

Mesoporous mixed Nb₂O₅-ZrO₂ catalysts for dehydration of glucose into 5-hydroxymethylfurfural

C. García-Sancho¹, J.A. Cecilia², R. Moreno-Tost², P. Maireles-Torres²

¹Instituto de Catálisis y Petroleoquímica, CSIC, c/ Marie Curie 2, Cantoblanco, 28049 Madrid, Spain

²Universidad de Málaga, Dpto. Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC), Facultad de Ciencias, Campus de Teatinos, 29071 Málaga, Spain

Introduction

Biomass is the world's most important renewable carbon source, whose major component, carbohydrates, can be valorized by transformation into biofuels and high value-added chemicals. Among the latter, 5-hydroxymethylfurfural (HMF), obtained by C6 carbohydrates dehydration, is a versatile and key intermediate for the production of a large spectrum of biobased chemicals. Different catalytic systems have been evaluated for HMF production, mostly based on heterogeneous catalysis as alternative to the use of conventional mineral acids [1]. Moreover, niobium oxide has shown interesting properties as acid catalyst for dehydration of sugars [2-3]. On the other hand, the high surface area and large pore size of mesoporous solids make them suitable for many catalytic processes.

In the present work, the dehydration of glucose to HMF has been evaluated by using different mesoporous mixed Nb₂O₅-ZrO₂ in a biphasic water–Methyl Isobutyl Ketone (MIBK) solvent system to avoid the HMF degradation. Different experimental parameters, such as reaction temperature and time, as well as the addition of CaCl₂ have been studied in order to maximize the HMF yield.

Experimental

Mesoporous Nb₂O₅-ZrO₂ have been synthesized using a neutral templating route [4-5]. Briefly, 7 mmol of the corresponding metal chlorides (NbCl₅ and ZrCl₄) were added to a template solution formed by 1 g of P-123 in 10 g of n-propanol. After vigorous stirring for 5 min, 0.54 mL of ionized water were added and the resulting solution was stirred for 30 min at room temperature. The solution was aged at 40 °C for 10 days. The structure-directing agent was removed by calcination in air at 450 °C for 6 h (1 °C·min⁻¹). Catalysts were labeled as Nb₂O₅ and ZrO₂ for pure metal oxides and Nb_xZr_y in the case of mixed oxides, where *x* and *y* indicate the molar content of Nb and Zr, respectively.

Catalysts have been characterized by X-ray diffraction (XRD), N₂ adsorption-desorption isotherms at -196°C, X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption of ammonia (NH₃-TPD) and Raman spectroscopy.

Catalytic tests have been carried out under batch, in a glass pressure tube with thread bushing with a magnetic stirring bar. In a typical experiment, 150 mg of glucose (Sigma-Aldrich, >99%), 50 mg of catalyst, 1.5 mL of deionized water and 3.5 mL of MIBK (Sigma-Aldrich) are poured into the reactor. The reaction mixture was heated with a thermostatically controlled oil bath. Reaction products were quantitatively analyzed by HPLC, equipped with a multiwavelength UV-visible and refractive index detectors.

Results and Discussion

N₂ adsorption-desorption isotherms have corroborated the mesostructured character of catalysts, being all isotherms of Type IV according to the IUPAC classification. BET surface

area decreases for catalysts with higher Zr content (Table 1). Likewise, pore volume and average pore diameter values diminish after Zr incorporation. Concerning the acid properties, a clear correlation between Nb and acidity can be observed, in such a way that total acidity, as deduced from NH_3 -TPD, decreases when the Zr content rises, and consequently the amount of Nb is reduced.

Table 1. Textural and acidic properties of mesoporous mixed Nb_2O_5 - ZrO_2

Catalyst	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_p ($\text{cm}^3 \cdot \text{g}^{-1}$)	dp (nm)	$\mu\text{mol NH}_3 \cdot \text{g}^{-1}$
Nb_2O_5	149	0.213	4.8	467.0
Nb_7Zr_3	150	0.161	4.2	411.7
Nb_5Zr_5	148	0.129	3.2	399.8
Nb_3Zr_7	104	0.104	3.8	309.2
ZrO_2	64	0.073	4.2	140.8

These mesoporous Nb-Zr catalysts have been tested in the dehydration of glucose to HMF at 175 °C under batch operation in aqueous solution, using MIBK as co-solvent (Figure 1A). It can be observed that both glucose conversion and HMF yield increase with the Nb content, being maximum (90% and 36%, respectively) after 90 minutes for Nb_2O_5 . This trend changes when CaCl_2 is added to the reaction medium (Figure 1B), improving the catalytic performance of mixed oxides and ZrO_2 , but Nb_2O_5 maintains similar results than without salt addition. This could be justified by the interaction between CaCl_2 and Lewis acid sites, since zirconium oxide possesses a higher amount of this acid sites type.

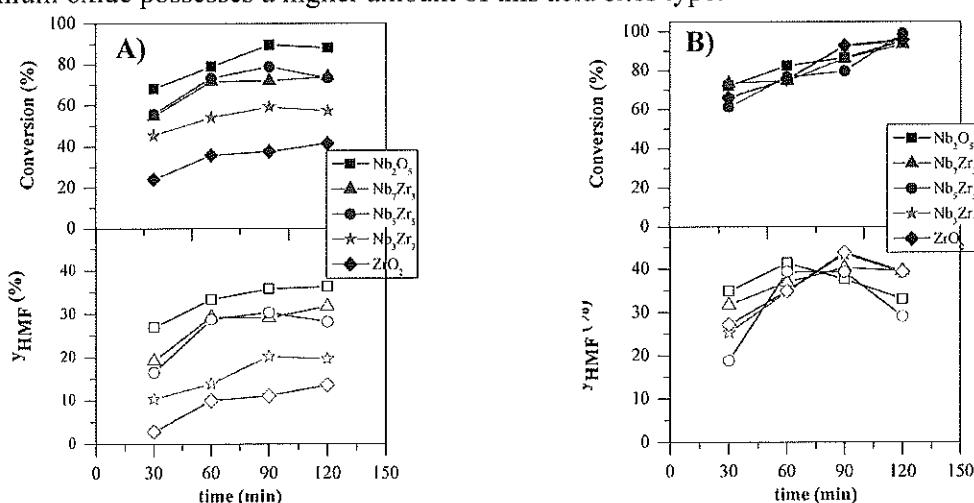


Figure 2. Glucose conversion and HMF yield as a function of reaction time, at 175 °C, without salt (A) and after addition of 0.65 g $\text{CaCl}_2 \cdot \text{g}_{\text{aq.sol.}}^{-1}$ (B) (glucose/catalyst weight ratio: 3)

References

1. T. Wang, M.W. Nolte, B.H. Shanks, *Green Chem.* 16 (2014) 548-572.
2. F. Yang, Q. Liu, X. Bai, Y. Du, *Bioresour. Technol.* 102 (2011) 3424-3429.
3. C. García-Sancho, J.M. Rubio-Caballero, J.M. Mérida-Robles, R. Moreno-Tost, J. Santamaría-González, P. Maireles Torres, *Catal. Today* 234 (2014) 119-124.
4. C. Tagusagawa, A. Takagaki, A. Iguchi, K. Takanabe, J.N. Kondo, K. Ebitani, S. Hayashi, T. Tatsumi, K. Domen, *Angew. Chem. Int. Ed.* 49 (2010) 1128-1132.
5. D. Stošić, S. Bennici, V. Pavlović, V. Rakić, A. Auroux, *Mater. Chem. Phys.* 146 (2014) 337-345.