



EUROPEAN COMMISSION
Innovation and Networks Executive Agency

HORIZON 2020 PROGRAMME
RESEARCH and INNOVATION ACTION
Call Identifier: H2020-LCE-2016-RES-CCS-RIA
Competitive Low-Carbon Energy

GA No. 727600



**Flexible Dimethyl ether production from biomass gasification
with sorption enhanced processes**

Starting date: 1st November 2016
Duration: 48 months

D 2.3 – Deliverable 2.3:

D2.3- Synthesis, characterization and catalytic performance of HPA and γ - Al_2O_3 catalysts for methanol dehydration

Dissemination level	PU Public CO Confidential, only for members of the consortium (including Commission Services)	PU
Written By	Sergio Rojas, Dalia Liuzzi, Miguel A. Peña (CSIC)	Date 2018-04-10
Due date	2018-04-30	Issue date 2018-05-18

Track changes

Version	DATE	Changes	CHECKED	APPROVED
V1	2018-04-10	First release	CSIC	S. Rojas
V2	2019-07-28	Acknowledgement section updated	CSIC	S. Rojas

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Contents

1	Executive summary	4
2	Introduction.....	5
3	DME synthesis from methanol	6
3.1	Synthesis of heteropolyacid based catalysts for methanol dehydration	6
3.2	Characterization of heteropolyacid based catalysts for methanol dehydration	6
3.3	Catalytic performance of acid catalysts for methanol dehydration	10
4	Conclusion	18
5	Acknowledgment.....	19

1 Executive summary

The activity for the production of dimethyl ether (DME) from methanol ($\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3$) with different acid based catalysts has been studied. Commercial catalysts γ -Al₂O₃ and HZSM5 show high activity for the production of DME in the temperature range between 240 and 310 °C.

An alternative family of acid catalysts based two commercially available heteropolyacids (HPA) based on Si or P (referred to as HSiW and HPW, respectively) supported on carriers such as TiO₂, Ce₂O₃, and BN have been prepared. HPAs display higher activity than γ -Al₂O₃ and HZSM5, at low reaction temperatures 140-180 °C, and ambient pressure.

2 Introduction

The synthesis of dimethyl ether (DME) from methanol ($\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$) is an exothermic catalytic process that takes place at pressures between 1-20 bar and 220-250 °C using acid catalysts. The state-of-the-art catalyst are γ -Al₂O₃ and H-ZSM-5, however, they have certain drawbacks such as hydrocarbon production under reaction conditions and deactivation by coke.

Heteropolyacids (HPAs) are polyoxometalates with very high acidity. They display a Keggin structure (although others are also possible) with a general formula $\text{H}_{8-n}(\text{X}\text{M}_{12}\text{O}_{40})^{n-8}$ where **X** is the central atom (P, Si...) and n the oxidation state of such atom. In addition, HPAs contain water molecules in their structure. The acidity of the HPAs, depends, among other features, on the nature of **X**. We have used two HPAs, namely tungstosilicic acid ($\text{H}_4[\text{W}_{12}\text{SiO}_{40}]$) and phosphotungstic acid ($\text{H}_3[\text{W}_{12}\text{PO}_{40}]$) referred to as HSiW and HPW, respectively.

In this report, the experimental results for synthesis, characterization, and catalytic performance of supported HPA, HZSM5 and γ -Al₂O₃ catalysts for methanol dehydration are presented. Heteropolyacids are very active for methanol dehydration reaction. However, they have very low surface area and their performance for DME synthesis might be compromised. When supported onto inorganic solids they show very high methanol conversion to DME at temperatures as low as 140 °C with 100% selectivity to DME under undesired hydrocarbon by-products. HZSM5 and γ -Al₂O₃ are used as acid benchmark catalysts to compare the methanol dehydration performance with supported HPA catalysts.

3 DME synthesis from methanol

3.1 Synthesis of heteropolyacid based catalysts for methanol dehydration

The synthesis of the supported heteropolyacid catalysts is based on the deposition of commercially available tungstosilicic acid ($H_4[W_{12}SiO_{40}]$) or phosphotungstic acid ($H_3[W_{12}PO_{40}]$), henceforward referred to as HWSi or HWP, on different inorganic carriers namely, TiO₂, BN, and CeO₂, denoted as HWSi/TiO₂, HWSi/BN, and HWSi/CeO₂, respectively. A loading of 4.5 KU/nm² was used. KU refers to Keggin Units.

3.2 Characterization of heteropolyacid based catalysts for methanol dehydration

Supported HPA catalysts have been characterized by N₂ adsorption-desorption isotherms and x-ray diffraction techniques. The BET specific surface area of the supports (TiO₂, BN, and CeO₂) and of the HSiW catalysts is shown in Figure 1. As observed, the area of the final catalyst is similar, yet slightly lower, than that of the bare support. The specific surface areas for the HSiW supported on TiO₂, BN, and CeO₂ are 40, 15, and 52 m²/g, respectively. The BET surface specific area for the TiO₂ supported HPW catalyst is 40 m²/g.

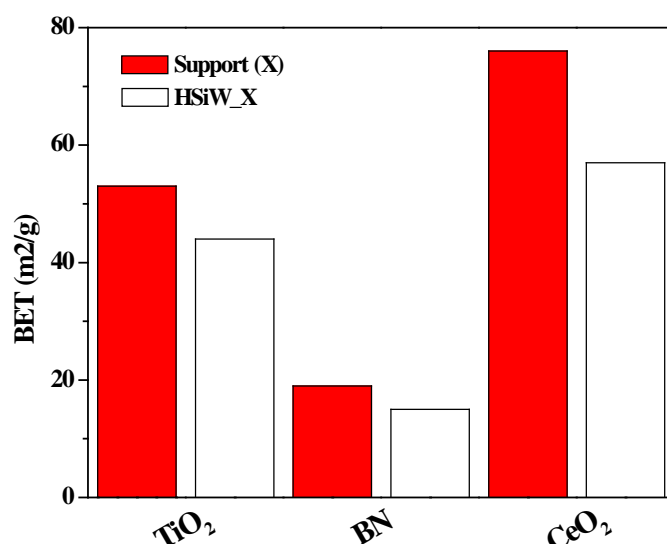


Figure 1. Specific surface area for the HSiW/X catalysts (red bars) and for the bare supports (white bars)

The thermal stability of the supported HPAs was studied by recording x-ray diffractograms at increasing temperatures in air, using an XRD equipped with an in situ chamber. The diffractograms obtained are shown in Figure 2. No changes are observed in the diffractograms of HPW/TiO₂ after treatments at 200 and 400 °C, indicating that removal of water to form anhydrous H₃PW₁₂O₄₀ is a reversible process, and the most stable phase of HPW over TiO₂ is the hexahydrated H₃PW₁₂O₄₀·6H₂O. At 500 °C, besides the diffraction lines of the hexahydrated, reflections attributed to crystalline WO₃ are observed in the diffractogram for HPW/TiO₂, indicating the coexistence phases with the Keggin structure along with WO₃ resulting from the collapse of the HPA. On the other hand, the treatment of between 25 and 400 °C does not modify significantly the diffractograms, and only reflections of highly hydrated H₄SiW₁₂O₄₀·xH₂O (x > 6) are observed. This suggests that highly hydrated HSiW is the most stable phase

in HSiW/TiO₂. The complete decomposition of the structure after thermally treating HSiW/TiO₂ catalyst at 500 °C leads to intense reflections assigned to crystalline WO₃.

