Influence of synthesis conditions in the catalytic performance of Nb-P catalysts

J.A. Cecilia, C. García-Sancho, J. Mérida-Robles, J. Santamaría-González, P.J. Maireles-Torres, A. Jiménez-López, R. Moreno-Tost*

Dpto. Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos s/n 29071 Málaga (Spain)

(*) rmtost@uma.es

Keywords: glycerol, acrolein, niobium, phosphorous

1 Introduction

Glycerol is a natural byproduct of the manufacture of soaps from the hydrolysis of animal fats and vegetable oils. Due to the incessant increment of the worldwide production of biodiesel, the production of glycerol, a by-product of the biodiesel industry, has notably increased causing as consequence a drop in its price. In this way, glycerol has been turned into an interesting starting raw material for others chemical products, where the double dehydration of glycerol to acrolein is one of proposed routes for glycerol valorisation.

Because of the crude glycerine is found diluted in water, the catalysts must be active and resistance to the presence of water avoiding a separation step of the glycerine from the water and therefore reducing the price of production of acrolein. Various solid acid catalysts have been tested in the dehydration of glycerol, including niobium oxide [1-3], phosphoric acid [4, 5] and zirconium niobium mixed oxides [6]. These catalysts reach the full conversion of glycerol and acrolein selectivities as high as 75mol% [3]. However, the main drawback of these catalysts is the deactivation with time on stream due to mainly to adsorption of high boiling point compounds. The characteristic features of the catalysts affecting to the catalytic activity are related to the amount of acid centers and the type of acid sites. The catalytic activity is related to Nb – OH groups and polymeric structures exposing Nb=O species [3, 6].

The main goal of this work is to evaluated how the preparation of the catalysts affect to the catalytic activity of supported niobia-phosporous on a mesoporous silica SBA-15 doped with zirconium. Doping with zirconium improves the acidity of the support and the stability of the catalysts as it has been shown previously [7].

2 Experimental

For the synthesis of mesoporous silica SBA-15 doped with zirconium (Si/Zr molar ratio of 5), 8 g of EO20-PO70-EO20 (Pluronic 123 from Aldrich) polymer was dissolved in 288 mL of a 1.7 M HCl aqueous solution and stirred at 313 K for 1 day. Then, 14.6 mL of tetraethoxysilane and 5.8 mL of zirconium n-propoxide were added, under vigorous stirring. The resulting solution was aged at room temperature for 3 days. The final product was filtered, washed with water and dried at 333 K. The solid was calcined at 823 K for 6 h. The support was labelled as SiZr

This solid was impregnated with niobium oxalate to achieve a 8wt% of Nb_2O_5 by using the incipient wetness impregnation. The catalyst was dried and calcined at 673 K during 4h (heating rate 2 K/min) and labelled SiZr_8Nb_2O_5. The niobium-phosphorous catalysts were prepared following to two different strategies. In the first one, the support was impregnated with a solution of niobium oxalate (8wt%Nb_2O_5) and then dried over night at 333 K. Following, the phosphorous was added by using H_3PO_4 (85wt%) wiith Nb/P molar ratio of 0.2. Finally, the catalyst was dried and calcined at different temperatures (523, 673 and 973 K) during 4 hours. The catalysts were labelled 0.2NbP-x where x is the temperature of calcination. In the second strategy, the support was impregnated with a solution containing niobium oxale and phosphoric acid with the Nb/P molar ratio of 0.2. This catalyst was calcined at 673 K for 4 hours and labelled 0.2NbP-400-I.

The support and catalysts were characterized by means of nitrogen adsorption, elemental analysis, XDR, XPS, TPD-NH_3 and adsorption of pyridine coupled to FTIR.

The dehydration of glycerol was performed, at atmospheric pressure, in a fixed-bed continuous-flow stainless steel reactor (9.1mm in diameter, and 230mm in length), operated in the down-flow mode Catalysts were pretreated in situ at atmospheric pressure under a nitrogen flow of 30 $mLmin^{-1}$ at 598 K for 30 min. The glycerol solution (10 wt.% in water) was supplied by means of HPLC pump at 0.05 $mLmin^{-1}$ feed rate in a N_2 flow (30$mLmin^{-1}$). The evolution of catalytic tests was studied by collecting liquid samples after 2, 5 and 8 h in a vial cooled in an isopropanol–liquid N_2 trap. These vials were sealed for posterior analysis by gas chromatography. The products measured were acrolein, acetaldehyde, hydroxyacetone and allyl alcohol.

