

Supported PdZn-ZnO/TiO₂ catalysts for CO₂ hydrogenation to methanol: effect of the preparation method on the PdZn formation, dispersion and activity

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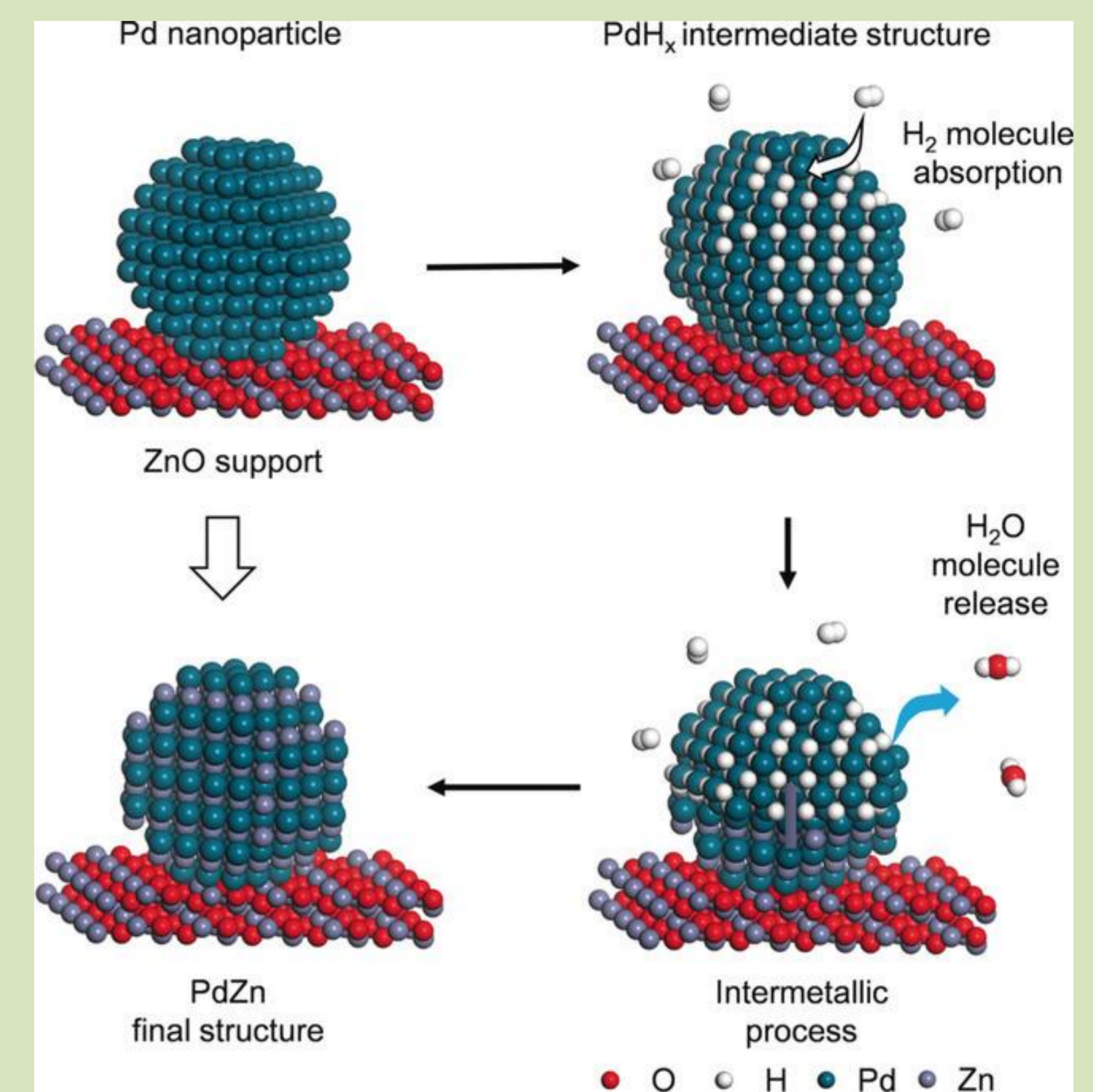


