Catalytic Activity of Tungstophosphorous Acid Supported on Mesoporous Silica for Glycerol Acetalisation to Glycerol Formal

ANCUTA TRIFOI¹, ANDREEA TURCANU^{1*}, RAMI DOUKEH¹, TIMEA GHERMAN¹, PETRU FILIP², MIHAELA BOMBOS^{3*}

¹Research Institute For Auxiliary Organics Products SA, 8 Carpati, 551022, Medias, Romania

²Romanian Academy, C. D. Nenitescu Organic Chemistry Centre, 202B Spl. Independentei, 060023 Bucharest, Romania ³National Institute for Research Development for Chemistry and Petrochemistry- ICECHIM-Bucuresti, 202 Spl. Independetei, 060021, Bucharest, Romania

For the acetalization reaction between glycerol and formaldehyde two mesoporous catalyst were prepared, characterized and tested. Mesoporous silicas (MCM-41 and HMS) were synthesized and used as supports for the phosphotungstic acid based catalysts. Glycerol was converted to glycerol formal through a solventless acetalization reaction with formaldehyde catalyzed by tungstophosphorous acid supported on two type of mesoporous silica (30PW/MCM41 and 30PW/HMS). The reaction was carried out in a batch reactor, at 120°C, using 2% catalyst. The highest yield > 98.5% was achieved over mesoporous 30PW/HMS catalyst. Catalyst characterization was performed by determining the textural characteristics, acid strength and by SEM analyses. The catalytic activity of the catalysts was compared, using the same conditions with two comercial acid catalysts : 5 and p-toluen sulphonic acid on polymer support (PTS/polymer).

Keywords: glycerol, MCM-41, HMS, 30PW/MCM41, 30PW/HMS

Glycerol is one of the most common by-product obtained from many industries like biodiesel production and it is becoming increasingly concerning how to valorize the raw glycerol into value-added molecules. Acetalization of glycerol is an excellent reaction for the synthesis of sixand five-membered cyclic products that exhibit a wide spectrum of commercial activities. Mainly, glycerol acetals and ketals are extensively used as additives, bases, scents, and flavors in several industries [1]. Glycerol formal is a mixture of 4-hydroxymethyl-1,3-dioxolane (5-membered cyclic ketal) and 5-hydroxy-1,3-dioxane (6-membered cyclic ketal) and the main methods used at industrial level are based on glycerol condensation with formaldehyde in the presence of acid catalyst [2].

Glycerol formal properties, recommend it as as potential substitute for most organic solvents used on an industrial scale, such as methyl-isobutyl ketone, cyclohexanone, terpenes and butyl-diglycol ether[3].

terpenes and butyl-diglycol ether[3]. For the synthesis of glycerol formal via homogenous catalysis process, strong mineral acids like H_sSO_s, HF, HCl or p-toluensuphonic acid [4-6] are used as catalysts. To ensure the continuous removal of the water from the reacting phase, Kaufhold et al. proposed in their patent [5] the use of entrainers (pentane, hexane), to shift the acetalization reversible reaction in the desired direction. There are also numerous studies performed for the acetalization of glycerol in heterogeneous catalysis using micro and mesoporous materials (zeolites, montmorillonite), polymeric resins (Dowex, Amberlyst etc.), active carbon, metal oxides or other catalysts such as ionic liquids, organic-inorganic hybrid catalysts [2]. Heteropolyacids (HPAs) are highly active heterogeneous catalysts in acid type reactions and to overcome disadvantages such as low thermal stability and surface area or separation problem from reaction mixtures and solubility, great variety of supports have been used as support to immobilize HPAs [7, 8]. Supporting the heteropolyacids on solids with high surface areas is also a useful method to improve catalytic performance in liquid-solid and gas-solid surface heterogeneous reactions. Bombos et al. [7] studied the

acetalization of glycerol with furfural, using toluene as a solvent. The yield in solketal was 88.8% after 80 min of reaction (catalyst amount of 8.5 wt% to glycerol, molar ration glycerol:furfural of 1:0.5).

The main objective of this research is to study the catalytic properties of tungstophosphorous acid (PW) supported on mesoporous silicas (HMS and MCM41) in the solventless condensation reaction of glycerol with p-formaldehyde. The general drawback of glycerol acetals synthesis is the formation of water in the process that favores the occurrence of the reverse reaction and also weakens the acid strength of the catalysts. In our work p-formaldehyde has been choosen as a formaldehyde source to avoid using more water in the system.

Experimental part

Material and methods

Catalyst preparation

Mesoporous silica support preparation

MCM-41 mesoporous silica support was obtained by conventional hydrothermal synthesis using cetyltrimethylammonium bromide as structuring agent and tetramethylammonium hydroxide as the mineralization agent. Two silicon sources were used: sodium silicate (28% SiO,, 8.6% Na,O, Merck) and high purity silica *fumed silica* (99.9% SiO2, Sigma). The hydrothermal synthesis was carried out at a temperature of 100-105°C, *pH* 12 for 48 h. The solid material was recovered by filtration from the resulting suspension after the synthesis was washed with distilled water and dried at ambient temperature. Elimination of incorporated surfactant during hydrothermal synthesis was performed by calcination in air at 550°C for 8 h. The calcination regime was conducted under controlled conditions with a heating rate of 1°/min for preservation of the mesoporosity of the MCM-41 structure.

