Bimetallic platinum/iridium modified mesoporous catalysts applied in the hydrogenation of HMF

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Abstract

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 hydrogen pressure for the maximum production of DMF were 120 °C and 15 atm, respectively. Increases in temperature and pressure decreased the selectivity to DMF. The catalysts were broadly characterized by different techniques, such as XRD, N₂-isotherms, XPS, TPR, TEM and NH₃-TPD. It was found that the metallic particles were well reduced and highly dispersed on the surface of supports having large surface areas and narrow pore size distributions. The PtIr alloy species catalytic sites were very active and selective towards the formation of the

desired DMF. PtIr-CMK-3 catalyst showed an excellent activity, selectivity and stability to be applied in this process.

Keywords: platinum; iridium; mesoporous carbon; SBA-15; 5-hydroxymethylfurfural, 2,5-dimethylfuran.

INTRODUCTION

Nowadays, depletion of fossil resources along with the greenhouse effect worldwide spread have encouraged the development of alternative eco-friendly energies. Biofuels are energy resources produced by humans from materials generated by living beings (animals and plants), which are generally called biomass. Particularly, lignocellulosic biomass can be converted into solid, liquid and gaseous products useful as biofuels or energy vectors; therefore, it has great potential as a current and future alternative source of energy that will replace fossil fuels in a considerable extend. 5-hydroxymethylfurfural (HMF) obtained 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 because it is considered an important precursor or platform molecule to produce high-value polymers, such as polyurethanes and polyamides, as well as several 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. In fact, DMF is considered a potential renewable fuel due to its interesting properties such as high-octane number, high energy density, among others.

Many chemical routes and catalysts for DMF production have already been described. Noble metals have been reported to be a promising alternative as high-performance catalysts for

HMF hydrogenation. Ru, Pt or Pd catalyst are the most commonly used for hydrogenation of HMF to DMF via hydrogenolysis [5-7]. Thus, 100% yield of DMF was obtained by using Pd/C with supercritical CO₂ mixture and water at 80 °C 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 several Pd/Au molar ratios in the presence of hydrochloric acid, under atmospheric hydrogen pressure [9]. In addition, DMF yield of 76% was achieved by Yang et al. [10] over Ni/Co₃O₄ catalyst at 130 °C and 10 atm, while 92% yield was attained by using CoPt over carbon nanotubes at 160 °C and 10 atm after 10 h of reaction [11].

There are few literature reports on the use of Ir as 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 [12]. Up to our knowledge, results for hydrogenation of HMF to DMF on bimetallic platinum-iridium catalysts were not found in the literature. On the other hand, the use of mesoporous supports for the preparation of well dispersed metal noble catalysts is an attractive alternative for researchers. The ordered mesoporous carbons and mesoporous silicas have characteristics of great interest such as stability of the mesoporous structure, uniform size of the pore system, large surface areas, and chemical, mechanical and thermal stabilities. In previous works carried out by our research group PtIr bimetallic catalysts supported in mesoporous materials were developed and applied successfully in HDT reactions [13, 14].

In order to obtain efficient catalytic systems to yield DMF starting from HMF, 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 their application in the hydrogenation of HMF to DMF under mild reaction conditions.

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 ref. [15]. 20 g of P123 were added and dissolved in 400 mL of 1 M HCl solution at 50 °C, always under stirring. Then, 40 g of TEOS were added to the mixture, and stirred during 24 h. Then the mixture was transferred to a PP bottle and aged at 100 °C during 72 h. The resulting material was recovered by filtration and washed until pH ~6 with deionized water. The molar composition of the solid was 1 Si: 0.018 EO20PO70EO20: 2.08 HCl: 112 H₂O. The solid was submerged in ethanol reflux during 6 h. Then it was filtered, washed and dried, and finally calcined at 600°C, in order to remove the template. .