Introduction

One of the strategies to reduce CO₂ emissions is its transformation into molecules of industrial interest. Methanol synthesis by CO₂ hydrogenation is a very interesting way to fix and to valorize the CO₂ molecule. Methanol is conventionally produced from syngas using Cu/ZnO/Al₂O₃ catalyst, however, its efficiency is significantly reduced when it is applied to methanol synthesis from pure CO₂. For this reason, work is being done to find alternatives to improve the efficiency of conventional Cu/ZnO catalysts. The most efficient and studied alternative catalysts are those based on noble metals and, more specifically, those based on Pd. Pd based catalysts are very active and robust in the CO₂ hydrogenation reactions and their selectivity to methanol depends, to a large extent, on the promoters and supports used. Pd supported on ZnO is able to form a PdZn intermetallic compounds when reduced at temperatures above 250 °C. PdZn intermetallic compound in close contact with ZnO is very active and selective for the synthesis of methanol from CO₂. The formation of PdZn and its contact with ZnO (active sites for the selective hydrogenation of CO₂ to methanol) will depend on the preparation and reduction conditions applied in the preparation of catalysts.

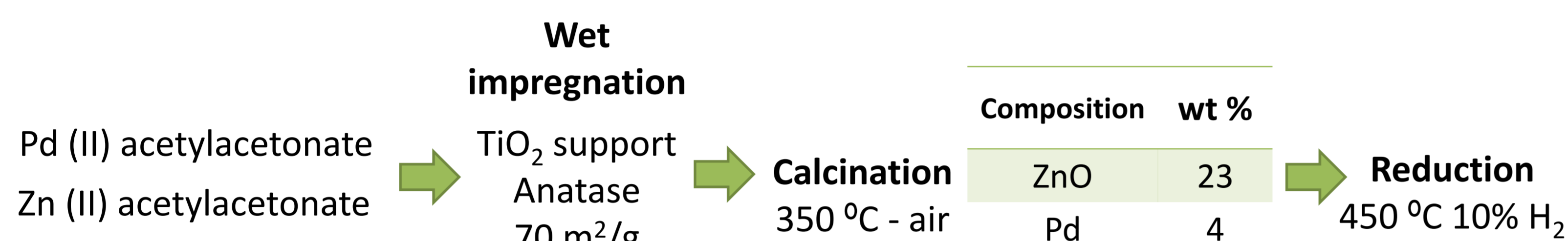
Objective

The aim of this work is to study the formation of PdZn intermetallic catalysts supported on TiO₂. Specifically, the study of the order of impregnation of Pd and Zn precursors on TiO₂ and their effect on the dispersion, crystallinity and contacts between PdZn and ZnO particles has been addressed.