For the synthesis of the *mesoporous HMS support*, tetraethylortosilicate was used as a silica source, dodecylamine as the structuring agent and ethanol and distilled water as solvents. The synthesis process was conducted in two stages, under the following conditions:

^{*} email: bombos.mm@gmail.com

The processing of the synthesized material was similar to the previous MCM-41 sample. The surfactant was removed by calcination at 550° C for 8 h with a temperature rise (25-550°C) of 1°C/min.

Preparation of the PW catalysts

The catalysts were prepared by impregnation of the mesoporous silica supports, in the form of calcinated powder, with a 12% solution of tungstophosphorous acid (PW), to a final concentration of PW of 30% [7].

Catalyst characterization

Catalyst characterization was performed by determining the textural characteristics acid strength and by SEM analyses. The acid strength distribution of the active center has been determined by the method of thermal desorption of diethyl-amine on a DuPont Instruments Thermal Analyst 2000/2100 coupled with a module 951 Thermogravimetric Analizer. The textural characteristics of the silica supports and PW/support catalysts were determined by nitrogen adsorption measurements at -196°C using the NOVA 2200e-Quantachrome apparatus. Prior to the adsorption measurements, the samples were degassed under vacuum in the following conditions: 300°C, 3 h (support material) and 250°C, 3 h (PW/support catalysts). From the adsorption / desorption isotherms recorded in the relative pressure range p/po = 0.005-1.0, the physical parameters of the porous texture were evaluated.

Reaction tests

The catalytic properties of the catalysts were studied in the acetalization of glycerol with formaldehyde, in a glass batchreactor. In a typical experiment, glycerol (1 mol) and formaldehyde (1 mol, usig p-formaldehyde as a source), was stirred and heated to 120° C. When the temperature reached 120° C, the catalyst (2% wt) has been added. According to Grajales et al., the p-formaldehyde depolymerization to gaseous formaldehyde, starts over 100° C

A sample of the reaction medium (the catalyst was removed from the solution for GC analysis using a 47 mm syringe filter, pore diam. of 0.45μ m) was injected into a gas chromatograph (Clarus 500) using a flameionization



detector (FID) with a Agilent 1909BD 113, 15 m \times 0.32 mm \times 0.25 μm capillary column for identification of the reaction products. The carrier gas was H₂ with 1 mL/min, injector temperature 300°C and furnance temperature 250°C. For the quantitative determination of glycerol formal a calibration curve between 0-100% concentration of glycerol formal has been created.

Results and discussions

Catalyst characterization

The stength of acid sites and total acidity

Diethylamine thermodesorption curves of the catalysts, from 20 to 600°C, are shown in figure 1. The three zones are assigned to weak, medium, and strong acidities. The weak acidic centers are obtained in the first region which ranges from 100 to 250°C, the medium acidic centers are in the second region from 250 to 400°C and the strong acidic centers are in the last region from 400 to 550°C.

The 30PW/HMS catalyst has a lower total acidity than the 30PW/MCM-41 catalyst. Both catalysts have a higher content of weak acidic centers than the medium and the strong acidic centers (table 1).

Textural characteristics

The textural properties (BET surface area, pore volume and average pore diameter) of the catalysts are summarized in table 2.

Tungstophosphorous acid supported on mesoporous silica (30 PW/MCM41 and 30 PW/HMS) present a high specific area (715-770 m^2/g), and have a narrow pore size distribution, with the average pore diameter between 2.98-3.12 nm.

Based on the isotherms presented in figure 3, it is noteworthy that both catalysts display a Type IV isotherm, with an hysteresis loop, that is observed with cilindrical pores [9, 10].

At a relative presure, $p/po \sim 0.33$ the HMS support present a significant increase of the adsorbed volume, due to the cappilary condensation of nitrogen (fig. 3A). After the impregnation with PW acid, the nitrogen adsorbed volume decreased, which is also observed from the textural data (table 2). The pore volume of the catalyst (30PW/HMS) decreased with 43,13% compared to the support.

 Table 1

 PORES ACID STRENGTH DISTRIBUTION OF THE CATALYSTS

Acidic type centers	Acidity strength (meq/g)	
	30 PW/MCM41	30 PW/HMS
Weak	1.174	1.154
Medium	0.271	0.217
Strong	0.164	0.155
Total	1.609	1.526



For the 30PW/MCM41 catalyst, the second hysteresis loop (p/po > 0.85), is more pronounced than the one of the support, indicating a decrease in the pore structure.

The small difference between the adsorption and desorption curves, with a narrow hysteresys loop, indicates the homogenity of the mesopores size.