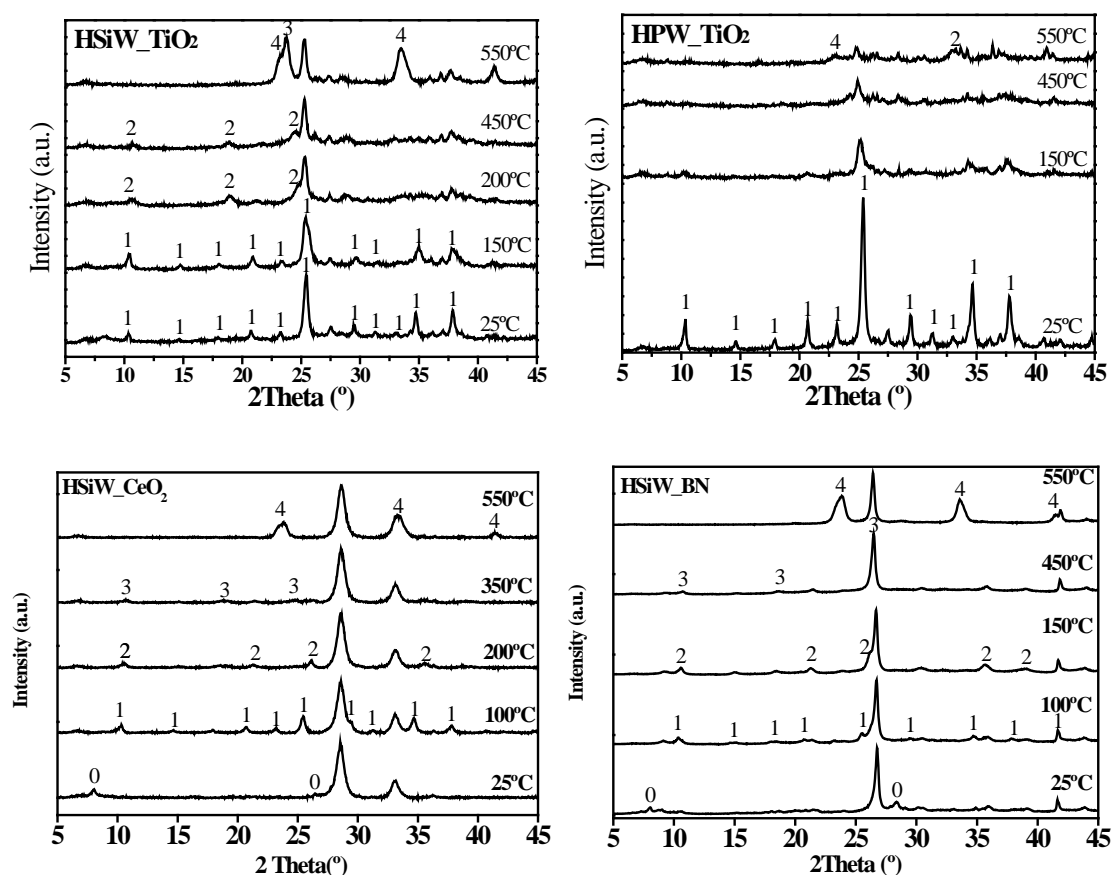


Figure 2. XRD patterns of HPW/TiO₂, HSiW/TiO₂, HSiW/CeO₂, and HSiW/BN treated at different temperatures in air. Assignment of reflections: 1: H₃PW₁₂O₄₀ · 6H₂O (or H₄SiW₁₂O₄₀ · 6H₂O); 2: H₄SiW₁₂O₄₀ · 6H₂O; 3: H₄SiW₁₂O₄₀ · H₂O (x > 6); 4: WO₃

As observed, the increasing temperature leads to a progressive dehydration of the HPAs losing water of crystallization molecules, until at ca. 500 °C the HPA structure collapses and diffraction lines ascribed to WO₃ crystalline phases are observed (marked as 4 in the diffractograms). In addition, a small fraction of totally dehydrated HPA phase is observed as a minor phase in the diffractogram.

The acidity of the catalysts was evaluated by recording temperature desorption of NH₃. The experiments were recorded in TPR/TPR2900 from Micromeritics equipped with a TCD. Around 50 mg of the sample are placed in a U-shaped quartz reactor and dried under flowing He at 220°C during 45 min. Next, NH₃ is adsorbed by flowing 60 mLmin⁻¹ of NH₃/He (5% NH₃) at 110°C during 30 min. Physisorbed NH₃ is removed under He flow at the same temperature. Once physisorbed NH₃ is removed, the temperature is increased until ca. 1000°C under a He flow of 50 mLmin⁻¹. The NH₃ desorption profile is recorded with a TCD reactor. The temperature at which NH₃ desorbs and the area under the curve give idea of the strength and number of acid sites.

The NH₃ desorption profiles for HPW/TiO₂, HSiW/TiO₂ and HSiW/CeO₂ are shown in Figure 3. All catalysts display the most intense desorption peak at ca. 480 °C the catalysts based on HSiW (the actual temperature depends on the nature of the support) and ca. 550°C for HPW/TiO₂. However, the CeO₂ based catalysts also shows a series of peaks at lower temperature and two peaks at higher temperature

of ca. 600 and 756 °C. As deduced from the XRD data above, the structure of the HPAs collapses at temperatures around 550°C and mostly WO₃ along with a minor fraction of the totally dehydrated HPAs are present. The fact that the NH₃ desorption peak appears at the same temperatures at which the HPA collapses indicates that the acidity of the HPAs is very high and that observed NH₃ desorption is due to the collapse of the catalyst's structure.