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 [16]. The procedure was as follow, 1.0 g of the template SBA-15 was immersed in an aqueous solution of 1.1 g of sucrose, 0.14 g of H₂SO₄ and 5.0 g of deionized water. Afterwards, the mixture was heated at 100 °C during 6 h and then, the temperature was raised till 160 °C and maintained during

another 6 h. A second wetness impregnation of the mixture was carried out with a solution of 0.65 g of sucrose, 90 mg of H_2SO_4 and 5.0 g of deionized water in order to ensure the filling of the pores of the template with sucrose. Another thermal treatment was performed at 100 °C and 160 °C during 6 h. In order to complete carbonization inside the pores of the template, the composite was treated at 900 °C in an inert atmosphere (N_2 , 20 mL/min). Finally, the removal of the template was done by immersing the composite in a solution of hydrofluoric acid (5 wt.%) at room temperature. The resulting material was filtered, washed and dried.

Synthesis of monometallic and bimetallic supported mesoporous material

Three different catalysts 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 chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$) as platinum source. A solution of this precursor was prepared in 50 mL of ethanol. The support (CMK-3), previously dried during 12 h at 120 °C, was added to this solution. Ethanol was removed by using a rotary evaporator at 50 °C and 60 rpm. Afterwards, the catalyst was dried at 120 °C during 12 h and a thermal treatment was done under nitrogen flow (20 mL/min) from 25 °C to 470 °C (rate = 4 °C/min), and maintaining this temperature during 5 h. After that, the catalyst was reduced under hydrogen flow (20 mL/min) at 470 °C. The bimetallic catalysts were obtained by co-impregnation method using iridium acetylacetonate ($\text{Ir}(\text{acac})_2$) and chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$) 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 a muffle furnace at 500 °C during 5 h before the reduction. The metals loading was 1 wt.% of Pt for Pt-CMK-3, 0.5 wt.% of Pt and 0.5 wt.% of Ir for the PtIr-CMK-3 and PtIr-SBA-15 bimetallic catalysts.

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 CuK α 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 1.2° (2 θ) min⁻¹. The scanning range was set between 0.5° and 5°. The sample was crushed previously and placed in an aluminium sample holder. Elemental analysis was performed by inductively coupled plasma-atomic emission spectroscopy (VISTA-MPX) equipment operated with high frequency emission power of 1.5 kW and plasma airflow of 12.0 L/min. TPR analysis was carried out by using a Micromeritics Chemisorb 2720 apparatus, with flow of 14 mL/min of 10 mol % of H₂/N₂ heating up 500 °C. N₂ adsorption/desorption isotherms at -196 °C were measured on ASAP 2420 from Micromeritics after degassing the samples at 400 °C, determining textural properties as surface area, pore volume, and pore size distribution. The carbon monoxide chemisorption was measured in ASAP 2420 equipment from Micromeritics, after in-situ reduction with pure H₂ at 300 °C during 3 h. The isotherms were measured at 35 °C and pressure range of 0-400 torr. X-ray Photoelectron Spectra (XPS) were obtained on a Microtech Multilb 3000 spectrometer, equipped with a hemispherical electron analyzer and MgK α (h ν = 1253.6 eV) photon source. An estimated error of ± 0.1 eV can be assumed for all measurements. Peak intensity was calculated from the respective peak areas

after background subtraction and spectrum fitting by a combination of Gaussian/Lorentzian functions. Textural characterization of solids was carried out by high-resolution transmission electron microscopy (HR-TEM) on a Jeol JEM-2100F equipment, working at a voltage of 200 kV. The HR micrograph analysis, lattice spacing, First Fourier Transform (FFT) and phase interpretation, were done with the Gatan Digital Micrograph software (Gatan Inc.) and the Java version of the Electron Microscope Software (JEM). Surface acid sites of catalysts were determined by NH_3 -TPD measurements using Micromeritics Chemisorb 2720 apparatus. The samples were first pre-treated with He at 400 °C during 1 h, cooled at room temperature, and then put in contact with NH_3 during another 30 min. The NH_3 -TPD patterns were collected under He at 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

Experiments of HMF hydrogenation were carried out in a 600 mL stirred autoclave (Parr Pressure Reactor 4536) at different temperatures and H_2 pressures. Typically, 150 mg of HMF, 50 mL of solvent and 150 mg of catalyst were used. The products were analyzed by means of a HP 5890 Series II GC equipped with a FID detector and a HP-5 capillary column, and identified by GC/MS.

