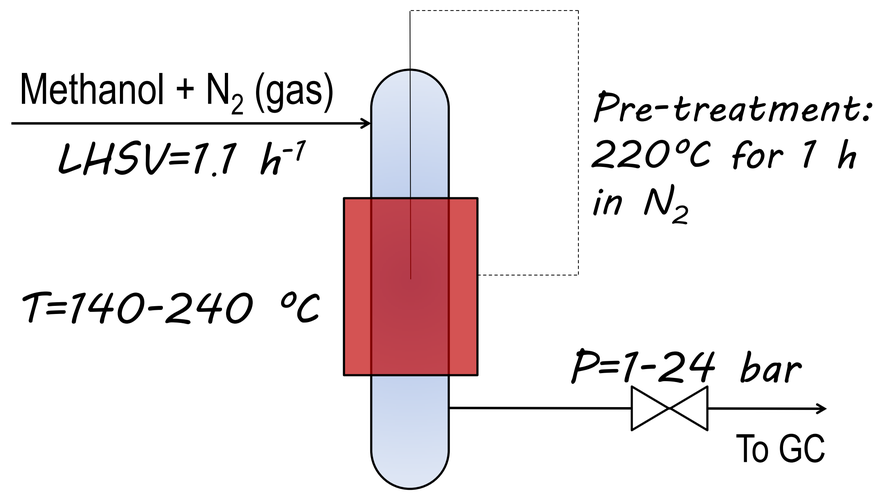
- $HSiW/TiO_2$
- $HSiW/SiO_2$
- $HSiW/ZrO_2$
- $HSiW/Al_2O_3$
- $HSiW/CeO_2$
- HSiW/BN

Different HSiW loading for each catalyst depending on the surface area of the corresponding support

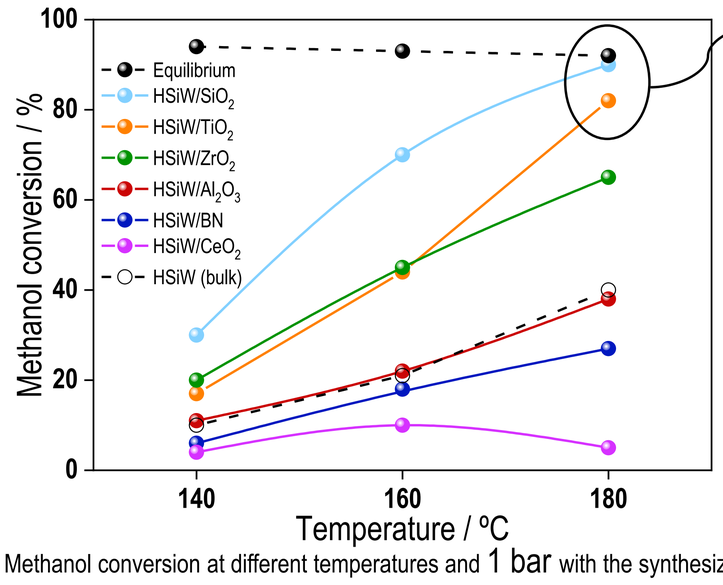
Characterization

N_2 adsorption-desorption
XRD
1H-NMR

Catalytic tests: fixed bed reactor



Results



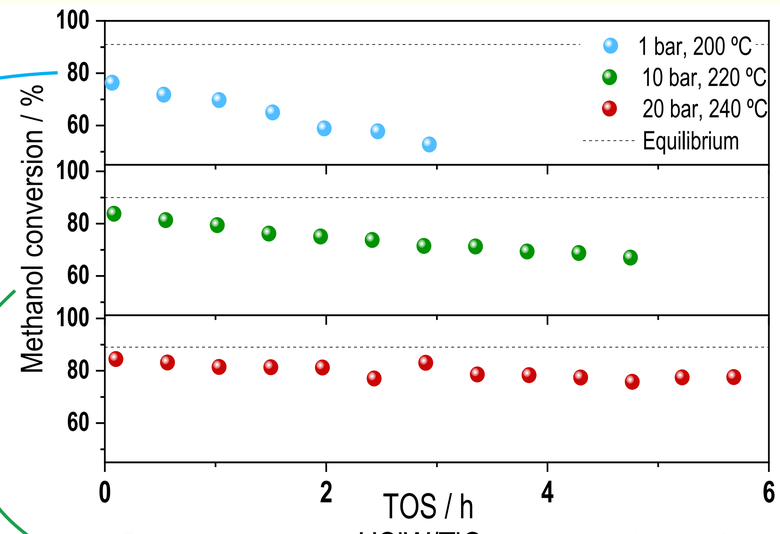
Methanol conversion at different temperatures and 1 bar with the synthesized HSiW/X

Obtained conversion close to equilibrium with the catalysts that showed weak interaction HSiW-support in ^{1}H-NMR measurements

100 % selectivity towards DME

- *Catalysts surface area higher than that of the bulk HSiW but lower than those of the corresponding supports: well dispersion of the HSiW*
- *XRD: all the catalysts except $HSiW/Al_2O_3$ presented the structure of the HSiW at temperatures up to 450 ºC*

Restore of the activity by increasing the pressure from 1 to 10 bar...



