2,5-DIMETHYLFURAN PRODUCTION BY BIOMASS VIA 5-HYDROXYMETHYLFURFURAL OVER BIMETALLIC CATALYST

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Resumen

En el presente trabajo se estudió la transformación catalítica de 5-hidroximetilfurfural (HMF) para producir 2,5-dimetilfurano (DMF) sobre catalizadores bimetálicos (PtIr) y monometálicos (Pt) soportados en materiales mesoporosos CMK-3 y SBA-15. Se estudiaron también la temperatura y presión óptimas para lograr la máxima producción de 2,5 DMF. Los catalizadores se caracterizaron ampliamente por XRD, isotermas de N2, XPS, TPR, TEM y NH3-TPD. En el estudio se observó que las partículas metálicas estaban bien reducidas y muy dispersas en la superficie del soporte debido a la gran área superficial y la distribución de poros del mismo. Los sitios de PtIr fueron muy activos y selectivos hacia la formación del 2,5 DMF. El catalizador PtIr-CMK-3 mostró una excelente actividad, selectividad y estabilidad para ser aplicado en este proceso.

Platino, iridio, carbón mesoporoso, SBA-15, 5-hidroximetilfurfural, 2,5-dimetilfurano.

Abstract #

The catalytic transformation of 5-hydroxymethylfurfural (HMF) to produce 2,5-dimethylfuran (DMF) was studied over bimetallic (PtIr) and monometallic (Pt) catalysts supported on CMK-3 and SBA-15 mesoporous materials. The optimum temperature and pressure for the maximum production of DMF were studied. The catalysts were broadly characterized by XRD, N2-isotherms, XPS, TPR, TEM and NH3-TPD. It was found that the metal particles were well reduced and highly dispersed on the surface of the support of large surface area and narrow pore distribution. The PtIr alloy species active sites were very active and selective towards the formation of the desired DMF. PtIr-CMK-3 showed an excellent activity, selectivity and stability to be applied in this process.

Platinum, iridium, mesoporous carbon, SBA-15, 5-hydroximethylfurfural, 2,5-dimethylfuran.

Estoy dispuesta a someter el trabajo al volumen especial dedicado al CICAT 2020 en alguna de las revistas internacionales: Catalysis Today o Topics in Catalysis en caso de que los revisores y el comité científico seleccionen su trabajo.

1. Introduction

Nowadays, due to exhaustion of fossil resources and greenhouse effect worldwide have encouraged the development of alternative eco-friendly energies. Biofuels are energy resources produced by humans from materials generated by living beings, which is called biomass. 5-hydroxymethylfurfural (HMF) through the dehydration reaction of sugars, is one of the most important approaches to transform biomass into useful chemicals [1,2]. The importance of obtaining HMF is that it is considered an important precursor for the production of high-value polymers, such as polyurethanes and polyamides, as well as for biofuels [3,4]. Through the hydrogenolysis process, HMF can be converted to 2,5-dimethylfuran (DMF), a compound that has the potential to become the biofuel of the future. DMF is considered a potential renewable fuel due to properties such as high octane number, high energy, density, amount others.

There have been many reported ways and catalysts for DMF production. Noble metals have been reported to be promising as high-performance catalysts for HMF hydrogenation. Ru, Pt or Pd catalyst are the most commonly used for hydrogenation of HMF to DMF by hydrogenolysis [5-7]. 100% yield of DMF was obtained using Pd/C, with supercritical CO_2 mixture with water at 80ºC and 10 atm [8]. The addition of a second metal has been proved to modify the catalytic properties and improve activity and stability. PdAu/C catalyst was tested with high conversion (96%) using various Pd/Au molar ratios in the presence of hydrochloric acid, under atmospheric hydrogen pressure [9].

There is very little literature on the use of Ir as a catalyst for this reaction despite being one of the most stable transition metals in acid media and much less expensive than Pt, Pd and Ru [10]. Results for hydrogenation of HMF to DMF on the bimetallic platinum-iridium catalysts was not found in literature.

In order to obtain efficient systems for obtaining DMF, the catalytic activity of different metallic and bimetallic modified mesoporous materials was studied. Bimetallic PtIr-CMK-3 and PtIr-SBA-15 and monometallic Pt-CMK-3 were synthesized for applying in the hydrogenation of HMF to DMF under mild conditions.