RESULTS AND DISCUSSION

Characterization of the catalysts

XRD

Figure 1 shows the low angle XRD diffraction patterns of the supports and the different metal supported catalysts.

The CMK-3 and SBA-15 low angle patterns exhibit a mesoporous ordered structure characteristic of the hexagonal crystallographic space group (P6mm). The diffraction pattern of the support presents two distinctive peaks, indexed to the (100) and (110) planes, typical of the ordered hexagonal mesostructure [16]. The incorporation of different metals onto the mesoporous support structure entails a slight distortion in the regularity of the structure, affecting the typical diffraction peaks. As it can be seen in Figure 1, the mesoporous carbon CMK-3 and SBA-15 keep their structures after the inclusion of Pt and PtIr particles, but there is a slight decrease in the intensity of the (110) diffraction plane in both catalysts. This loss of intensity can be explained by considering the introduction of scattering material (Pt, PtIr) inside the nanopores of the support [17].

Figure 1

Figure 2 presents the wide-angle diffraction pattern of the different catalysts. The wide peak at $\sim 25^\circ$ can be indexed to the (002), characteristic peak of mesoporous carbons [18]. In the case of the monometallic catalyst (Pt-CMK-3), the pattern presents the typical diffraction peaks of metallic Pt, with the planes (111) and (200), which implies that the reduction process

has been effective [19]. The bimetallic catalysts show two broad diffraction peaks around $\sim 40\text{-}45^\circ$, indicative of a bimetallic PtIr alloy formation, which was also corroborated by TPR analysis (see next sections) [20].

The absence of prominent diffraction peaks in all the catalysts is a good sign that the metal nanoparticles incorporated on the solids are well dispersed and possess nanometric size.

Figure 2

Adsorption/desorption isotherms analysis

Nitrogen adsorption/desorption isotherms at -160°C for the supports and for the different metal supported catalysts are presented in Figure 3(a), while pore size distributions are shown in Figure 3(b). The CMK-3 based catalysts show N_2 adsorption/desorption isotherms type IV curves with hysteresis loops of type H_2 , while SBA-15 based catalysts present hysteresis loops of type H_1 , in agreement with IUPAC classification. There is a reduction in pore volume and size when adding the metals onto the supports (Table 1), because of a gradual decrease in length of the inflection. The mesoporous carbon used as support presents microporosity in the nanochannel walls, this explaining why it has higher surface area compared with the SBA-15 used as template. It also presents a regular array of nanopores, with a pore diameter of 5.2 nm. With the addition of metals there is a small reduction in the pore diameter, indicating the presence of metal nanoparticles inside the mesopores of the support. The analysis suggests regularity in the mesoporous channels of the catalysts, consistent with the XRD analysis, that indicates no modification of the CMK-3 structure with the incorporation of the metal nanoparticles. Additionally, there is a slight reduction in the surface area for Pt-CMK-3 and PtIr-CMK-3 in comparison with the support. A 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 nanochannels of the pure CMK-3 or SBA-15. ICP analysis established the metallic content for the different catalysts (Table 1).

Figure 3

Table1

CO Chemisorption

Characterization of the metal supported materials here prepared by carbon monoxide chemisorption is presented in Table 1. The stoichiometry used for calculations is 1:1 for metal : CO. The results indicates that the catalyst with the higheest dispersion is Pt-CMK-3, according with its smaller metal nanoparticle size, followed by the two bimetallic systems: PtIr-SBA-15 and PtIr-CMK-3.

TEM

Figure 4 shows the ordered mesoporous structure and the metal particle size distribution for the bimetallic and monometallic catalysts. In both cases, the incorporation of the metal active species has not modified the mesoporous structure of the support. The metal 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.

