STUDY OF NI CLUSTERS ON Al_2O_3 FOR SABATIER REACTION

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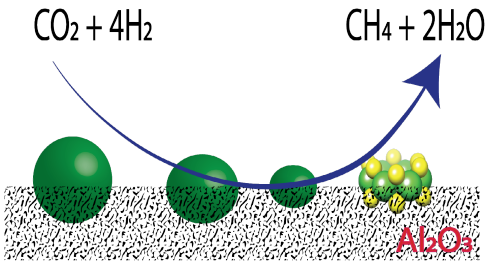
INTRODUCTION

One of the most promising approaches in *carbon capture and utilization* is the Sabatier reaction, leading to the removal of carbon dioxide pollution and at the same time converting it in energy. The Sabatier reaction produces methane from carbon dioxide and hydrogen ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$)[1]. Ni-based catalysts are the most widely investigated materials for Sabatier reaction due to their high activity, high selectivity and low cost. The main drawback of Ni-based catalysts is carbon formation that is strongly influenced by temperature and operating pressure [2]. Nickel particle size or nickel dispersion are frequently discussed as factors influencing the CO/CH_4 selectivity of CO_2 hydrogenation. Nanosized metal clusters have demonstrated exceptional properties and play an important role in many catalytic applications.

In this work, we evaluated the influence of particle size in the catalytic behavior of Ni/Al_2O_3 catalysts in the Sabatier reaction. Four different preparation routes are explored, from the conventional incipient wetness impregnation or deposition-precipitation to the preparation of Ni nanoclusters.



EXPERIMENTS

Powder catalysts were synthetized with 15% of Ni supported in Al_2O_3. To obtain this type of powder catalysts, three techniques have been developed: Two catalysts were prepared using `All in one method´; which consists in preparing an aqueous suspension with all that is necessary, that is, the support, the metal precursor salt and the additives. These two catalysts were named as `Ni_tdu_pva´ and `Ni_tdu´. Another catalyst was prepare using pore volume impregnation method named as `Ni_imp´. By this technique, the precursor salt of the metal, to be supported, is introduced into a volume corresponding to the pore volume of the support, and finally, the last catalyst was prepared by precipitation-deposit method (Ni_PD), a homogeneous precipitation with the presence of a support that in our case was alumina. To obtain the powder catalysts, the solutions were dried at 120 ºC and calcinated for two hours at 550 ºC. To control the particle size and structure we prepare $Ni_6(SC_2H_4Ph)_{12}$ nanoclusters based on reported methods [3] and supported on Al_2O_3 by impregnation.

The physical-chemical properties of the prepared catalysts were studied by several techniques such as: N_2 physisorption (BET), CO chemisorption, X-ray Diffraction, Temperature programmed reduction/adsorption/desorption (TPR/D/O) and the catalytic performance has been tested in the Sabatier reaction at CO_2/H_2 feed molar ratio of 1:4. Kinetic tests have been done between 150-500 ºC at atmosphere pressure, with a feed molar ration of CO_2/H_2 1:4. In all the test flow reactor was

used, loaded with 200mg of catalysts, and the outgas connected for analysis with a GC-chromatograph.

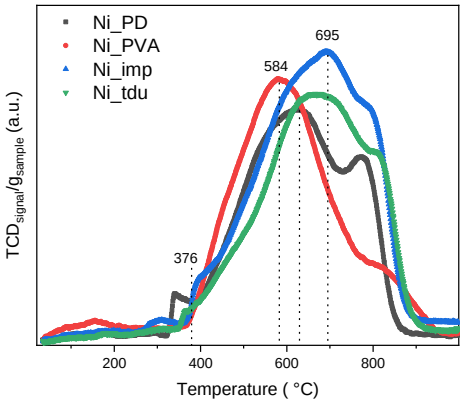
RESULTS AND DISCUSSION

The preparation protocol had a strong effect on the surface of the catalysts. Table 1 showed differences in dispersion and particle size depending on the sample. PVA and PD protocols leads to higher dispersion and smaller particle size.

These results were correlated with the reduction profiles shown in Fig.1. Therefore, high homogeneous surfaces with smaller particle sizes are required to optimize the catalytic performance. Then, the next step is the atomically precise nanoclusters. The preliminary results showed the possibility to obtain highly pure Ni_6 cluster.

CONCLUSION

The PVA and PD methods lead to the most homogeneous surface and optimal candidate for better catalytic performance. However, the straightforward and highly reproducible route is the PVA. Then, once the nanocluster catalysts will be prepared, the final comparison in catalytic activity will be obtained.



	Metallic surface (m^2/g_{sample})	Dispersion (%)	Grade of reduction (%)	Dp Ni^0 (nm)
Ni_tdu_pva	20.65	20.7	65.19	4.89
Ni_tdu	11.66	11.7	74.72	8.66
Ni_PD	21.07	21.1	68.87	4.79
Ni_imp	13.62	13.6	70.2	7.42

Figure 1: *(left)* H_2 reduction profiles by TPR and *(right)* Physic-chemical characterization results

REFERENCES

[1] M. Saric, J.W. Dijkstra, W.G. Haije, J. CO2 Util, **2017**, 20, 81-90

[2] K. Stangeland, D. Kalai, H. Li, Z. Yu, Energy Procedia, **2017**, 105, 2022-2027

[3] Kagalwala H., et al. *Inorganic chemistry*, **2013**, 52, 9094-9101.