2. Experimental

Synthesis of SBA-15

For the synthesis of SBA-15, triblock copolymer Poly (ethyleneglycol)-block-poly(propylene glycol)-block-poly (ethylene glycol), (EO20PO70EO20, P123-Sigma-Aldrich), was used as surfactant and orthosilicate (TEOS, Sigma-Aldrich, reagent grade 98%) as source of silica. The synthesis has been made according to [11].

Synthesis of CMK-3

The mesoporous carbon used as a support was synthesized by nanocasting strategy using the mesoporous silica SBA-15 as template and sucrose as carbon source [12].

Synthesis of monometallic and bimetallic supported mesoporous material

Three different catalyst containing Pt and Ir were prepared by wetness impregnation of the mesoporous carbon (CMK-3) and mesoporous silica (SBA-15). The mono metallic catalyst was prepared using cloroplatinic acid (H2PtCl6xH2O)) as platinum source. The bimetallic catalysts were obtained by co-impregnation method using iridium acetylacetonate (Ir(acac)2) and cloroplatinic acid (H2PtCl6xH2O)) as metal precursors. A solution of these precursors in ethanol was obtained at 50°C under reflux. Then, the support (CMK-3 or SBA-15) was added to the solution. The rest of the procedure was the same described above. In the case of SBA-15, the catalyst was calcined in muffle at 500°C for 5 h previous to the reduction. The loading of the different metals was 1 wt.% of Pt in Pt-CMK-3, 0.5 wt.% of Pt and 0.5 wt.% of Ir for the bimetallic catalysts PtIr-CMK-3 and PtIr-SBA-15.

Characterization of the catalysts

XRD patterns were collected by using a continuous scan mode. The scan speed was 0.02 deg (2 θ)/min in the Philips X'Pert PRO PANalytical diffractometer, operating with CuKa X-ray radiation (X-ray generator current and voltage set at 40 mA and 45 kV), using small divergence and scattering slits of 1/32 mm and a goniometer speed of 1.2º (2θ) min-1. The scanning range was set between 0.5º and 5º. Elemental analysis was performed by inductively coupled plasma-atomic emission spectroscopy (VISTA-MPX) operated with high frequency emission power of 1.5 kW and plasma airflow of 12.0 L/min. TPR was performed using a Micromeritics Chemisorb 2720 apparatus, with flow of 14 mL/min of 10 mol % of H2/N2 heating up 500ºC. N_2 adsorption/desorption isotherms at -196°C were measured on ASAP 2420 from Micromeritics after

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degassing the samples at 400°C, determining textural properties as surface area and pore volume and pore size distribution. The carbon monoxide chemisorption measurements were performed in ASAP 2420 equipment from Micromeritics, after in-situ reduction with pure H_2 at 300°C for 3 h. The isotherms were measured at 35°C and torr pressure range of 0-400. X-ray Photoelectron Spectra (XPS) were obtained on a MicrotechMultilb 3000 spectrometer, equipped with a hemispherical electron analyzer and MgKα (hν = 1253.6 eV) photon source. An estimated error of ±0.1 eV can be assumed for all measurements. Textural characterization of solids was performed by high definition transmission electron microscopy (HR-TEM) on a Jeol JEM-2100F equipment, working at a voltage of 200 kV. Surface acidic sites of catalysts were determined by NH_3-TPD using Micromeritics Chemisorb 2720 apparatus. The samples were first pre-treated with He at 400 °C for 1 h, cooled at room temperature and then put in contact with NH3 for another 30 min. The NH3-TPD patterns were collected under Heat a flow rate of 30 mL/min by heating from room temperature to 600°C with a heating rate of 10 °C/min.

Catalytic activity

Hydrogenation of HMF was conducted in a 600 mL stirred autoclave (Parr Pressure Reactor 4536) at different temperatures and pressures of H_2. For the reaction, 150 mg of HMF, 50 mL of solvent and 150 mg of catalyst were used. The products were analyzed with a HP 5890 Series II GC and HP-5 capillary column and identified by GC/MS.

3. Results y discussion

Characterization of the catalysts

XRD

Figure 1 shows the low angle XRD diffraction patterns of the support and the different catalysts.