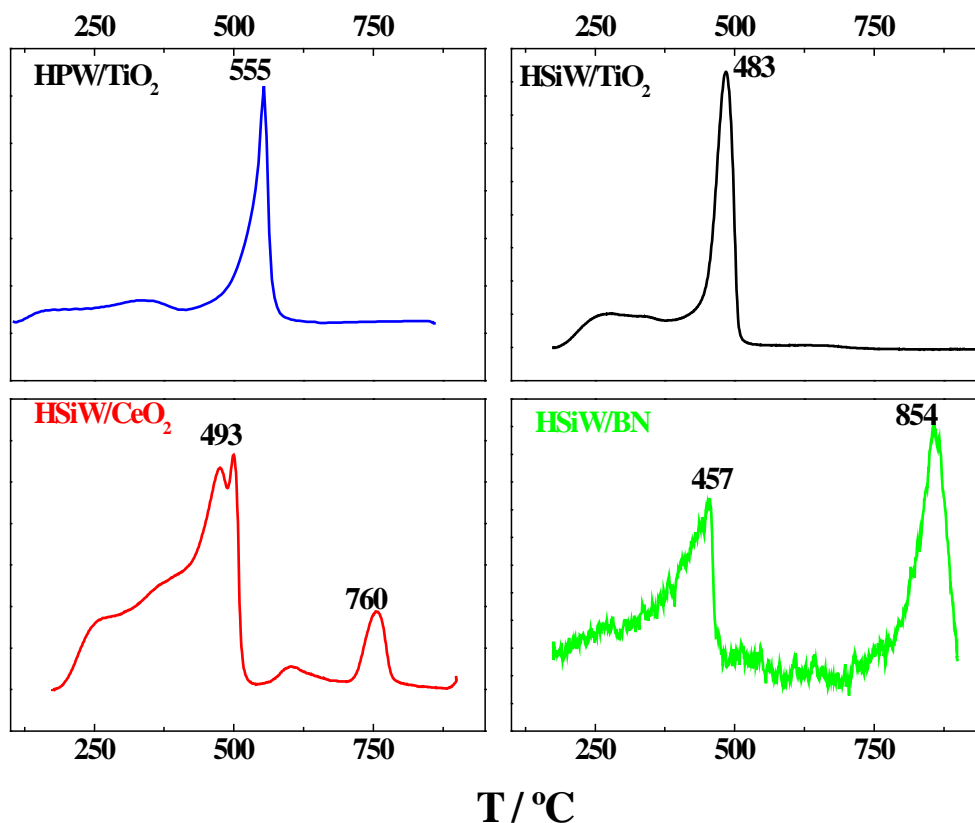


Figure 3. NH₃-TPD profiles for the HPAs under study. NH₃ desorption is characterized by a strong peak between ca. 480 and 550 °C

As stated above, the TPD profiles for the CeO₂ catalyst also show a series of NH₃ desorption peaks at higher and lower temperatures, indicative of NH₃ adsorption on acid sites on CeO₂.

The ¹H-NMR spectra of HSiW on the different supports is shown in Figure 4. The main signals appear at ca. 7.0 ppm. Signals at around this shift are usually ascribed to protons of the HPA interacting with the support.

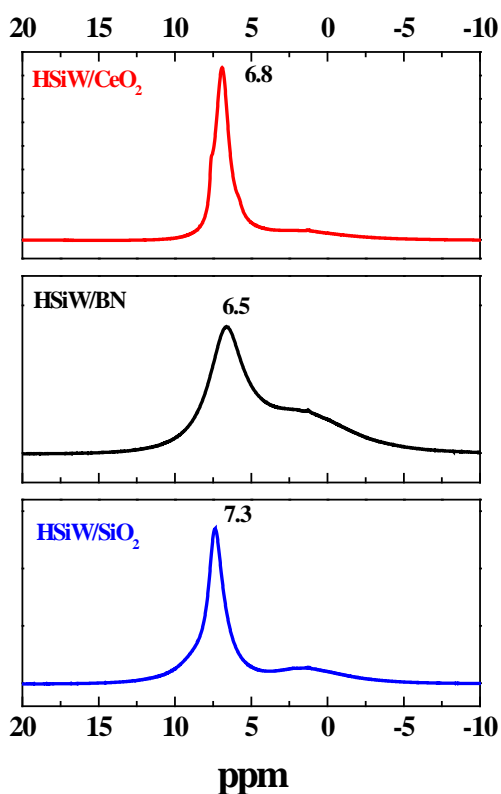


Figure 4. Solid ¹H-NMR of the HSiW-catalysts on the different supports..

The surface of the HSiW/TiO₂ and HPW/TiO₂ catalysts was studied by XPS. Figure 5 shows the W 4f core-level region of the catalysts under study. The spectra show a doublet with W 4f_{7/2} at ca. 35.7 eV in both samples. This peak is similar to that of the commercial HSiW and HPW, indicating that the structure of the HPA remains stable after incorporation on the TiO₂. The peak at 37.5 eV is due to the 3p core-level of Ti⁴⁺ ions on TiO₂.

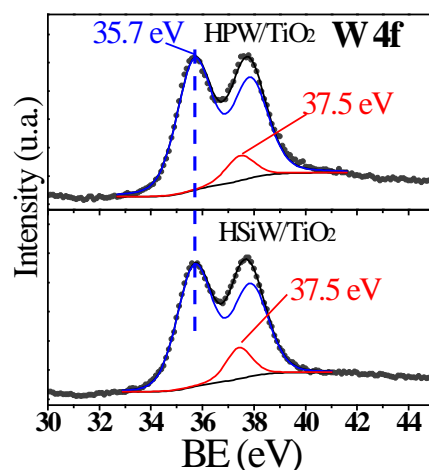


Figure 5. X-ray photoelectron spectra of W 4f and O 1s regions for HPW/TiO₂ and HSiW/TiO₂.

The hydrophobicity of the catalysts was assessed by placing a drop of H₂O on the surface of the catalyst and observing the contact angle. As deduced from the images in Figure 6, HSiW/BN is a more hydrophobic catalyst than HSiW/CeO₂ and HSiW/TiO₂. Whereas the drop of H₂O can be clearly observed at the surface of the BN catalyst can be clearly observed, H₂O absorbs rapidly (less than 2 seconds) on HSiW/CeO₂ and HSiW/TiO₂ indicating that the surface of those catalysts is highly hydrophilic.



Figure 6. From left to right pictures of H₂O drop on HSiW/BN, HSiW/CeO₂, and HSiW/TiO₂

3.3 Catalytic performance of acid catalysts for methanol dehydration

Previous to the assessment of the catalytic performance of the catalysts for the production of DME, the possibility of co-feeding methanol and H₂O in our reactor setup was extensively explored. CH₃OH/H₂O mixtures with different compositions (ranging between 90/10 to 10/90 v/v) were prepared and fed with a single Gilson HPLC pump. First, the reproducibility of the feed was analysed. GC results indicated the lack of reproducibility in the feed, regardless of the actual composition of the mixture. Then, the catalytic reactor has been modified to allow liquid CH₃OH and H₂O to be fed separately (as liquid), mixed and evaporated in the pre-reactor chamber and fed into the catalytic reactor.