3 Results and discussion

The support and catalysts were studied by XRD to confirm the presence of the mesoporous structure which was mantained after the impregnation and calcination of the active phases. Moreove, it was not detected neither niobium phase nor phosphate phaser at higher 2θ.The SiZr catalyst show a high glycerol conversion even higher than the SiZr_8Nb_2O_5 within the 8 hours of time on stream (TOS) although the selectivity of the SiZr_8Nb_2O_5 towards acrolein is higher (Table 1). This issue is related to higher Brönsted acid sites present in the SiZr_8Nb_2O_5 since the SiZr support only shows Lewis acid sites. When phosphorus is added to the SiZr_8Nb_2O_5 catalyst (Table 1), the catalytic performance is improved both in terms of glycerol conversion and acrolein selectivity. It is observed an increase of Brönsted acid sites, probably the presence of P – OH speccies and a decrease of Lewis acid sites compared to the SiZr_8Nb_2O_5 catalyst. This improvement is only shows when the catalyst is calcined at 673 K (Figure 1) higher and lower calcination temperatures had not beneficial effect on the catalytic activity.

It was also compared the catalytic activity when the impregnation with phosphorous and niobium was carried out in one step (Figure 2). In this case, the catalytic performance is drastically improved since the acrolein yield is increased in a 20mol%. This fact point out the presence of an active phase, no detected by XRD analysis, formed by interaction of niobium and phosphorous.

Fig. 1. Glycerol and acrolein selectiviy of the 0.2NbP-x catalysts. Glycerol conversion open symbols and full symbols acrolein yield

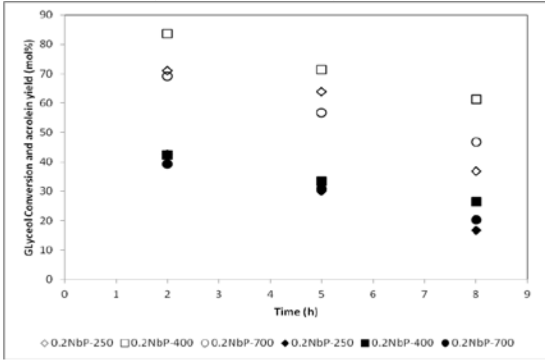

Fig. 2. Effect of the method of impregantion on the catalytic activity

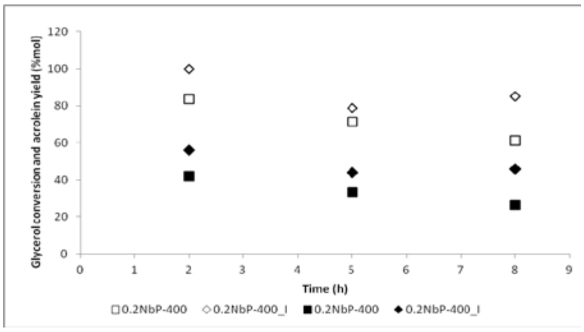

Table 1. Catalytic Performance of SiZr and niobium and Nb-P catalysts after 8 hours TOS

Catalyst	**Glycerol Conversion (%mol)**	**Acrolein Selectivity (%mol)**	**Acetaldehyde Selectivity (%mol)**	**Acetol Selectivity (%mol)**	**No detected (%mol)**
SiZr	72.4	23.3	20.2	6.8	49.8
SiZr_8Nb_2O_5	51.2	34.4	8.7	6.3	50.6
SiZr5_0.2NbP-400	61.2	43.3	0	7.3	49.4

4 Conclusions

The catalytic performance of a Nb-P catalyst supported on a mesoporous silica SBA-15 doped with zirconium is ameliorated when the impregnation of the two active phases is carried out in one step reaching an acrolein yield of 46mol% and a glycerol conversion of 85mol%.

Acknowledgements

The authors are grateful to financial support from the Spanish Ministry of Science and Innovation (ENE2009-12743-C04-03 project), Junta de Andalucía (P09-FQM-5070) and FEDER funds. RMT would like to thank this Ministry of Science and Innovation for the financial support under the Program Ramon y Cajal (RYC-2008-03387).

References

1. S.H. Chai, H.P. Wang, Y. Liang, B.Q. Xu, J. Catal. **250** (2007) 342.
2. N.R. Shiju, D.R. Brown, K. Wilson, G. Rothenberg, Topics Catal. **53** (2010) 1217.
3. M. Massa, A.Andersson, E. Finocchio, G. Busca, F. Lenrick, L.R. Wallenberg, J. Catal. **297** (2013) 93
4. W. Yan, G. J. Suppes, Ind. Eng. Chem. Res., **48** (2009) 3279.
5. W. Suprun, M. Lutecki, T. Haber, H. Papp, J. Mol. Catal. A **309** (2009) 71.
6. P. Lauriol-Garbay, J.M.M. Millet, S. Loridant, V. Bellière-Baca, P. Rey, J. Catal. **280** (2011) 68.
7. B. Katryniok, S. Paul, V. Bellière-Baca, P. Rey, F. Dumeignil, Green Chemistry **12** (2010) 2079