The CMK-3 and SBA-15 low angle pattern exhibits a mesoporous structure order of the hexagonal crystallographic space group (P6mm) [12]. The incorporation of different metals into the mesoporous support structure involve a slight distortion in the regularity of the structure, affecting the typical diffraction peaks. As it can be seen in Figure 1, the overall structure of the mesoporous carbon CMK-3 and SBA-15 is maintained after the inclusion of Pt and PtIr particles, but there is a slight decrease in the intensity of the (110) diffraction plane in both

catalyst. This loss of intensity can be explained in terms of to the introduction of scattering material (Pt, PtIr) inside the nanopores of the support [13].
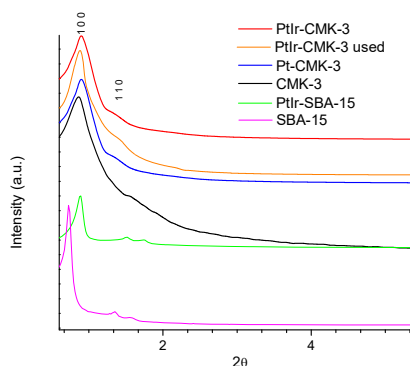

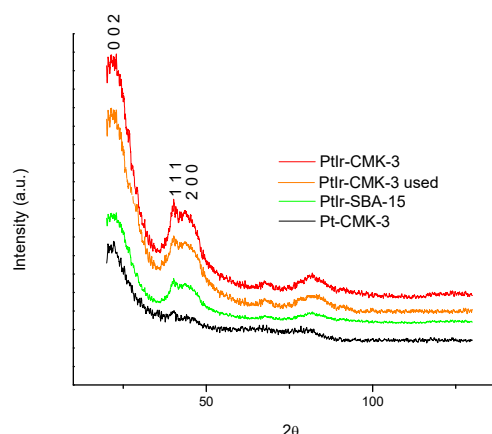**Figura 1.** Small-Angle XRD

Figura 2. Wide angle XRD diffraction patterns

Figure 2 presents the wide-angle diffraction pattern of the different catalyst. The bimetallic catalysts show two broad diffraction peaks around ~40-45° indicative of a bimetallic PtIr alloy formation, corroborated below by TPR analysis [14].

The absence of prominent diffraction peaks in all the catalysts implies that the metal nanoparticles are well dispersed and with nanometric size.

Adsorption/desorption isotherms analysis

The CMK-3 catalysts show N_2 adsorption/desorption isotherms type IV curves (not showed) with hysteresis loops type H_2 and SBA-15 catalyst with hysteresis loops type H1, in agreement with IUPAC classification. There is a reduction in the volume and size of the pores when adding the metals into the support (Table 1),

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because of a gradual diminution of the length of the inflection. With the addition of metals there is a small reduction in the pore diameter, indicating the presence of nanoparticles inside the mesopores of the support. The analysis suggests regularity in the mesoporous channels of the catalysts, consistent with the XRD analysis. Additionally, there is a slight reduction in the surface area for Pt-CMK-3 and PtIr-CMK-3 when comparing with the support. Similar trend was observed with PtIr-SBA-15 compared with pure SBA-15 used as support. This indicates that some metal nanoparticles are present inside the nanochanels of the pure CMK-3 or SBA-15.

Table1. Structural and textural properties

Sample	Area $(m^2/g)^a$	V_P $(cm^3 g^{-1})$ b	Metal cluster average size $(nm)^e$#	$Dp(nm)^d$#
1%Pt-Al$_2$O$_3$	131	0.34	2.5	6.8
SBA-15	961	1.23	--	8.6
CMK-3	1323	1.10	--	5.2
Pt-CMK-3	920	1.05	1.1	4.8
PtIr-CMK-3	890	0.83	1.8	4.5
PtIr-SBA-15	750	1.15	1.6	8.3

[a] Pie de figura (10 pt). [a]Total specific surface area obtained by the multi-point BET method; [b]Total pore volume; [c]Mesopore volume, calculated as Vmes=Vp-Vmic; [d]Pore size calculated by NLDFT method for siliceous and QSDFT method for carbonous.

CO Chemisorption

The carbon monoxide chemisorption characterization (not showed) indicates the catalyst with higher dispersion is Pt-CMK-3, according with the small particle size, followed by the bimetallic PtIr-SBA-15 and PtIr-CMK-3.

XPS

XPS results for Pt-CMK-3, PtIr-CMK-3 and PtIr-SBA-15 for mesoporous carbon catalysts show C1s binding energy corresponding to C- C sp3 and C= C sp2 (284-286 eV) are characteristic of CMK-3 as graphitic and disordered carbon species [15,17], also the strong presence of –CO species are determined by the presence of O1s at about 532 eV. O1s at 533.6-533.7 eV was attributed to Pt-O or Ir-O in the monometallic and bimetallic catalysts [15]. Chemisorbed oxygen and oxygen atoms in adsorbed water at higher eV were not detected [16, 17].