The catalytic activity in methanol dehydration reaction of all catalysts was measured in a fixed bed continuous flow reactor. The catalytic bed is formed by mixing 0.2 g of catalysts with 2.0 g of SiC (0.25-0.30 mm pellet size) to avoid hot spots. The reactor is equipped with a Gilson HPLC pump to feed liquid methanol. Methanol is evaporated in the pre-heating chamber and mixed with N₂ before entering the catalytic reactor. Effects such as GHSV (LHSV), P, and T have been evaluated.

Two commercial catalysts: i) γ -Al₂O₃ (AlfaAesar) and ii) HZSM5 (ACS Material Molecular Sieve ZSM-5, SiO₂/Al₂O₃ molar ratio=38), and a series of homemade heteropolyacids (HPA) have been tested.

γ -Al₂O₃ catalyst is a bimodal 70-5000 Å, 255 m²/g and 1.60 cm³/g. H-ZSM-5 catalyst is an ACS Material Molecular Sieve ZSM-5 Catalyst with SiO₂/Al₂O₃ molar ratio equal to 38 and a BET surface area \geq 250 m²/g.

Before the catalytic tests, the catalysts were pre-treated in a N₂ flow at 220°C for 60 min. Unless otherwise stated, 100% selectivity towards DME was obtained.

3.3.1 DME production from methanol dehydration using commercial catalysts

The catalytic performance of two commercial catalysts (γ -Al₂O₃ and HZSM5) for DME production has been evaluated under different reaction conditions relevant for the project. P = 1 and 20 bar; T between 210 and 340 °C, and LHSV (mL_{CH₃OH}/mL_{cat}/h) 1.11 and 2.47 h⁻¹. Figure 7 shows the performance of the alumina at different pressures and temperatures.

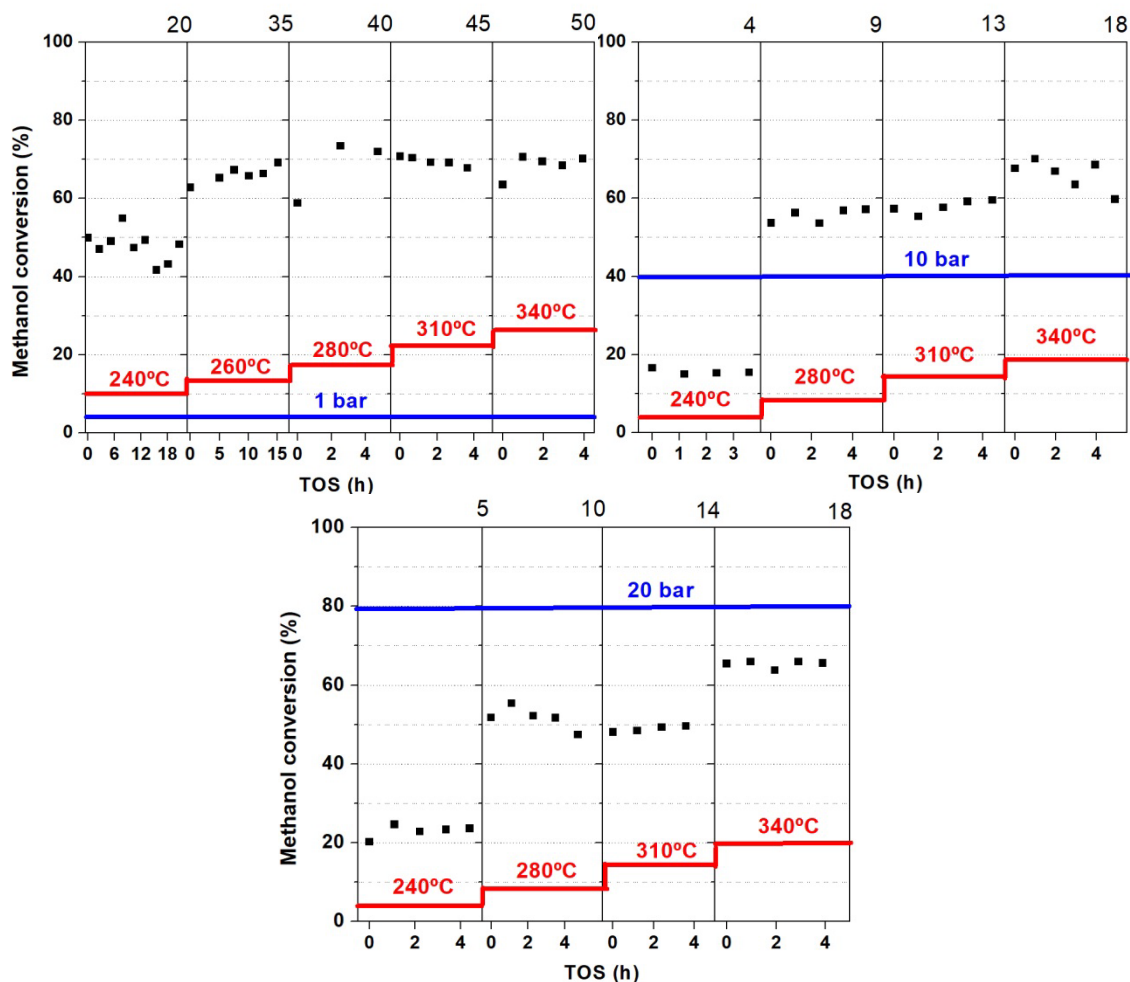


Figure 7. Methanol conversion with γ -Al₂O₃ at different temperatures and pressures measured at LHSV=1.11 h⁻¹. Catalyst pre-treated at 220°C in N₂ for 60 min. (bottom x-axes indicates time under a give reaction conditions, upper x-axes indicates cumulative time under reaction).

The effect of the contact time (or LHSV) in the methanol conversion with γ -Al₂O₃ can be observed in Figure 8. As expected, methanol conversion decreases with the increasing LHSV.

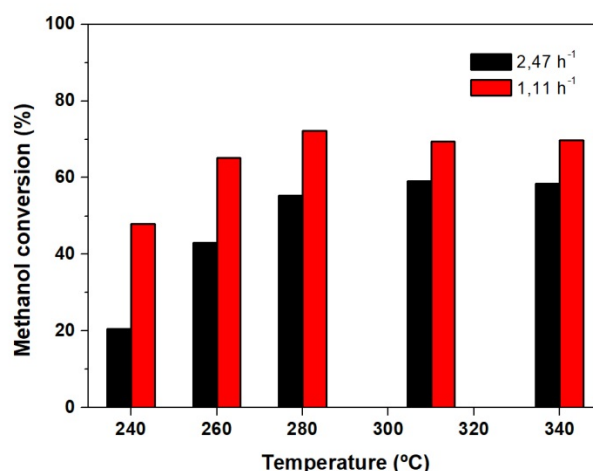


Figure 8. Effect of the LHSV for the methanol dehydration reaction. Catalyst: γ -Al₂O₃, atmospheric pressure, catalyst pre-treated at 220°C in N₂ for 60 min.

