

Hydrogenation of platform molecules to obtain biofuels with $\text{WO}_x/\text{TiO}_2\text{-ZrO}_2$.

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1. Introduction

Furfural (FF) is typically used as a precursor in the production of furfuryl alcohol (FA), FF is one of the most used chemicals obtained from the lignocellulosic biomass, and is known as a platform molecule able to produce high added value chemicals. FA can be obtained by the hydrogenation of the C=O bond in the FF (Merve 2020) and this can be converted into biofuels as 2-methylfuran (2MF) and 2-methyltetrahydrofuran (2-MTHF). Mixed oxides have been used in the transformation of molecules from biomass, converting them into molecules with high added value that allow the production of biofuels. $\text{TiO}_2\text{-ZrO}_2$ oxides, among some characteristics include their acid-base properties, high surface area, and resistance to deactivation. This study aims to synthesize Ti-Zr-W catalysts modified with Pt to increase the FA yield obtained by the FF hydrogenation reaction to hydrogenate FA and produce 2-MTHF.

2. Materials and methods

Ti-Zr-W catalyst supports were synthesized by the sol-gel method with Ti-Zr:1 molar ratio, using as precursors: titanium butoxide $\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$ (Aldrich brand, purity 97%) and zirconium butoxide $\text{Zr}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$ (Aldrich brand, purity 80% weight in 1-butanol) adding 1-butanol $\text{CH}_3(\text{CH}_2)_3\text{OH}$ (Aldrich brand, purity 99.9%) as solvents. The catalysts were modified with ammonium metatungstate $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot\text{H}_2\text{O}$ (Aldrich brand and purity 99.99%), 10% by weight as described by Silahua Pavón. In order to increase the selectivity of the catalysts, 1% platinum was added using chloroplatinic acid hydrate $\text{H}_2\text{PtCl}_6\cdot x\text{H}_2\text{O}$ (Aldrich brand, purity >99.9%) at pH=1 in a suspended bed reactor. Furfural ($\text{C}_5\text{H}_4\text{O}_2$, Aldrich brand, purity 99%) was used as a platform molecule, the identification standard of furfuryl alcohol ($\text{C}_5\text{H}_6\text{O}_2$, Aldrich brand, purity 98%), and isopropyl alcohol ($\text{CH}_3\text{CHOHCH}_3$, as solvent Meyer brand, purity 99.5%). The catalysts were structural, textural, morphological and elemental analysis characterized by means of X-ray diffraction (XRD, Bruker D8 Advanced), N_2 physisorption analysis at -196°C (BELSORP-Max-LP), Scanning Electron Microscopy (Zeiss Gemini 500, equipped with EDS), the quantification of the basic and acidic sites was carried out by TPD of CO_2 and TPD of NH_3 (BEL JapanBelcat-B) equipment. The catalytic hydrogenation reactions were carried out in a high pressure reactor with a capacity of 50 ml, with a pressure of between 4-8 MPa at 175°C for 5 hours using 0.1 g of catalyst, isopropyl alcohol as a solvent and a furfural initial concentration of 21000 ppm. The samples were filtered and subsequently analyzed by gas chromatography in a Perkin Elmer Clarus® 580 equipment, flame ionization detector (FID) with an Agilent HP-5 19091J-413 capillary column. Finally, the calibration curves were evaluated using FF and FA to determine the yields and the conversion of FF to FA was calculated.

3. Results and discussion

X-ray diffraction patterns of TZW10SG and TZW10SG of the as prepared samples, present amorphicity, likewise, the induced phase of the tetragonal ZrO_2 is observed with a slight shift at $30^\circ 2\theta$ that corresponds to the (111) plane; while the sample TZW10SG_Pt shows a slight signal at $40^\circ 2\theta$ attributed to (020) plane, that confirms the presence of platinum. Physisorption results of TZW10SG and

TZW10SG_Pt samples present mesoporosity, with 243.59 m²/g of surface area, 0.28 cm³/g of pore volume and 3.24 nm of pore diameter; and 224.79 m²/g, 0.26 cm³/g and 3.86 nm respectively. CO₂-TPD analyzes of TZW10SG and TZW10SG_Pt samples show a desorption temperature peak at 185°C and 163°C respectively, associated to very weak basic sites predominating in both samples; from NH₃-TPD measurements, it was observed, weak acid sites predominating in both samples.

