On the selective transformation of oxygenated compounds present in aqueous fractions derived from biomass over tungsten oxides bronzes

J.M. López Nieto [a,*], **D. Delgado Muñoz** [a], **N. La Salvia** [a], **E. García-González** [b], **A. Fernández-Arroyo** [a], **M. E. Domine** [a]

[a] *Instituto Tecnología Química, UPV-CSIC, Universitat Politecnica de Valencia, 46022 Valencia, Spain*
[b] *Departamento Química Inorgánica, Universidad Complutense, 28040 Madrid, Spain*
**Corresponding author: +34963877809, jmlopez@itq.upv.es;*

Abstract: Unsupported and KIT-6 supported tungsten oxide-based bronzes have been prepared (with different Nb/W ratios and different amount of KIT-6), characterized and tested in the selective transformation of oxygenated compounds (such as ethanol, propanal, hydroxyacetone and acetic acid) present in aqueous fractions derived from lignocellulosic biomass processing. The catalysts are active and selective in both consecutive condensation and ketonization of oxygenated compounds. Consequently, intermediates such as 2-methyl-2-pentenal (2M2P), C_5-C_8 and C_9-C_{10+} hydrocarbon fractions can be selectively achieved depending on both the catalyst composition and the reaction conditions.

Keywords: tungsten-niobium oxide bronzes, aqueous phase condensation, ketonization.

1. Introduction

The liquid phase selective transformation of oxygenated compounds present in aqueous effluents (obtained by phase separation of biomass-derived pyrolytic oils) is an important target in the development of biorefineries.[1] In this case, acid catalyzed condensation and ketonization reactions seem to be the most interesting processes to be considered for the upgrading of light oxygenates into high added value products.[2]

Recently, an alternative type of catalysts for the selective liquid phase transformation of oxygenated compounds, based on unsupported and supported tungsten oxide type bronzes ($W_{1-x}Nb_xO_z$ catalysts; $0 < x < 1.0$), have been proposed. From all of these those presenting hexagonal tungsten bronze (HTB) structure seems to be highly effective to carry out both the consecutive condensation and the ketonization reactions, in one-pot synthesis.[3] We will show how it is possible to achieve high performance for the desired products using supported and unsupported catalysts, but also how optimized catalysts can be used for several cycles without significant loss of catalytic performance.

2. Experimental

Unsupported and supported (KIT-6) catalysts have been prepared by reflux of the corresponding aqueous solutions of precursors during 24 h at 100ºC.[4] The resulting solids were finally, dried and heat-treated in N_2 at 500ºC. The catalysts were characterized by several techniques, N_2 adsorption, XRD, HRTEM and TPD-NH_3, as well as by Raman and XPS spectroscopies.

The liquid-phase catalytic tests have been carried out in autoclave-type reactors, at 180 or 200ºC, and 13 bar of N_2 pressure by using an aqueous mixture including ethanol, acetic acid, propanal and hydroxyacetone. Reaction mixtures were analyzed by GC and GC-MS. [5]

3. Results and discussion

The characterization results (XRD, HRTEM, and Raman Spectroscopy) clearly demonstrate the effective incorporation of niobium in the HTB-type framework, with a final density of acid sites depending on both the Nb/W ratio and the amount of support in catalysts. On the other hand, the number and strength of acid sites, as determined by TPD-NH_3, strongly depend on the Nb/W ratio and the amount of support in catalysts

The catalysts were evaluated in terms of conversion of starting oxygenated compounds (Fig. 1a) and in total organic product yield, TOY, i.e. 2-methyl-2-pentenal (2M2P), C_5-C_8 and C_9-C_{10+} hydrocarbon fractions (Fig.1b), which are the main reaction products. However, we must notice that acetone and ethyl acetate have been also observed as minorities.

The catalytic results indicate the importance of both the chemical composition as well as the presence or absence of support. This can be well correlated with the density of acid sites on the surface of the catalysts. The product distribution is also discussed in terms of the nature of acid sites and the ratio between Brönsted and Lewis acid sites. The optimized supported tungsten based bronze yields an organic fraction containing hydrocarbons and aromatic~~s~~ products for fuel applications, and they show a good catalyst stability compared with reference material in literature (i.e. Ce-Zr mixed oxides)[2].