Figure 9 illustrates the effect of temperature in the methanol conversion reaction with both commercial catalysts, γ -Al₂O₃ and HZSM5, measured at 1 bar and 1.11 h⁻¹. As observed, the activity of γ -Al₂O₃ is higher than that of HZSM5 at all temperatures studied. Pressure only has a moderate effect in the methanol conversion in the γ -Al₂O₃, while the zeolite produces products other than DME when the pressure is increased. Finally, LHSV affects the performance of both catalysts.

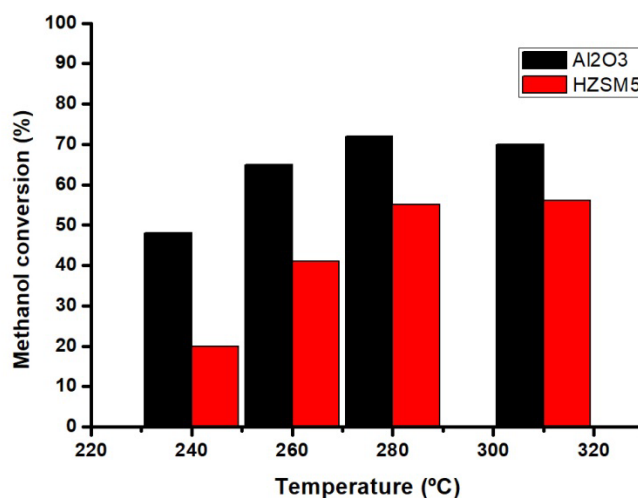


Figure 9. Methanol conversion with γ -Al₂O₃ and HZSM5 at P=1 bar, LHSV=1.11h⁻¹. Catalysts pre-treated at 220°C in N₂ for 60 min.

3.3.2 DME production from methanol dehydration using heteropolyacids

Effect of the nature of HPA

HPAs are very active for the DME production, probably due to their high acidity. Therefore, their activity can be actually measured at lower temperatures than γ -Al₂O₃ and HZSM5. Temperatures between 140 - 180 °C, pressures between 1 – 20 bar and LHSV at 1.11 and 2.47 h⁻¹ were investigated.

First, the effect of the nature of the HPA was evaluated. Two commercially available HPAs, HSiW, and HPW were selected and deposited onto TiO₂. Extensive characterization details are provided above. DME production using HSiW/TiO₂ and HPW/TiO₂ was compared under the same reaction conditions. The results obtained are shown in Figure 10.

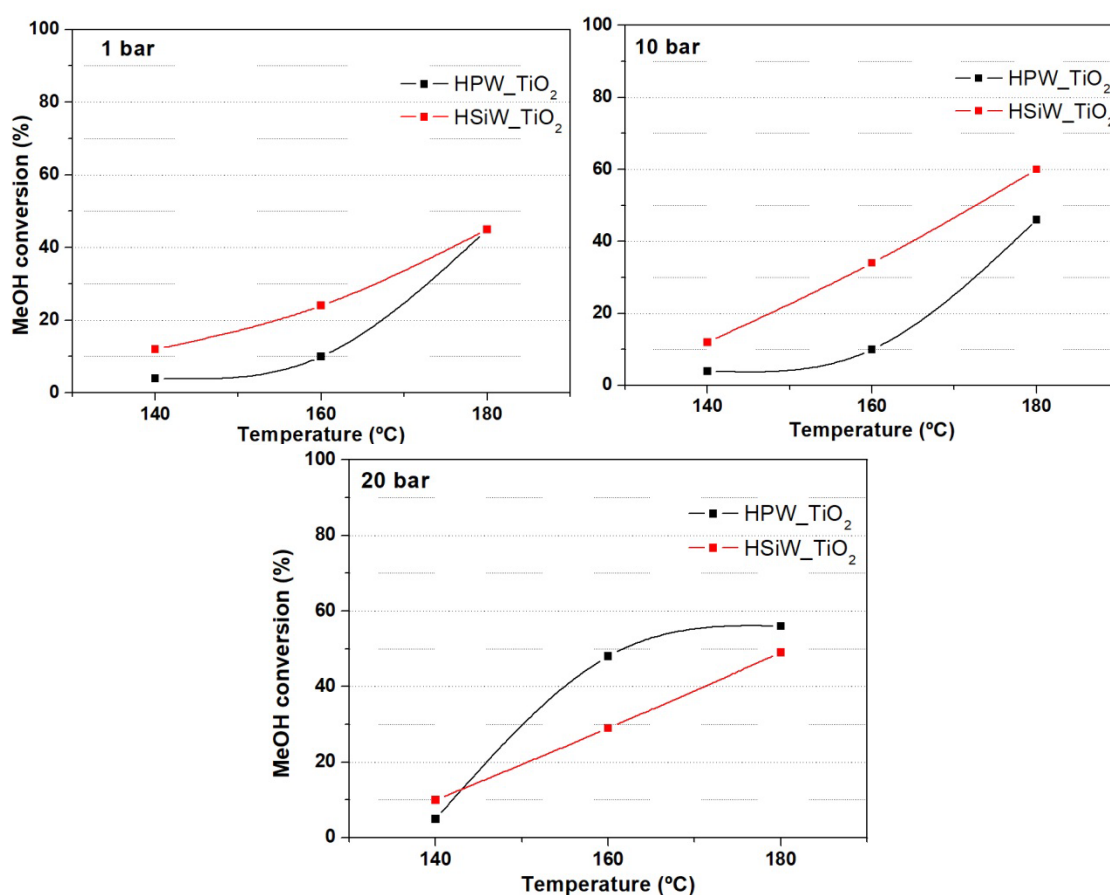


Figure 10. Methanol conversion with HPW/TiO₂ and HSiW/TiO₂ at different temperatures and pressures as indicated in the figures. LHSV 1.1 h⁻¹.

As shown in Figure 10 both HPW/TiO₂ and HSiW/TiO₂ record high activity for DME production from methanol at temperatures as low as 140°C. Nevertheless, HSiW/TiO₂ shows higher methanol conversions at every temperature than HPW/TiO₂ at pressures of 1 and 10 bar. This trend is reversed at P=20 bar; however, it should be taken into account that this effect could be due to the larger time on stream of HSiW/TiO₂.

Effect of the nature of the support.