Figure 4

Table 2 presents the XPS results obtained for Pt-CMK-3, PtIr-CMK-3 and PtIr-SBA-15. In the case of the mesoporous carbon catalysts, 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 [21-26], 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 [21]. Chemisorbed oxygen and oxygen atoms in adsorbed water at higher eV were not detected [22, 23].

Table 2 also shows the analysis of the contribution of Pt⁰, Ir⁰ and Pt²⁺, Ir²⁺ in the metallic and bimetallic catalysts. According to the literature, BE of Pt4f_{7/2} at 71.0 is assigned to Pt⁰ and 72.0 eV is assigned to Pt-O, while BE of Ir4f_{7/2} at 61.0 eV is assigned to Ir⁰ and 62.0 eV is assigned to Ir-O [27-29]. Pt-CMK-3 shows the BE of 4f_{7/2} at 71.4 eV for Pt⁰ and at 72.9 eV for Pt²⁺, metal-support interaction or small cluster-size effects being responsible for the slight shift in the signals. In this sample, 88% of platinum was reduced to metallic platinum. In the case of bimetallic PtIr-CMK-3 and PtIr-SBA-15, a shift to higher BE in the case of Pt4f_{7/2} together with a shift to a lower value in the case of Ir4f_{7/2} were observed. This could be related to a lower electron density on the Pt sites due to the presence of Ir (higher electron affinity), this suggesting the formation of a bimetallic Ir-Pt alloy [28-30]. Pt⁰ and Ir⁰ contents are very high in PtIr-CMK-3, indicating the success of the reduction procedure. The small values of the atomic surface ratios here determined indicate that the metal crystallites could be in the inner surface of the mesoporous carbon or silica.

Table 2

TPR

Figure 5 shows the temperature reduction programmed profiles obtained for the catalysts here studied. Only one reduction temperature was detected for all samples. Pt-CMK-3 presents the reduction peak at 177 °C and PtIr-CMK-3 at 184 °C. In a previous work, a reduction temperature for monometallic Ir-CMK-3 of 208 °C was obtained [14]. 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 bimetallic species [31]. The reduction temperature of bimetallic PtIr-CMK-3 sample is lower than the one obtained using siliceous SBA-15 as support, whose reduction temperature is 194 °C. This could be explained in terms of a weaker anchorage of the bimetallic crystallites on the carbonaceous surface compared with SBA-15, also taking into account the different nature of the surface in these cases (CMK-3 vs SBA-15).

Figure 5

TPD of NH₃

To investigate the amount and strength of the acid sites on the different catalysts, NH₃-TPD measurements were performed, and the results are shown in the last column of Table 1. PtIr-SBA-15 material presented a broad peak, between 200 °C and 300 °C, which is characteristic of weak acidity. . In this sense, SBA-15 support is known to present very low acidity mainly

given by the presence of silanol groups [32-34]. According to Table 1, it was observed that PtIr-SBA-15 catalyst was slightly acidic catalyst compared to the mesoporous carbon-based materials that present almost no acidity.

Catalytic activity

Scheme1 shows complete reaction paths of HMF conversion, according to literature [7]. As it can be seen in the proposed scheme, DMF is produced from selective hydrogenation of HMF. The reaction can proceed through two different routes: i) selective hydrogenation of the C=O double bond to form BHMF and subsequent hydrogenation and hydrogenolysis to MFA and successive formation of DMF as the main route, [7] and ii) alternatively through the hydrogenation/hydrogenolysis to give first 5-MF and successive hydrogenation to MFA, then following the above-mentioned route until finally getting the DMF. Nevertheless, undesired paths producing FA or FF, involving decarbonylation and demethylation, respectively, can also take place during the process. Catalytic results here obtained are analyzed and discussed by considering this reaction network.