SEM

The two catalysts, have very similar morphologies, as observed in the SEM images (fig. 4).

Catalytic activities of PW catalysts in the acetalization of glycerol with formaldehyde

A typical GC chromatogram of reaction medium is shown in figure 5. The peaks sum at 5.57 min correspond to the two glycerol formal isomers. The other peaks are

side products [32]. The hemiacetals are not seen in the GC chromatogram, due to the reversal of reactions [11].

A series of experiments was performed to determine the glycerol formal yield with reaction time over the PW catalysts supported on mesoporous silica and over two commercial macaroporous catalysts, Amberlyst 15 and PTS/polymer. Both catalysts synthesized and characterized in this work exhibit excellent catalytic behaviour in the reaction (fig. 6).

30PW/HMS has demonstrated the best catalytic activity in the reaction of glycerol with formaldehyde, using paraformaldehyde as a source of formaldehyde and in the absence of a solvent. Figure 6 and 7 show a maximum yield of 98% glycerol formal, after 3h, over the 30PW/HMS catalyst. With similar textural properties and synthesis conditions, the 30PW/MCM-41 catalyst presents similar



Fig. 3. The isotherm of nitrogen adsorption / desorbtion on the catalyst; A-HMS and 30 PW/HMS; B-MCM41 and 30PW/MCM41

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Fig. 6. Glycerol formal yield in time, over various catalysts. Reaction conditions: glycerol:formaldehyde molar ratio of 1:1, temperature 120°C, 2% catalyst

catalytic behaviour as 30PW/HMS. The glycerol formal yield slowly increased from 30 to 150 min, reached a maximum of 90.61% at 180 min and after thar started to deacrease.

Amberlyst 15, a commercial catalyst used in other studies for glycerol acetalization, exhibit good catalytic properties in the first 30 min of the reaction, when the glycerol formal yield reached 85%. After 2 h of reaction, the glycerol formal yield was 93.1% and after that, started to decrease. The catalytic activity of PTS/polymer is much lower than those of the other heterogeneous catalysts. The strength of PW is higher than H_2SO_4 and paratoluenesulfonic acid [12].





Conclusions

Solventless acetalization of glycerol with acetone was performed over 30%PW/HMS and 30%PW/MCM-41 catalysts. Under the reaction conditions molar ratio glycerol:formaldehyde of 1:1, reaction temperature of 120°C, reaction time of 3 h and catalyst amount of 2%, glycerol formal yield was 98.5% over 30%PW/HMS catalyst and 90.61% over 30%PW/MCM-41 catalyst. Using pformaldehyde as a source of formaldehyde, avoided the additional introduction of the water in the system.

References

1.MALLESHAM, B., et al., Design of highly efficient Mo and W-promoted SnO2 solid acids for heterogeneous catalysis: acetalization of bioglycerol. Green Chemistry, 2013. **15**(2): p. 478-489.

2.TRIFOI, A.R., P.S. AGACHI, T. PAP, Glycerol acetals and ketals as possible diesel additives. A review of their synthesis protocols. Renewable and Sustainable Energy Reviews, 2016. **62**(Supplement C): p. 804-814.

3.GARCIA, J.L, H. GARCIA-MARIN, E. PIRES, Glycerol based solvents: synthesis, properties and applications. Green Chemistry, 2014. **16**(3): p. 1007-1033.

4.FRUSTERI, F., et al., Oxygenated additives production for diesel engine emission improvement. Chemical Engineering Journal, 2007. **134**(1): p. 239-245.

5.KAUFHOLD M., E.-C.M., Process for preparing acetaldehyde diethyl acetal, H. Aktiengesellschaft, Editor 1996.

6.TW., G., Protective groups in organic synthesis, ed. Willey1981, New York.

7.BOMBOS, D., BOMBOS, M., VASILIEVICI, G., OPRESCU, E.E., Ecological Component for Motor Fuels Based on Furfural Derivates. Rev. Chim. (Bucharest), **67**, no. 4, 2016

8.GADAMSETTI, S., et al., Acetalization of glycerol with acetone to bio fuel additives over supported molybdenum phosphate catalysts. Journal of Molecular Catalysis A: Chemical, 2015. **410**(Supplement C): p. 49-57.

9.S. LOWELL, J.E.S., Powder Surface Are and Porosity 3rd ed1991, New York Chapman&Hall.

10.LIEBAU, F., Ordered microporous and mesoporous materials with inorganic hosts: definitions of terms, formula notation, and systematic classification. Microporous and Mesoporous Materials, 2003. **58**(1): p. 15-72.

11.AGIRRE, I., et al., Glycerol acetals, kinetic study of the reaction between glycerol and formaldehyde. Biomass and Bioenergy, 2011. **35**(8): p. 3636-3642.

12.CHEN, L., B. NOHAIR, S. KALIAGUINE, Glycerol acetalization with formaldehyde using water-tolerant solid acids. Applied Catalysis A: General, 2016. **509**(Supplement C): p. 143-152.

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