Experimental

Catalyst preparation

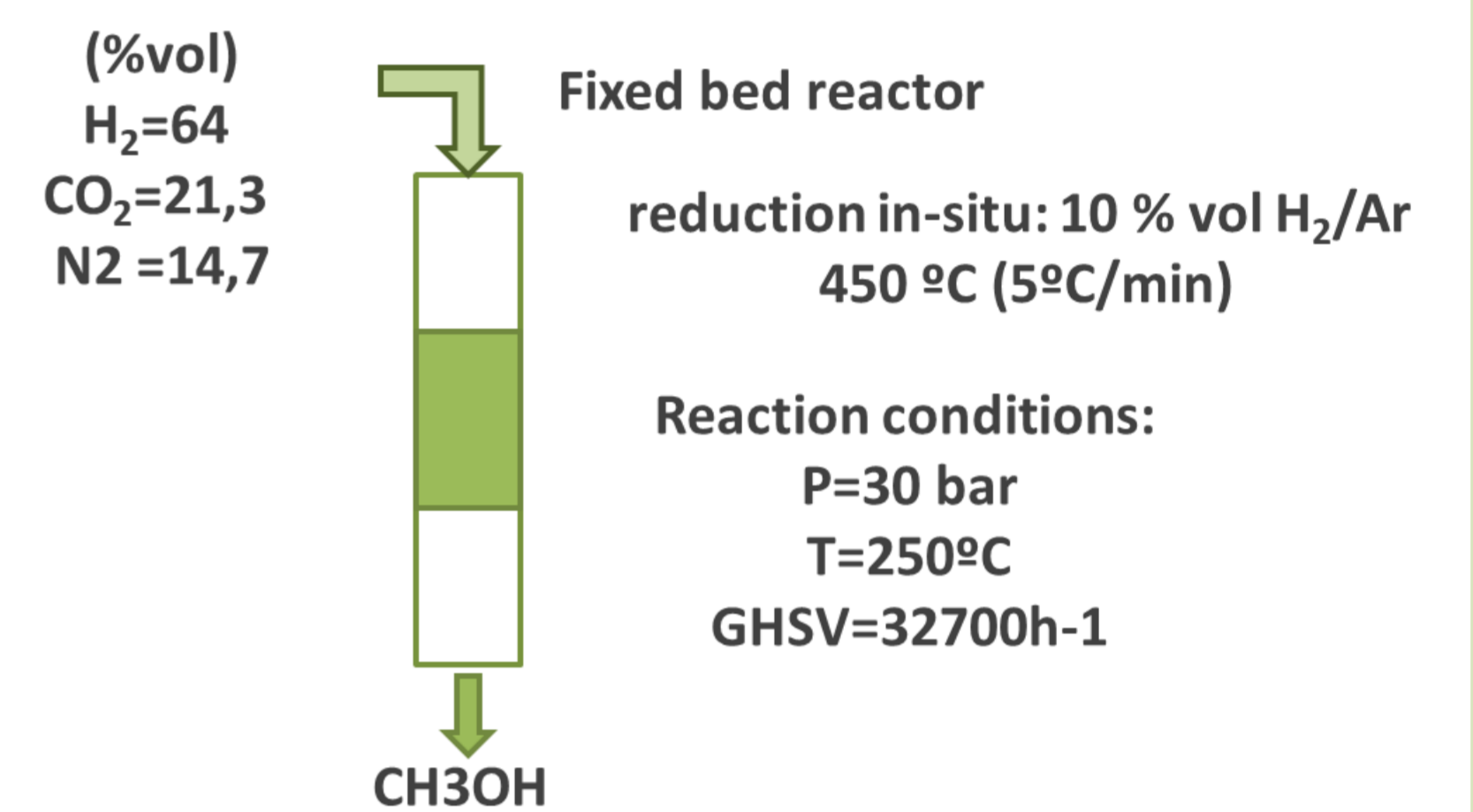


1 st impregnation	Calcinat. (350 °C)	2 nd impregnation	Calcinat. (350 °C)	Reduction (450 °C)	Sample
Pd(acac) ₂	✓	Zn(acac) ₂	✓	✓	(Zn)Pd/TiO ₂
Zn(acac) ₂	✓	Pd(acac) ₂	✓	✓	(Pd)Zn/TiO ₂
Zn(acac) ₂	✗	Pd(acac) ₂	✓	✓	(Zn-Pd)/TiO ₂
Zn(acac) ₂ + Pd(acac) ₂	✓	✗	✗	✓	(Zn+Pd)/TiO ₂