In view of the results above, HSiW was selected as the HPA of choice for further catalytic tests. The effect of the nature of the support has been studied by comparing three different supports, namely TiO₂, CeO₂, and BN. TiO₂ was used because previous studies indicate that this support leads to the most active catalysts for DME production. CeO₂ support was used due to its higher surface area. Finally, and despite of its low specific surface area, BN was investigated as support material because of its hydrophobicity (see Figure 6).

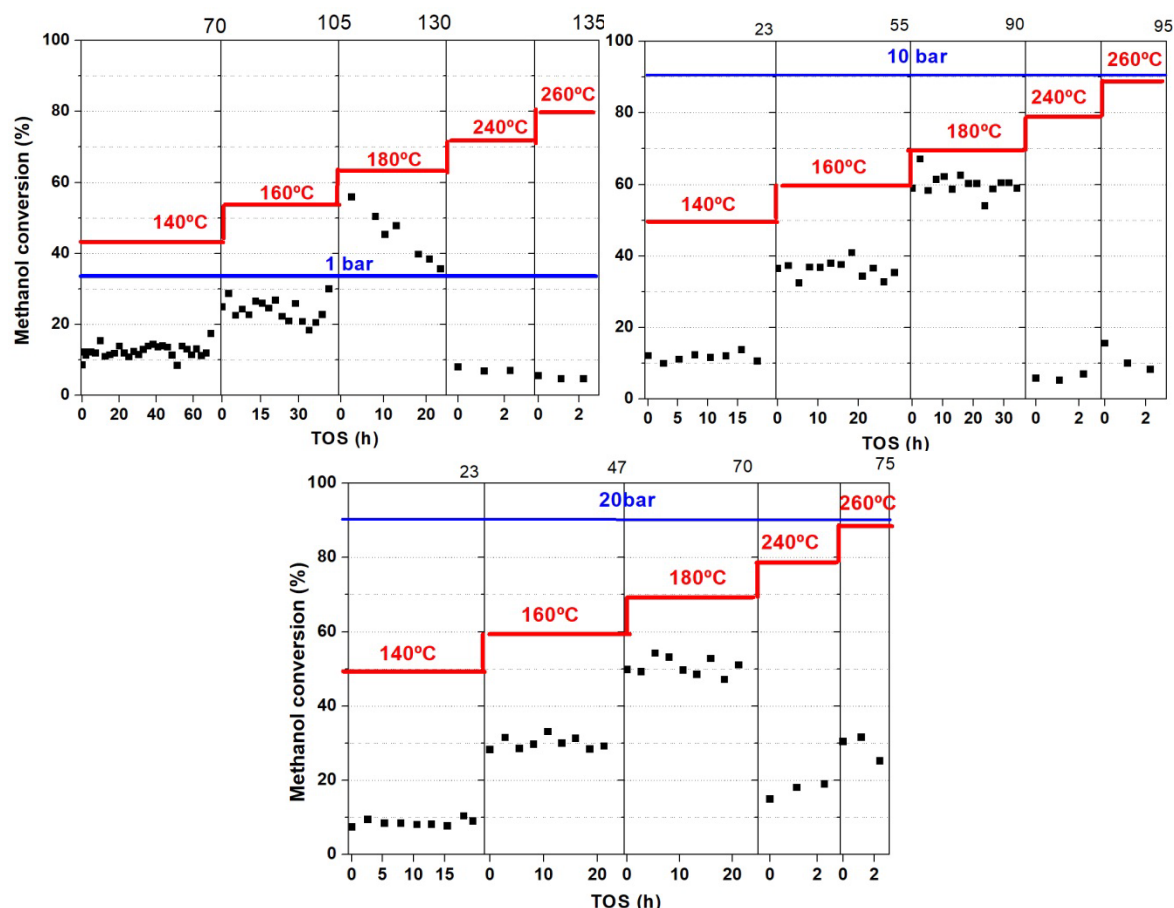


Figure 11. Methanol conversion with HSiW/TiO₂ at different temperatures and P as indicated in the Figure; LHSV 1.11h⁻¹. Lower axis indicate the time-on-stream (TOS) at a given reaction conditions whereas the upper axis indicate the cumulative time on reaction (h). Bottom x-axes indicates time under a give reaction conditions, upper x-axes indicates cumulative time under reaction)

As observed in Figure 11, HSiW/TiO₂ is very active for the DME production from methanol. The activity increases (moderately) with pressure. On the other hand, methanol conversion increases with temperature between 140 and 180 °C. However, methanol conversion drops at 240 °C remaining unaffected at higher temperatures. Nevertheless, it can be also observed that methanol conversion at higher temperature can be increased by increasing temperature. For instance, methanol conversion at 240°C of ca. 10% is observed at 1 bar, but increases to ca 20 % at 20 bar. Although at this point we do not have a definitive explanation for this observation, we hypothesize that the loss of the crystallization water of the HPAs could be responsible for this behaviour. It is known that crystallization H₂O plays a key role in the catalytic properties of HPAs (pseudo-homogeneous catalytic pathway). At high temperatures crystallization H₂O is lost thus decreasing the catalytic activity. However, increasing reaction pressure prevents H₂O vaporization thus resulting in a moderate increase of methanol conversion.

Finally, methanol conversion is significantly affected by the LHSV, decreasing from $\text{LHSV} = 1.11$ to 2.47 h^{-1} , as observed in Figure 12. The effect of LHSV, i.e., methanol conversion decreases with the higher LHSV, is observed at all pressures under study, 1, 10 and 20 bar.

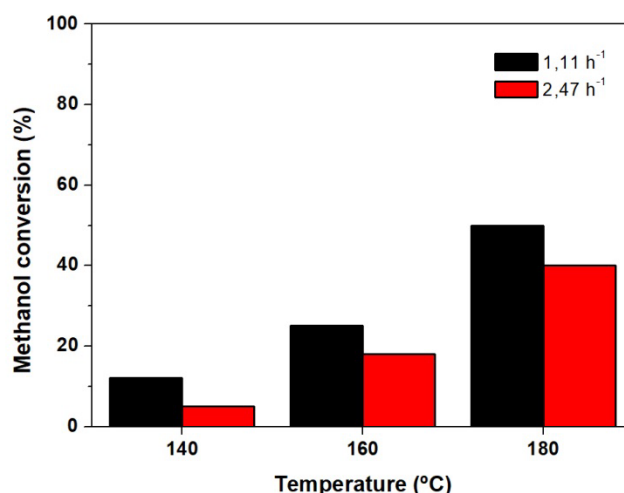


Figure 12. Influence of LHSV for the methanol conversion with HSiW/TiO₂ at 1 bar. Catalyst pre-treated at 220°C in N₂ for 60 min.