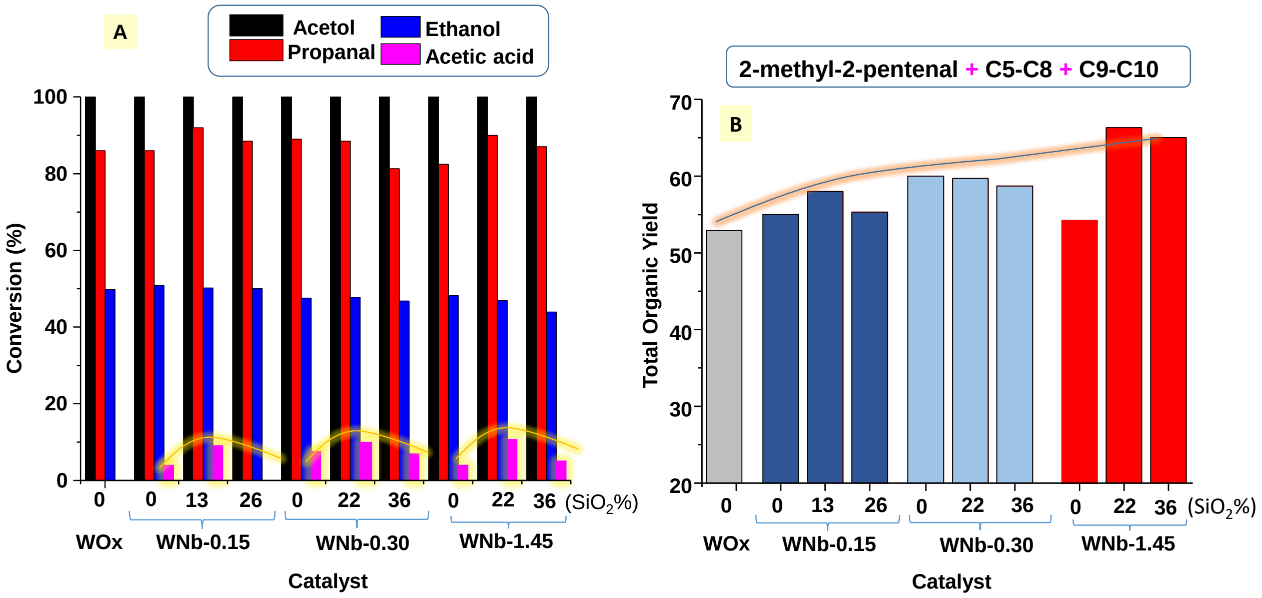

Figure 1. Conversion of acetol, ethanol, propanal and acetic acid (A) and evolution of total organic products yield, TOY (2M2P + C_5-C_8 + C_9-C_{10} fractions), with the composition of catalysts (B). Reaction conditions: 3.0 g of aqueous model mixture, 0.15 g of catalyst; at 200 ºC and P_{N2} = 13 bar; time on stream of 7h.

.

4. Conclusions

In conclusion, unsupported and supported (KIT-6) tungsten-niobium oxide based catalysts with HTB type structure, prepared by reflux synthesis, with tuned acid properties, show high activity and selectivity for the valorization of oxygenated compounds in aqueous effluents obtained by phase separation of pyrolytic bio-oils. These optimized W-Nb-O materials show good stability (after several reuses) and higher catalytic activity than those previously reported by other authors,[2] mainly because they are highly water resistant catalysts.

References

1. G.W. Huber, S. Iborra, A. Corma, Chem. Rev. 106 (2006) 4044.
2. A. Gangadharan, M. Shen, T. Sooknoi, D.E. Resasco, R.G. Mallinson, Appl. Catal. A: Gen. 385 (2010) 80.
3. M.E. Domine, J.M. López Nieto, A. Fernández Arroyo, D. Delgado, WO 2017162900 A1 (2017).
4. N. La Salvia, D. Delgado, L. Ruiz-Rodríguez, L. Nadji, A. Massó, J.M. López Nieto, Catal. Today 296 (2017) 2.
5. A. Fernández-Arroyo, D. Delgado, M. E. Domine, J.M. López Nieto, Catal. Sci. Technol. 7 (2017) 5495.