Characterization

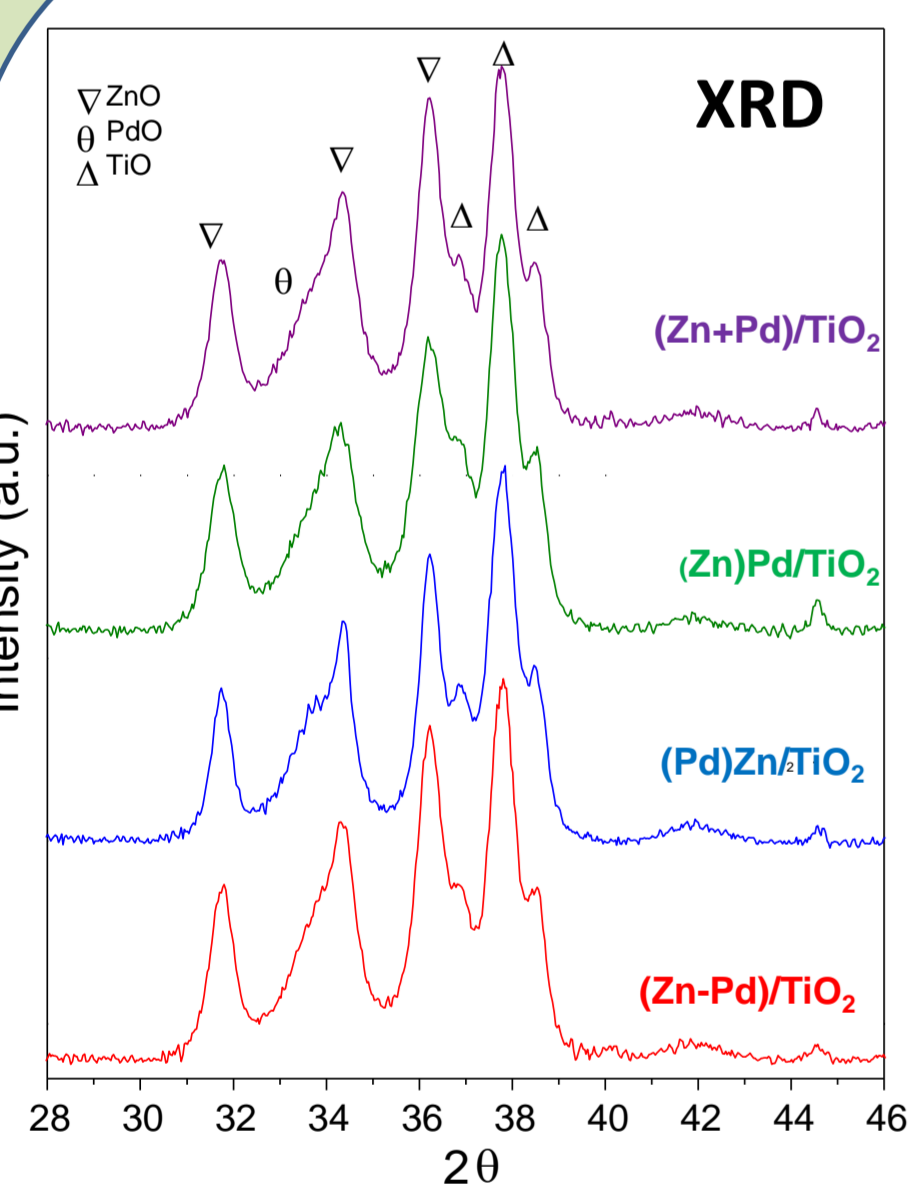
- XRD
- H₂-TPR
- N₂-Isoterm
- ICP

Methanol synthesis tests

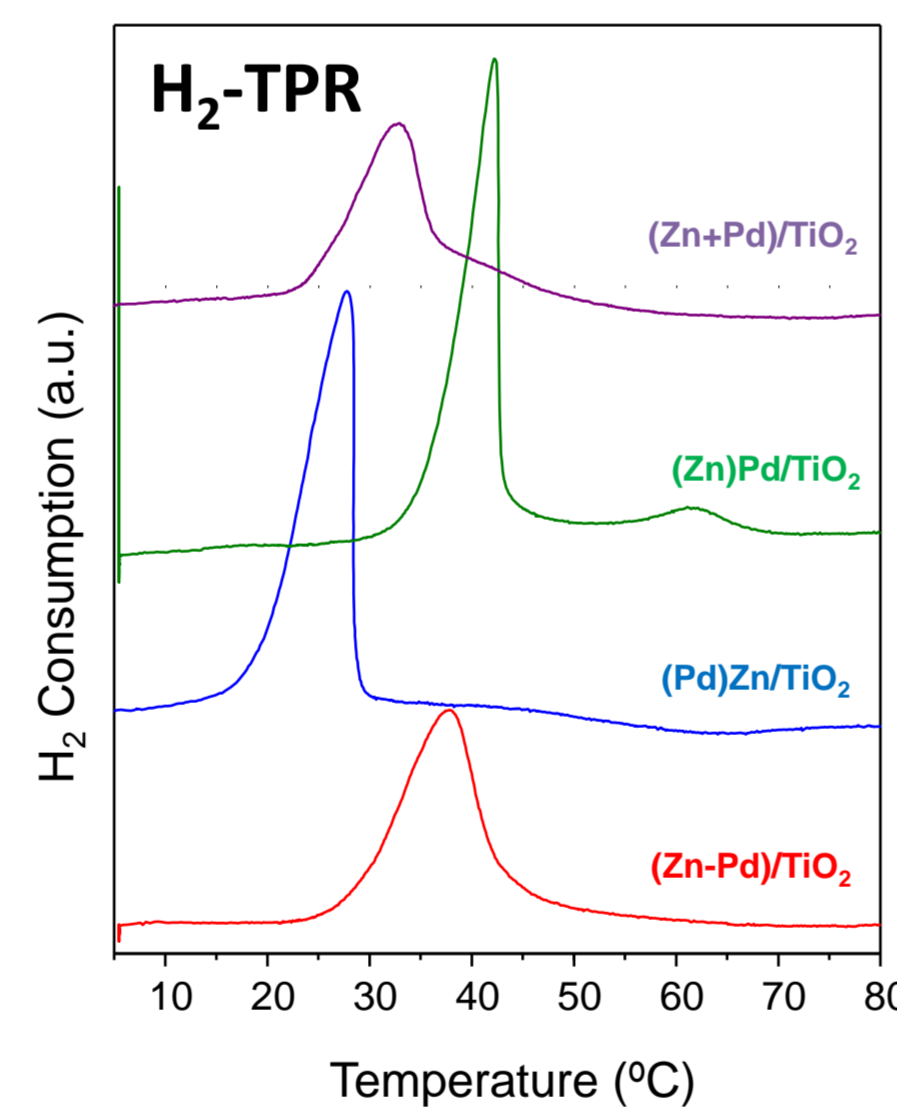


Results and Discussion

Calcined catalysts