The activity performance of HWSi/BN and HWSi/Ce₂O₃ has been also evaluated under similar conditions; T between 140 - 180 °C, P= 1 and 20 bar and $\text{LHSV} = 1.11$ and 2.47 h^{-1} . Figure 13 shows the methanol conversion over HWSi/BN. As observed, the methanol conversion is lower than that observed for HWSi/TiO₂. This is probably due to the lower loading of HPA in the BN catalyst. Note that all catalysts have been prepared with an HPA loading of 4.5 KU/nm^2 . Since the specific surface area of BN is lower than that of TiO₂, the actual loading of HPA in BN is the lowest in the series.

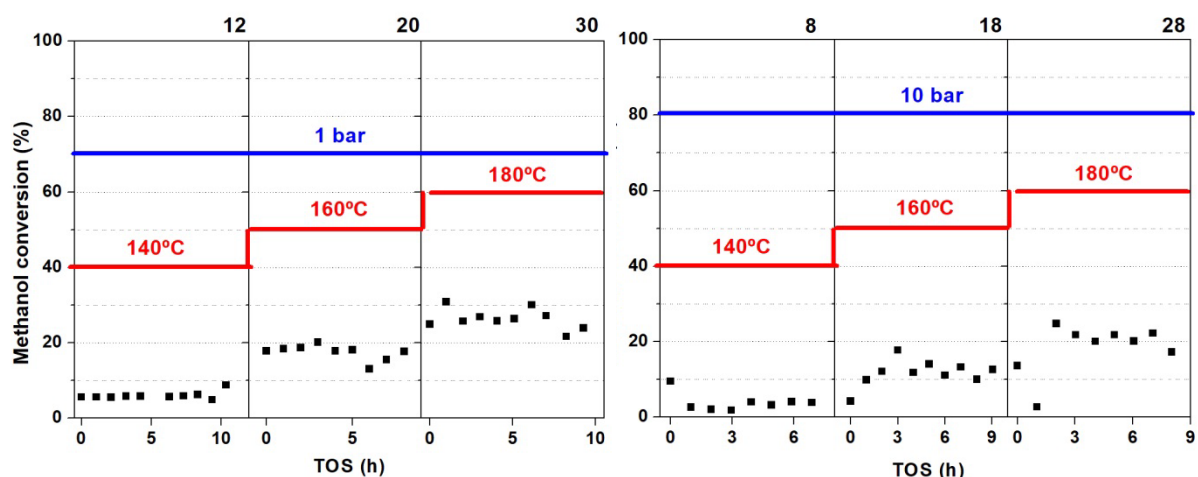


Figure 13. Methanol conversion with HSiW/BN at different temperatures and P as indicated in the Figure; $\text{LHSV} = 1.11 \text{ h}^{-1}$. Lower axis indicate the time-on-stream (TOS) at a given reaction conditions whereas the upper axis indicate the cumulative time on reaction (h). Catalyst pre-treated at 220°C in N₂ for 60 min.

Methanol dehydration performance with CeO₂ supported HPA catalysts resulted in very low methanol conversion (<10 %) at the same reaction conditions under which the other HPA catalysts were studied.

For a further comprehension of the performance of the HSiW on the different supports, Figure 14 compares the methanol conversions obtained with the three catalysts investigated. Irrespectively of the reaction conditions, TiO_2 supported HSiW shows a better performance for the methanol dehydration reaction.

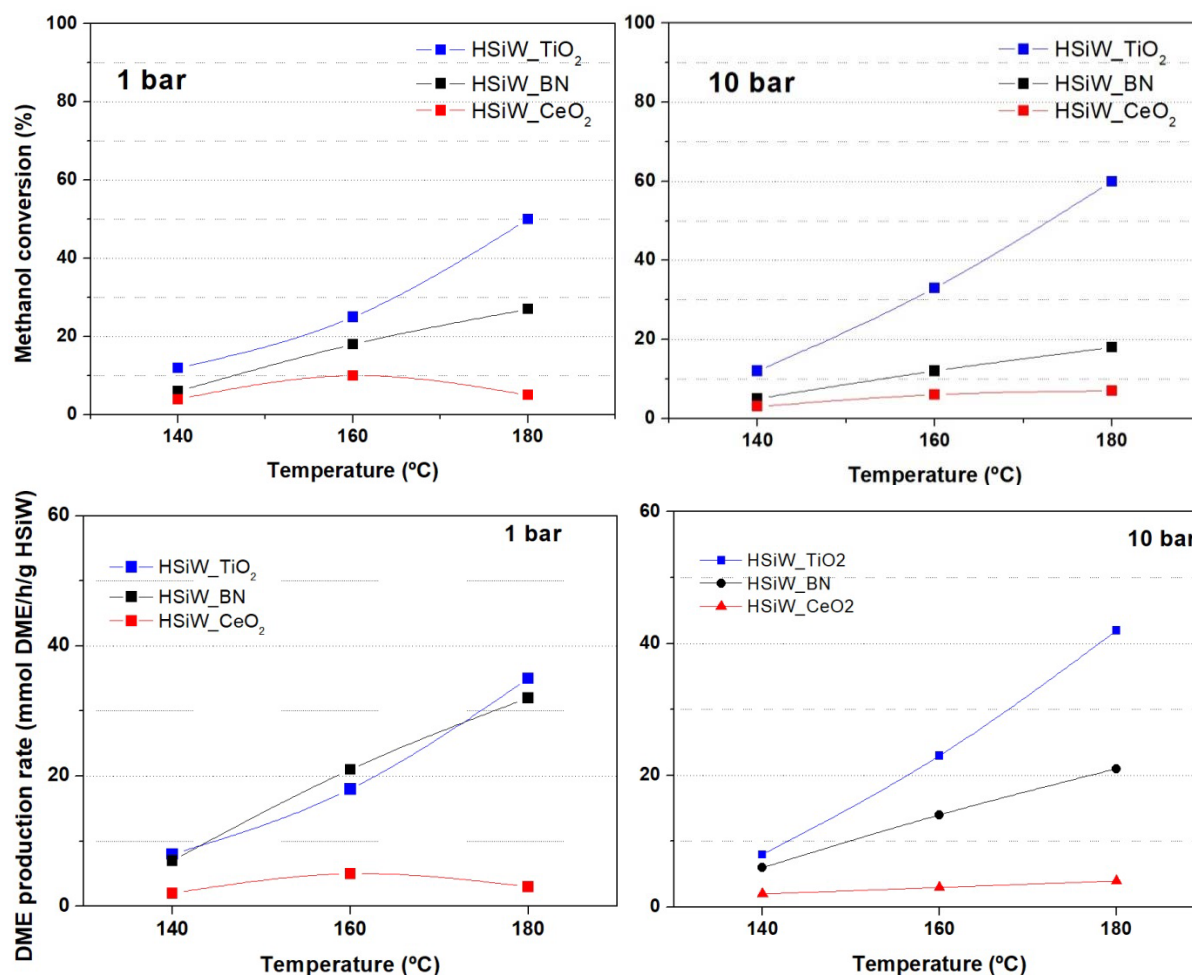


Figure 14. HSiW over TiO_2 , BN, and CeO_2 catalytic activity at T and P as indicated in the figure. LHSV 1.11 h^{-1} . Catalysts pre-treated at 220°C in N_2 for 60 min. DME production normalized to the actual content of HPA (in grams) is shown in the lower panel.