Scheme 1

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 tests performed at different temperatures, maintaining the hydrogen pressure at 15 atm, are shown in Figure 6. When increasing

temperature from 100 to 120 °C (Figures 6a and 6b), the conversion of HMF improves for every catalyst. In the case of the most active PtIr-CMK-3 and PtIr-SBA-15 catalysts, conversion increases by about 40% in 4 h and selectivity to DMF was noticeably higher. However, if temperature continues rising until 150°C (Figure 6c), the yield of DMF dramatically decreases and the reaction goes towards other products (Table 3). Pt-Al₂O₃ sample is not selective to DMF at any studied temperature. According to the results, only bimetallic PtIr-CMK-3 catalyst was very active and selective to DMF, reaching complete conversion of HMF and 86% yield of DMF at 120 °C and 15 atm in 4 h of reaction.

Figure 6

Hydrogenation of HMF at different pressures

Figure 7 shows the performance of the synthesized catalysts for the hydrogenation of HMF to DMF at different hydrogen pressures, keeping temperature at 120 °C. Conversion of HMF decreased and yield of DMF was zero when pressure decreased from 15 to 8 atm (Figure 7a). Significant amounts of by-products were detected at low pressure (see Table 3). In addition, a strong increase in hydrogen pressure from 15 to 25 atm (Figure 7b) had a negative effect on DMF production, mainly because of the consecutive hydrogenation of DMF to DMTHF and HOL (scheme 1), by-products included in the “others” column in Table 3.

Figure 7

Table 3 summarizes the overall results of the experiments carried out at different reaction conditions for the synthesized catalysts. According to these data, the three metal supported catalysts presented higher conversions of HMF at the highest temperatures and pressures studied. Nevertheless, secondary reactions could occur during the HMF conversion, apart from dehydration and hydrogenation reactions [7, 35, 36], such as demethylation and decarbonylation. DMF formation was found to be very sensitive to the operating conditions. At higher temperatures and/or pressures good conversions of HMF were obtained, but either the predominant product is FA and FF (especially in PtIr-SBA-15) or the hydrogenation and dehydration reactions are too fast, giving DMTHF, HOL, 5-MF, etc., their values are contained in the “others” column (Table 3). This trend is observed for the three metal supported catalysts, as it can be seen in the increment of the “others” products. Mild conditions (lower temperature and/or lower hydrogen pressure) involve low conversion of HMF and the occurrence of either the undesired path to FF or the incomplete path to DMF, giving the corresponding intermediate products, such as BHMF, MFA, etc. In summary, the optimal conditions for the HMF selective hydrogenation to DMF were 120 °C and $P_{H_2} = 15$ atm, and the most active and selective catalyst was PtIr-CMK-3.

Table 3

In the case of the best catalyst PtIr-CMK-3, the good activity and selectivity to the 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 Ir. The good performance of the alloy compared to the monometallic Pt-CMK-3

was already 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 [37-40]. 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 H_2 molecules and/or the enhancement of the hydrogenation reaction pathway. On the other hand, the catalyst with acid nature could cause the loss of one of the radicals presented in the HMF molecule and/or the degradation of DMF [7]. Thus, 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 product. Shi et al. [36] have reported platinum modified carbon materials showing higher DMF yields (73%) than SiO_2 , Al_2O_3 , Fe_3O_4 and MgO . The authors claim that the selectivity towards DMF depends on its capacity of adsorption on the catalyst surface. According to Iriondo et al. [7], the neutral nature of the support positively influences the selectivity toward the target product. Thus, the neutral nature of PtIr-CMK-3 could be the reason why PtIr-CMK-3 catalysts is more selective to DMF than slightly acidic PtIr-SBA-15 material.

The correlation between the dispersion and activity of noble metal particles was calculated using the turnover number (TON). TON was calculated using the number of converted moles of HMF to DMF (at 120 °C, $P_{H_2} = 15$ atm and 4 h of reaction time) divided per the number of metal active sites of the catalysts determined by carbon monoxide chemisorption (Table 1). The TON for PtIr-CMK-3 sample was much higher than the others catalysts (values are listed in Table 1). This may imply that the prominent performance of bimetallic PtIr-CMK-3 is not only related to the high dispersion achieved, but also to the nature of the bimetallic catalytic centers involved in the reaction and the nature of the support and metal-support interaction [16, 17]. The higher values of TON for PtIr-CMK-3 catalyst, even when the

dispersion is lower, proves the bimetallic sites to be different and more active than the monometallic sites.