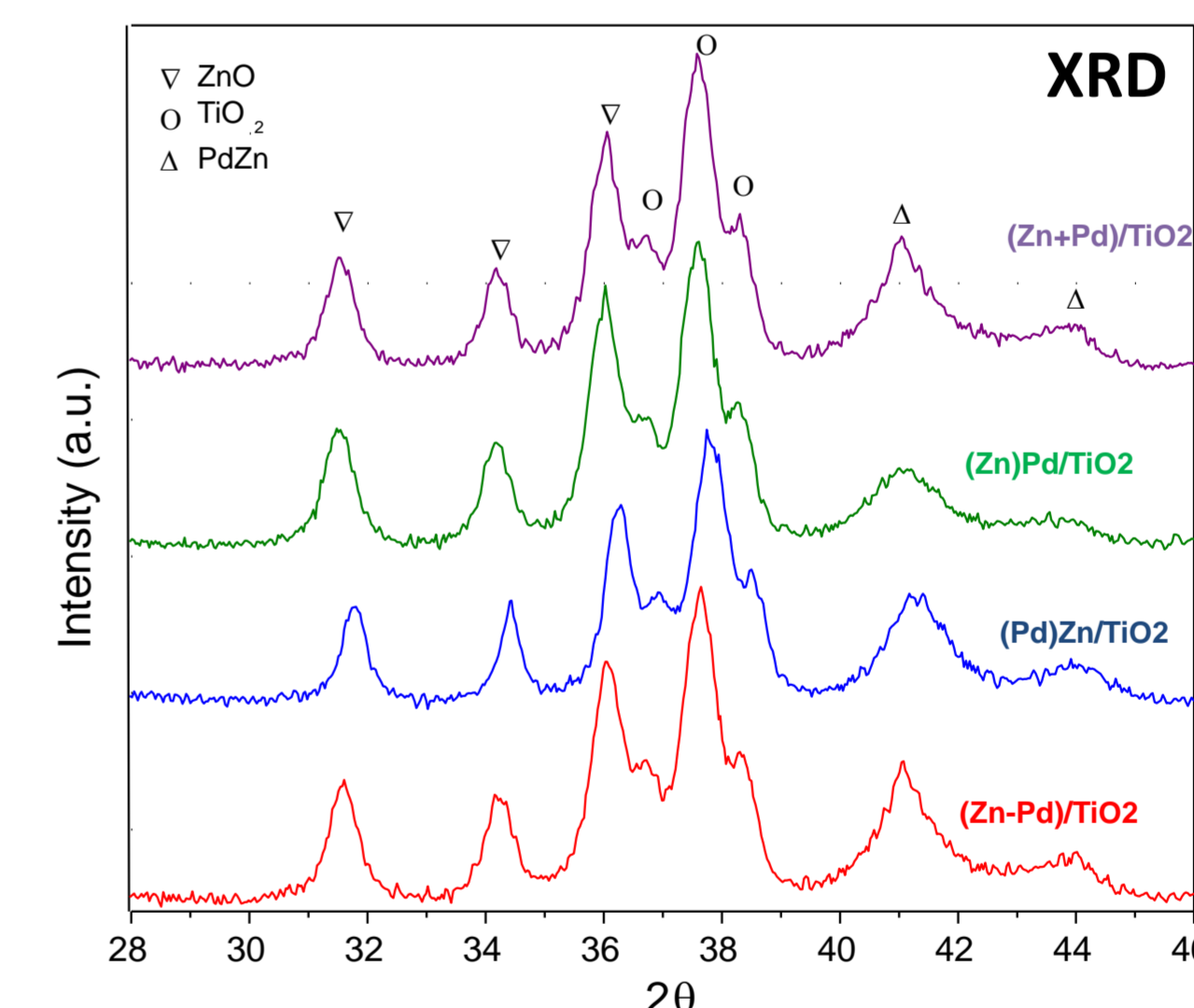


Sample	ZnO size (nm)	PdO size (nm)
(Zn+Pd)/TiO ₂	14,9	6,9
(Zn)Pd/TiO ₂	14,1	7,9
(Pd)Zn/TiO ₂	18,4	8,0
(Zn-Pd)/TiO ₂	15,4	7,8



Sample	PdO reduction T. (°C)	H ₂ Consumption (a.u.)
(Zn+Pd)/TiO ₂	33,2	131
(Zn)Pd/TiO ₂	42,2	172
(Pd)Zn/TiO ₂	28,2	185
(Zn-Pd)/TiO ₂	37,8	140

Reduced catalysts



Sample	ZnO size (nm)	PdZn size (nm)
(Zn+Pd)/TiO ₂	16,6	8,1
(Zn)Pd/TiO ₂	14,8	6,5
(Pd)Zn/TiO ₂	15,2	7,3
(Zn-Pd)/TiO ₂	15,8	8,0