Contribution of Pt[0], Ir[0] and Pt[2+], Ir[2+] in the metallic and bimetallic catalysts was determined. According to the literature, BE of Pt4f7/2 at 71.0 is assigned to Pt[0] and 72.0 eV is assigned to Pt-O and BE of Ir4f7/2 at 61.0 eV is assigned to Ir0 and 62.0 eV is assigned to Ir-O [18-20]. Pt-CMK-3 shows the BE of 4f7/2 at 71.4 eV for Pt[0] and at 72.9 eV for Pt[2+], metal-support interaction or small cluster-size effects can be responsible for the slight shift. In this sample 88% of platinum was reduced to metallic platinum. In the case of bimetallic PtIr-CMK-3 and PtIr-SBA-15, we observe a shift to higher BE in the case of Pt4f7/2 and a shift to a lower value in the case of Ir4f7/2. This could be related to a lower electron density on the Pt sites due to the presence of Ir (higher electron affinity), suggesting the formation of a bimetallic Ir-Pt alloy [19-21]. Pt[0] or Ir[0] content is very high in PtIr-CMK-3, indicating the success of the reduction procedure. The small values of the atomic surface ratios indicate that the crystallites could be in the inner surface of the mesoporous carbon or silica.

TEM

Figure 3 shows the ordered mesoporous structure and the distribution of metal particles for the bimetallic and monometallic catalysts. It is observed that in both cases, the incorporation of the active species has not modified the mesoporous structure of the support. The particle size looks slightly larger for the bimetallic catalysts and their dispersion decreases. The metal cluster average size obtained from the histogram is listed in Table 1.
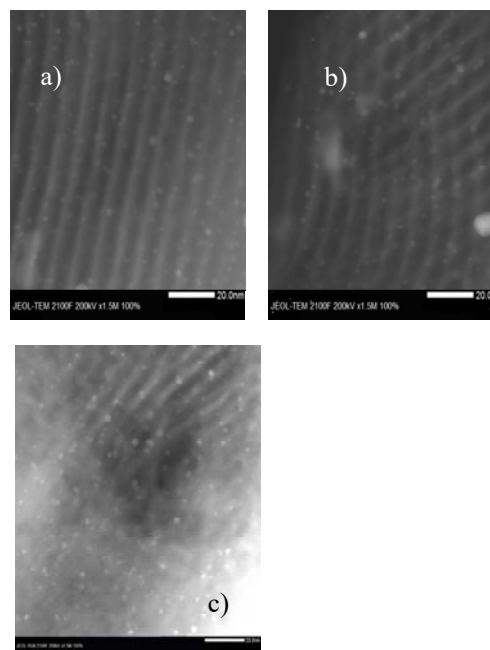

Figura 3. TEM images, a) PtIr-SBA-15, b) Pt-CMK-3 c) PtIr-CMK-3.

TPD of NH3

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To investigate the amount and strength of the acidic sites on the catalysts, NH3-TPD was performed (not showed). PtIr-SBA-15 presented a broad peak, between 200° and 300°C, characteristic of weak acidity. It is known that SBA-15 support presents very low acidity given by silanol groups [23,24]. According to results, it was observed that catalyst PtIr-SBA-15 was slightly acidic catalyst compared with the mesoporous carbons that present almost no acidity.

TPR

P-CMK-3, PtIr-CMK-3 and PtIr-SBA-15 were analyzed by temperature programmed reduction (not showed). We observe only one reduction temperature for all samples. Pt-CMK-3 presents the reduction peak at 177°C and PtIr-CMK-3 at 184°C. The presence of only one peak at the intermediate temperature of 184°C, in the case of the bimetallic PtIr-CMK-3 is indicative of the formation of a bimetal [22]. The reduction temperature of bimetallic PtIr-CMK-3 is lower than the obtained using siliceous SBA-15 as support, which reduction temperature is 194°C. This could be explained in terms of a weaker anchorage of the bimetallic crystallites on the carbonous surface compared with SBA-15, taking account the different nature of the surface.

Catalytic activity

Complete reaction paths of HMF conversion, was considered according to literature [7], where 2,5DMF is produced from selective hydrogenation of HMF. The reaction can proceed through two different routes; hydrogenation of the C=O double bond and subsequent hydrogenation and hydrogenolysis to MFA (methyl furfuryl alcohol) and successive formation of DMF as the main route [7] and to the undesired path to produce FA (Furfuryl alcohol) or FF (Furfuryl furan), involving demethylation and decarbonylation.