As observed in Figure 14, DME production normalized to the actual loading of HSiW on each catalyst follows a similar trend and HSiW/ TiO_2 is the best catalyst in the series. However, it should be indicated that DME production normalized to the HSiW loading of HSiW/BN matches that of HSiW/ TiO_2 at 1 bar, although is still lower at 10 bar.

These catalysts did not show an improvement in the activity when studied at 20 bar at the temperatures indicated in the Figure 14. Thus, at 20 bar and 140°C, methanol conversion was ca. 3, 1, and 9% for BN, CeO_2 , and TiO_2 supported HSiW, respectively.

3.3.3 Comparison between commercial catalysts and HPA for DME production

For the sake of comparison, Figure 15 compares the catalytic activity of the commercial catalysts (when relevant in the corresponding conditions) with that of the HPA catalyst that showed the best catalytic performance, *i.e.*, HSiW/TiO₂.

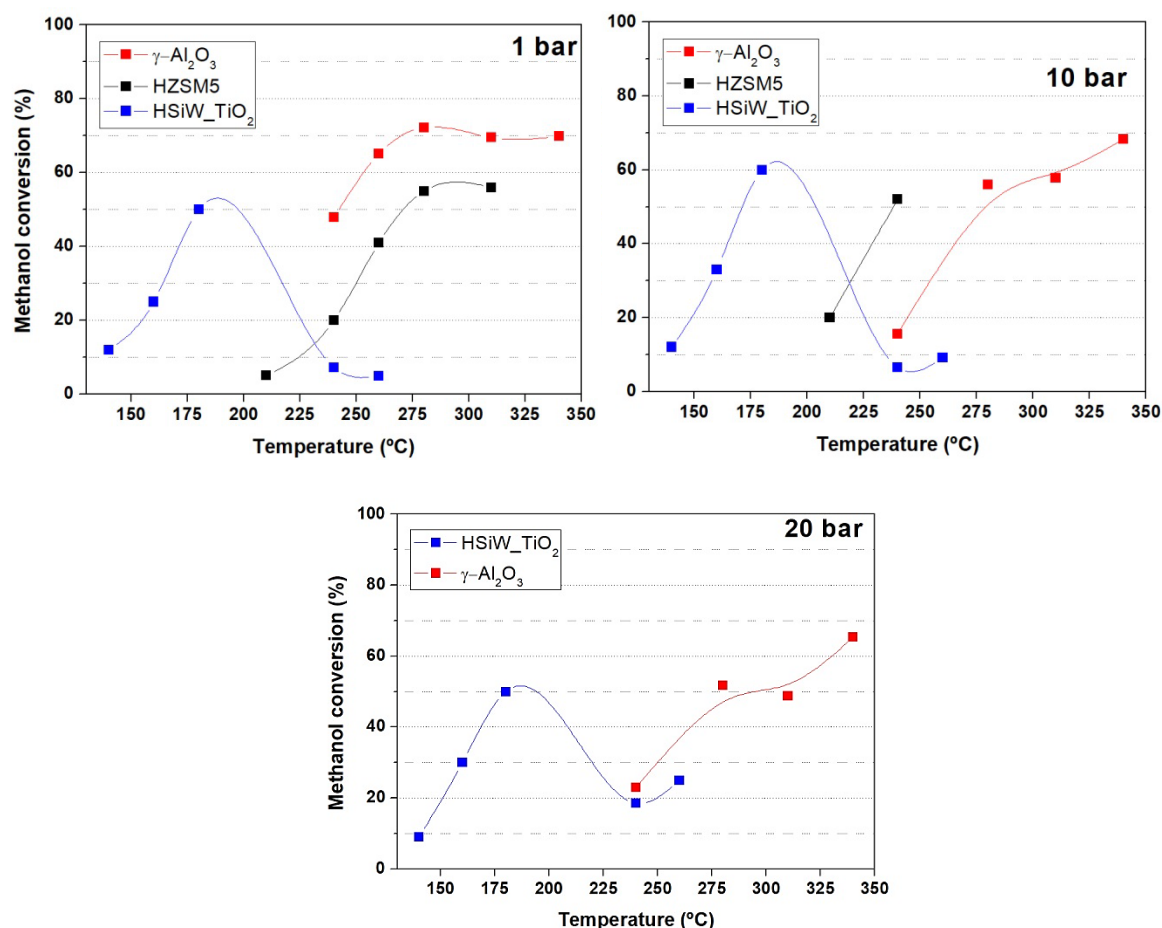


Figure 15. Comparison of the studied catalysts for the methanol dehydration reaction at different conditions as shown in the Figure. LHSV=1.11 h⁻¹. Catalysts pre-treated at 220°C in N₂ for 60 min.

As deduced from results above and as clearly summarized in Figure 15 the optimum reaction temperature for DME production is different for the HPA than for the commercial catalysts. Thus, HPA catalysts are very active towards methanol dehydration at low temperatures yielding their maximum productivity at ca 180°C. However, a significant decrease of methanol conversion is observed at higher temperatures, above 200°C. Note that this trend applies to all HPA based catalysts studied in this deliverable, although the actual methanol conversion are characteristic of each individual HPA-based catalysts. On the other hand, the commercially available catalyst, namely γ -Al₂O₃ and HZSM5, are active at higher temperatures, showing the highest conversions at T ≥ 275 °C. DME is the only product detected with the HPA-based catalysts and with γ -Al₂O₃. However, olefins are also detected during methanol conversion with HZSM5. The effect of LHSV is similar for all catalyst. As for the pressure, HPA-based catalysts seem to be only moderately affected by pressure at low temperatures, but a positive effect in methanol conversion at T > 200 °C with the increasing pressure is observed.

4 Conclusion

We have studied (synthesized, characterized and tested) heteropolyacids (HSiW and HPW) supported on TiO₂, CeO₂, and BN. In addition, we have measured the methanol dehydration activity of two commercial catalysts, namely γ -Al₂O₃ and HZSM5. All catalysts studied show activity for DME production from methanol. The HPA based catalysts are very active for DME production at low temperatures, below ca. 200°C, but their activity drops at higher temperatures. A partial recovery of their activity at high temperatures is observed at increasing pressures. Among the commercial catalysts, γ -Al₂O₃ shows the best results, displaying high activity between 260 and 350 °C.

5 Acknowledgment

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727600

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