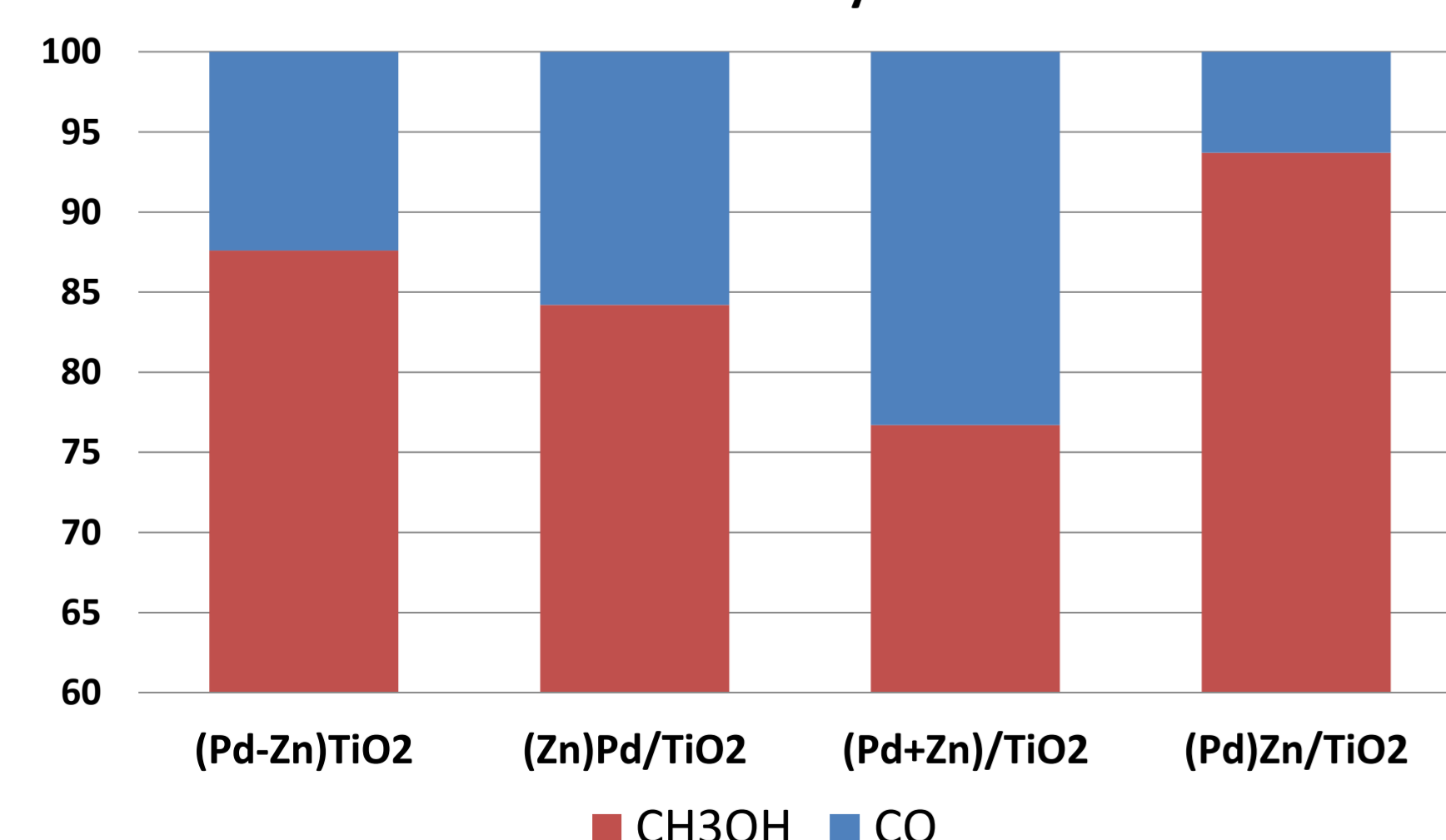
- ZnO and PdO of small crystallite domains are identified in all calcined catalysts
- No significant differences in the crystallinity or size of the PdO and ZnO between samples

- Differences in reducibility of PdO: (Pd)Zn > (Zn+Pd) > (Zn-Pd) ≈ (Zn)Pd
- Different H₂ consumption: (Pd)Zn > (Zn)Pd > (Zn-Pd) ≈ (Zn+Pd) → different interaction and contact of PdO with TiO₂ and/or ZnO

- Formation of PdZn in all samples after reduction → crystallite size of PdZn increases in the order: (Zn)Pd/TiO₂ < (Pd)Zn/TiO₂ < (Zn-Pd)/TiO₂ ≈ (Zn+Pd)/TiO₂
- PdZn/ZnO intensity ratio decreases in the order: (Pd+Zn)/TiO₂ ≈ (Pd-Zn)/TiO₂ > (Pd)Zn/TiO₂ > (Zn)Pd/TiO₂