Hydrogenation of HMF using different solvents

The effect of the solvent in the hydrogenation of HMF was studied over PtIr-CMK-3 catalyst at 120 °C, P_{H_2} = 15 atm and 4 h of reaction time. The reactions were carried out with the following solvents: acetonitrile, THF and methanol, and the results are shown in Table 4. It can be observed that better yield is obtained with a less polar aprotic solvent as THF. Polar solvents like protic methanol and aprotic acetonitrile could be strongly adsorbed by the catalytic surface, competing with the reactive molecule and becoming a barrier for the diffusion of substrates and products, thereby hindering the catalytic performance [41, 42]. This is either interpreted in terms of hindrance of adsorbed solvent molecules in the mesoporous channels [43, 44] or by electronic effects of the adsorbed solvent molecule on the catalytic active center [45]. In this work, the use of the aprotic and slightly polar THF was found to effectively reduce the by-product formation giving a high yield of DMF.

Table 4

Deactivation of the catalyst

Stability and reusability of the catalyst was studied because of the great importance for practical application in industrial processes (Figure 8). Recycling experiments were carried out after washing several times with THF and methanol, desorption in inert atmosphere and

reduction under H₂ flow. The reusability of PtIr-CMK-3 catalyst was evaluated through three reaction cycles. There was only a marginal decrease in the HMF conversion and DMF selectivity after these three reaction cycles. The catalyst used after the third recycle was characterized by XRD (Figure 1 and 2) and XPS (Table 2). Results of fresh and used catalyst had almost no difference, indicating stability of the support and the metal nanoparticles during the selective hydrogenation process to convert HMF into DMF.

Figure 8

CONCLUSION

According to the results, all metal supported tested catalysts 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 P_{H2} = 15 atm. When varying temperature or hydrogen pressure, the yield of DMF drastically falls down, indicating that the reaction pathway is very sensitive to changes in temperature and pressure. TF polar aprotic solvent was the more adequate for this reaction. The design of a catalyst with high dispersion of bimetallic nanoparticles and a neutral nature of the support was decisive to achieve a high selectivity towards DMF. In this sense, the high activity and selectivity of PtIr-CMK-3 catalyst was explained in terms of the presence of electronic deficient species that avoid the irreversible adsorption of the hydrocarbon compounds. Moreover, the optimal metal-support interaction between the PtIr alloy species together with the neutral character of the high surface area mesoporous carbon are also responsible for the high selectivity to DMF. Finally, reusability tests demonstrated that this catalyst could have potential application in an industrial process.

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Table1. Structural and textural properties of the catalysts.

Sample	Area (m ² /g) ^a	V_P (cm ³ g ⁻¹) ^b	V_{mes} (cm ³ g ⁻¹) ^c	D_p (nm) ^d	Metal cluster average size (nm) ^e	Pt/Ir (wt.%) ^f	CO(mmol/g); D(%) ^g	Acidity (mmol NH ₃ /g catalyst) ^h	TON ⁱ
1%Pt-Al ₂ O ₃	131	0.34	--	6.8	2.5	0.99/--	--	--	--
SBA-15	961	1.23	1.19	8.6	--	--	--	--	--
CMK-3	1323	1.10	0.85	5.2	--	--	--	--	--
Pt-CMK-3	920	1.05	0.80	4.8	1.1	0.95/--	0.069;80	0.03	57
PtIr-CMK-3	890	0.83	0.65	4.5	1.8	0.48/0.46	0.059; 70	0.04	115
PtIr-SBA-15	750	1.15	1.08	8.3	1.6	0.51/0.48	0.061;73	0.15	39

^aTotal specific surface area obtained by the multi-point BET method; ^bTotal pore volume; ^cMesopore volume, calculated as $V_{mes}=V_p-V_{mic}$; ^dPore size calculated by NLDFT method for siliceous and QSDFT method for carbonous; ^eEstimated by TEM; ^fDetermined by ICP; ^gDispersion determined by CO chemisorption. ^hNH₃-TPD; ⁱTON calculated using HMF conversion to DMF (yield) at 120°C, 15 atm and 4 h of reaction time (initial HMF/catalyst ratio =1 g/g).