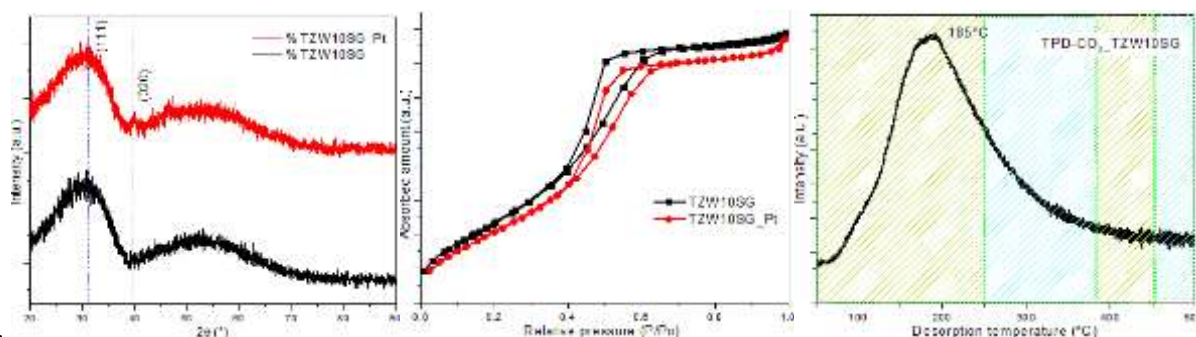


Figure 1. a) X-ray diffraction patterns, b) Adsorption isotherms, c) TPD-CO₂

The results of the hydrogenation reactions reveal that the Pt incorporation to Ti-Zr-W catalyst improve the selectivity of the reaction.

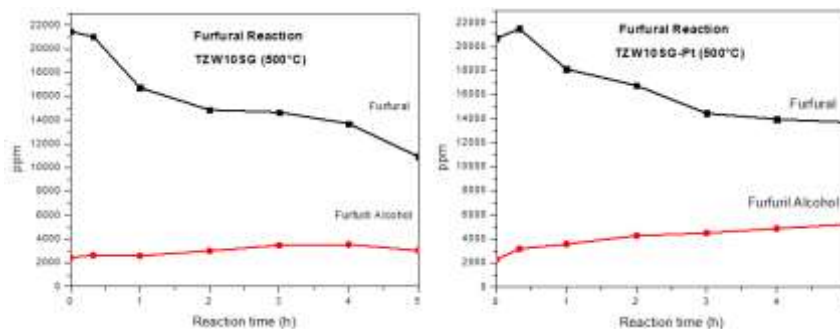


Figure 2. a) Hydrogenation of TZW10SG b) Hydrogenation of TZW10SG_Pt

That is, the activity for the sample without platinum is conversion 49%, selectivity 29%, total yield 14%, while with 1% platinum, conversion 37%, selectivity of 67.6% total yield 25%

4. Conclusions

Mixed oxides catalysts of WO_x/TiO₂ZrO₂, and 1% of platinum added, were successfully synthesized by the sol-gel/ suspension method. The catalytic activity results show that the performance of the synthesized materials is mainly attributed to a mixture of weak acidic and basic sites and that despite having a lower conversion, the total performance is favored with the sample containing Pt, the above is due to an increase of 2.5 in selectivity.

References

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Keywords

hydrogenation; mixed oxides; WO_x/TiO₂-ZrO₂, sol-gel, biofuels