Hydrogenation of HMF at different temperatures

The effect of temperature in the transformation of HMF to DMF was evaluated for the synthesized catalysts. The results of the reaction test at different temperatures, maintaining the pressure at 15 atm. We can observe that when increasing temperature from 100 to 120°C, the conversion of HMF increased for all the catalysts. In the case of the most active PtIr-CMK-3 and PtIr-SBA-15 catalysts, increases by about 40 % in 4 h and the selectivity to DMF was noticeably higher. However, if the temperature continues to rise to 150 ºC (Figure 6c), the yield of DMF dramatically

decreases and the reaction path goes to other unknown products. Pt-Al2O3 is not selective to DMF at any studied temperature. According the results, only bimetallic PtIr-CMK-3 was very active and selective to DMF, reaching complete conversion of HMF and yield of DMF of 86% at 120°C and 15 atm in 4 h.

Hydrogenation of HMF at different pressures

Tests of the performance of the synthesized catalysts for the hydrogenation of HMF to DMF at different pressures, maintaining temperature at 120ºC were made. Conversion of HMF decreased and yield of DMF was zero when pressure decreased from 15 to 8 atm. Significant amounts of by products were detected at low pressure. In addition, a strong increase in pressure from 15 to 25 atm had a negative effect because of the consecutive hydrogenation of DMF. In resume, the optimal conditions were 120°C and 15 atm and the most active and selective catalyst was PtIr-CMK-3. In the case of the best catalyst PtIr-CMK-3, the good activity and selectivity to desired product DMF, can be related to the high hydrogenating capacity of the bimetallic sites, the neutral support characteristics and the high dispersion achieved on the mesoporous carbon support. The PtIr alloy combines the hydrogenating capacity of Pt and the hydrogenolysis capacity of iridium. The good performance of the alloy compared to the monometallic Pt-CMK-3 was explained in terms of the presence of electronic deficient species that avoid the irreversible adsorption of the hydrocarbon compounds. These sites are also more resistant to poisoning and coke formation. In this way, Nishimura et al. [9], affirm that the formation of the electronically poor states in the noble metal in the alloy plays a crucial role in the activation of H2 molecules and/or the enhancement of reaction pathway of hydrogenation. On the other hand, the catalyst with acid nature could cause the loss of one of radicals presented in the HMF molecule and/or the degradation of DMF [7]. The use of neutral supports improves catalyst selectivity toward DMF, avoiding the C-C bond cleavage of tertiary carbon of the HMF and preventing the formation of FA products. According to Iriondo et al. [7] the neutral nature of the support influenced positively on the selectivity toward the target product. The neutral nature of PtIr-CMK-3 could be the reason why PtIr-CMK-3 is more selective to DMF than slightly acidic PtIr-SBA-15.

Table 2. Yields of the catalysts at different

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temperatures and pressures

Sample	T(°C);P(atm)	HMF Conv. %	DMF Yield, %#
Pt-CMK-3	100; 15	55	1
	120; 15	90	50
	150; 15	92	0
	120;8	65	0
	120;25	93	0
PtIr-CMK-3	100; 15	60	3
	120; 15	98	86
	150; 15	100	0
	120;8	70	0
	120;25	100	0
PtIr-SBA-15	100; 15	57	0
	120; 15	97	30
	150; 15	100	0
	120;8	64	0

Reutilization of the catalyst

The reusability of PtIr-CMK-3 was evaluated through three reaction cycles. There was only a marginal decrease in the HMF conversion and 2,5-DMF selectivity after three reaction cycles.

4. Conclusion

Se According to the results, all of tested catalyst have shown a significant activity in the hydrogenation of HMF. However, only PtIr-CMK-3 catalyst exhibited very good selectivity to DMF at 120°C and 15 atm. An incensement of temperature or pressure, the yield of DMF drastically drops indicating that the desired path of reaction is very sensitive to changes in temperature and pressure. The design of the catalyst with high dispersion of bimetallic particles and the neutral nature of the support was determinant to achieve a high selectivity towards DMF. The high activity and selectivity of PtIr-CMK-3 was explained in terms of the presence of electronic deficient species that avoid the irreversible adsorption of the hydrocarbon compounds. The optimal metal-support interaction between the PtIr alloy species and the high area neutral mesoporous carbon are the responsible for the high selectivity to DMF.

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