Table 2. XPS Binding energies and atomic surface ratios.

Sample	C1s	O1s	Si2p	Pt4f _{7/2}	Ir4f _{7/2}	Pt/C	PtIr/C	PtIr/Si
Pt-CMK-3	284.8 (69) 286.4 (14)	531.8 (65) 533.7 (35)	--	71.4 (88) 72.9 (12)	--	0.001018	--	--
PtIr-CMK-3	284.8 (72) 286.1 (28)	532.0 (66) 533.6 (34)	--	71.8 (94) 73.3 (6)	60.6 (93) 62.0 (7)	--	0.002033	--
PtIr-CMK-3 used	284.8 (71) 286.2 (29)	532.2 (65) 533.5 (35)	--	71.9 (92) 73.8 (8)	60.7 (90) 62.2 (10)	--	0.002214	--
PtIr-SBA-15	--	--	103.4	71.7 (80) 73.4 (20)	60.1 (89) 62.4 (11)	--	--	0.003254

Table 3. Yields of the catalysts at different temperatures and pressures.

Sample	T(°C);P(atm)	HMF Conv.%	Yield, %						
			DMF	5-MF	FA	MFA	BHMF	OMBM	Others
Pt-CMK-3	100; 15	55	1	15	0	5	25	0	9
	120; 15	90	50	12	0	18	5	0	5
	150; 15	92	0	0	17	0	0	12	63
	120;8	65	0	17	16	0	16	0	16
	120;25	93	0	0	7	0	0	11	75
PtIr-CMK-3	100; 15	60	3	18	0	3	30	0	6
	120; 15	98	86	5	0	5	0	0	2
	150; 15	100	0	0	15	0	0	10	75
	120;8	70	0	20	15	0	21	0	14
	120;25	100	0	0	10	0	0	15	75
PtIr-SBA-15	100; 15	57	0	5	26	3	10	0	13
	120; 15	97	30	7	30	0	15	5	10
	150; 15	100	0	4	45	0	18	0	33
	120;8	64	0	8	30	0	20	0	6
	120;25	99	0	5	28	4	15	8	39

Table 4. Hydrogenation of HMF over PtIr-CMK-3 using different solvents.

Solvent	HMF Conv.%	Yield						
		DMF	5-MF	FA	MFA	BHMF	OMBM	others
Methanol	80	4	28	4	0	12	0	32
THF	98	86	5	0	5	0	0	2
Acetonitrile	90	14	9	9	0	18	0	40

Captions

Figure 1: Small-Angle XRD patterns of the samples synthesized.

Figure 2: Wide-angle XRD diffraction patterns of Pt-CMK-3, PtIr-CMK-3 and PtIr-SBA-15.

Figure 3: (a) Nitrogen adsorption (solid symbols)-desorption isotherm (open symbols) at 160 °C and (b) pore size distribution of the samples synthesized.

Figure 4: TEM images of (a) PtIr-SBA-15, (b) Pt-CMK-3, (c) PtIr-CMK-3.

Figure 5: TPR of the samples synthesized.

Scheme 1: Reaction pathway for HMF conversion.

Figure 6: Conversion of HMF and yield of DMF over the catalysts synthesized and Pt-Al₂O₃ as reference. (a) T=100 °C, (b) T=120 °C and (c) T=150 °C. Reaction conditions: 15 atm, 360 rpm, solvent= tetrahydrofuran (THF), t=4h.

Figure 7: Conversion of HMF and yield of DMF over the synthesized catalysts and Pt-Al₂O₃ as reference. (a) P=8 atm, (b) P=25 atm. Reaction conditions: 120 °C, 360 rpm, solvent= tetrahydrofuran (THF), t=4h.

Figure 8: Reusability test of PtIr-CMK-3.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Scheme 1

Figure 6

Figure 7

Figure 8