Rapid deactivation of $HSiW/TiO_2$ at the specified conditions

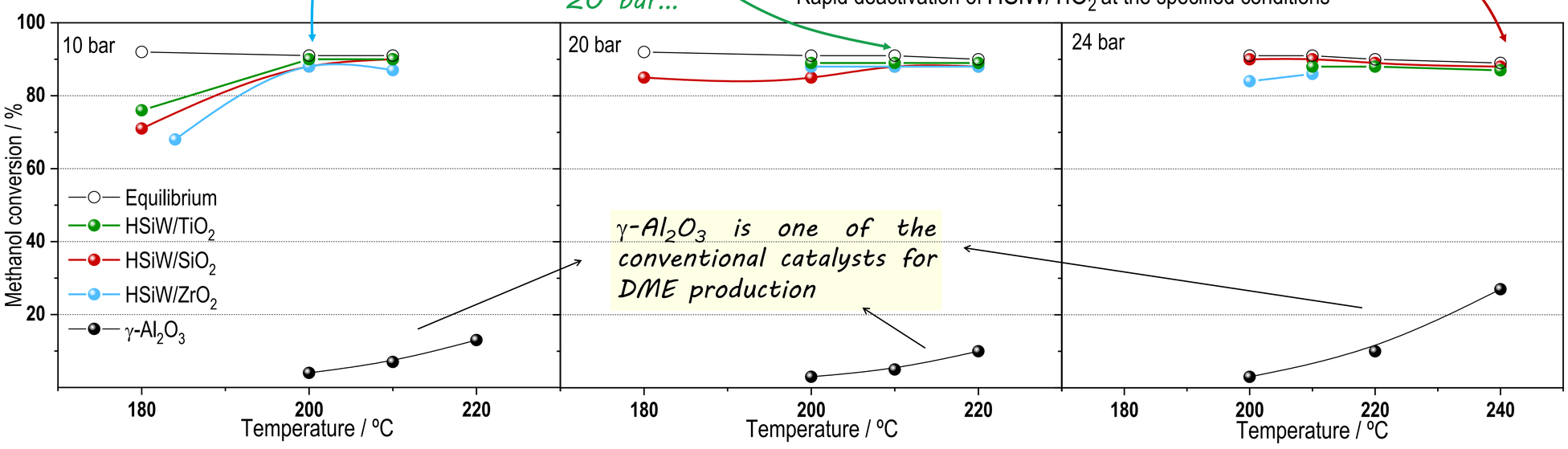
Activity decline ascribed to a loss of the pseudo-liquid catalysis contribution

...and from 20 to 24 bar.

...from 10 to 20 bar...

HSiW/X and methanol behave like a liquid-gas system:

- *Methanol absorbs into the interpolyanion space of the HSiW*
- *High temperatures decrease the solubility of the gas in the "liquid"*
- *High partial pressures of methanol increase its solubiliuty between Keggin units (Henry's law)*



γ-Al_2O_3 is one of the conventional catalysts for DME production

Stable methanol conversions (maintained at least for 6 h) for the HSiW/X catalysts and γ-Al_2O_3 at different conditions of P and T

Conclusions

- *The synthesized HSiW/X catalysts presented higher activity for the DME production than bulk HSiW and γ-Al_2O_3, especialy those supported on TiO_2, SiO_2 and ZrO_2. The nature of the support is crucial for the activity of these catalysts.*
- *Operating at high temperatures prevents the pseudo-liquid catalysis, but this effect can be avoided by increasing the operating pressure.*

Bibliography and acknowledgements

1. Ladera, R.M., et al., *TiO2-supported heteropoly acids for low-temperature synthesis of dimethyl ether from methanol.* Journal of Catalysis, 2014. **312**: p. 195-203.
2. Schnee, J., A. Eggermont, and E.M. Gaigneaux, *Boron Nitride: A Support for Highly Active Heteropolyacids in the Methanol-to-DME Reaction.* ACS Catalysis, 2017. **7**(6): p. 4011-4017.

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