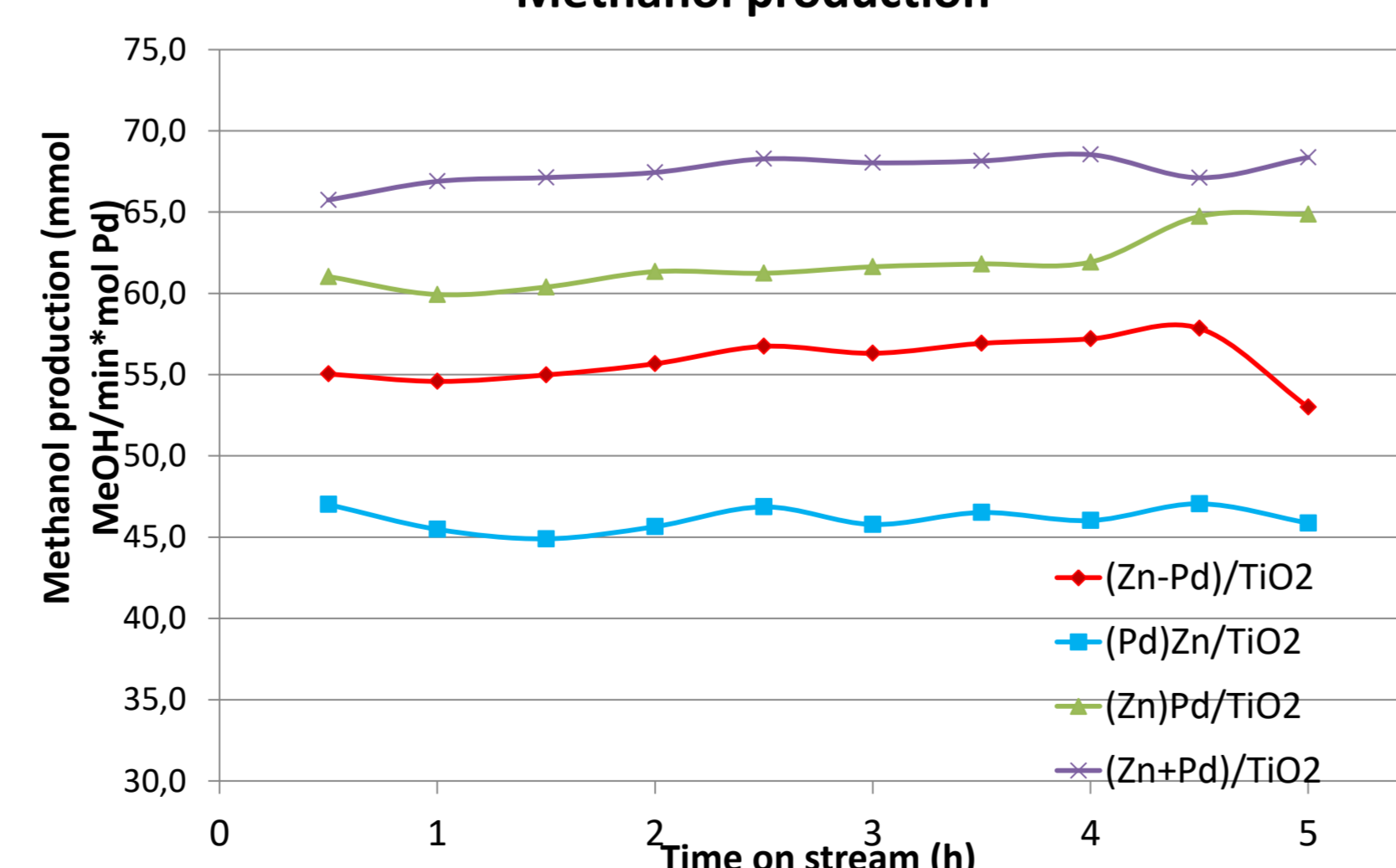
Methanol activity tests

Selectivity



- CH₃OH selectivity decrease according the sequence: (Pd)Zn/TiO₂ > (Zn-Pd)/TiO₂ > (Zn)Pd/TiO₂ > (Zn+Pd)/TiO₂
 - Methanol synthesis sites → more extensive formation of the PdZn-ZnO-interfaces
 - RWGS sites → isolated Pd⁰ or PdZn sites
- Methanol yield increase inversely with selectivity → the number of active sites for methanol synthesis increases in parallel with RWGS sites →
 - CH₃OH sites/RWGS sites: (Pd)Zn/TiO₂ > (Zn-Pd)/TiO₂ > (Zn)Pd/TiO₂ > (Zn+Pd)/TiO₂

Methanol production



Conclusions

- The order of impregnation of metal precursors affects the formation and contacts between ZnO and PdZn particles → differences in the contact between those domains lead to changes in both selectivity and yield for methanol production
- When Pd is impregnated on calcined ZnO/TiO₂ it is achieved the highest relative number of selective sites for methanol synthesis associated with the more extensive formation of the PdZn-ZnO-interface
- The other impregnations lead to the formation of a larger number of sites for methanol synthesis but also sites for the undesired RWGS reaction.
- Additional characterization is underway to further characterize the formation of the PdZn particles and their contact with the ZnO

Acknowledgements

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