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Continuous gas phase condensation of bioethanol to 1-butanol over bifunctional Pd/Mg and Pd/Mg-carbon catalysts

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Abstract: The condensation of ethanol into 1-butanol, in the presence of different catalytic systems based on Pd dehydrogenating/hydrogenating component and magnesium hydroxide derived materials as basic ingredient, was studied in a fixed bed reactor. The incorporation of metal was done by wetness impregnation and the resulting material was then reduced in-situ with hydrogen at 573 K for 1 h before reaction. The bifunctional catalysts were tested in a fixed bed reactor operated in gas phase at 503 K and 50 bar using a stream of helium and ethanol. Bifunctional catalyst supported over synthetized composite based on Mg and a carbon material: high surface area graphite, was also studied. Improved catalytic performance in terms of selectivity towards 1butanol and stability was shown by the Pd catalyst supported on Mg-HSAG composite after thermal treatment in helium at 723K, presumably due to the compromise between two parameters: the adequate size of Pd nanoparticles and the concentration of strong basic sites. Our results indicate the optimal density of strong basic sites is a key aspect in designing superior bifunctional heterogeneous catalytic systems for the condensation of ethanol to 1-butanol.

Introduction

The interest in 1-butanol production has grown in recent years because it is contemplated as a promising alternative to ethanol as petrol substitute. Butanol offers many advantages when used as fuel over ethanol due to its properties such as its lower volatility, immiscibility with water, less corrosive nature (which leads to improved safety) and mainly its higher heat of combustion, similar to that of gasoline.^[1,2] Also unlike other alcohols, butanol has the air-fuel ratio closer to that of petrol, which makes it more suitable when used in current cars as no modification in combustion engine is required.^[3] As a matter of fact, the application of butanol as biofuel has already been demonstrated, and at the same time a reduction in emission of pollutants was attained with a very low increase in fuel

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[c] Prof. A. Guerrero-Ruiz, Prof. I. Rodríguez-Ramos Grupo de Diseño y Aplicación de Catalizadores Heterogéneos, Unidad Asociada UNED-CSIC (ICP), Spain consumption compare to petrol.^[4] Furthermore, apart from its fuel properties, 1-butanol finds applications in the paint, solvents and plasticizers and it is also the raw material for acrylic acid and acrylic esters.

Traditionally, butanol has been produced through the acetonebutanol-ethanol (ABE) bacterial fermentation. But in the 1950s this method was substituted by the petrochemical route known as the Oxo process, where propylene is hydroformylated using syn-gas over a homogeneous rhodium catalyst to yield butanal, which is then hydrogenated to butanol.^[5] However, this route would not endure owing to the rising prices in crude oil, which has favored the industrial ABE fermentation to emerge again in many countries. Nevertheless, some studies have pointed out to the limitations of this fermentation process such as low butanol yield and by-product formation (acetone and ethanol).^[6] On the contrary, the direct conversion of butanol from ethanol has been suggested to be a more desirable route, since the reaction proceeds faster when compared to the fermentation process and fewer steps are necessary to get the product. Bearing in mind that ethanol could also be a biomass derivative (bioethanol),[7] the catalytic conversion of bioethanol into butanol represents a promising alternative for fuel production from renewable biomass resources^[8].

The synthesis of higher alcohols from light alcohols is known as Guerbet reaction and has been used for more than 100 years.^[9] Traditionally, it was carried out employing a homogeneous base (alkali metal hydroxide) in presence of a metal. The chemical route for the synthesis of 1-butanol from ethanol implies a multistep mechanism (see Figure 1): Step (1) is the dehydrogenation of ethanol to acetaldehyde, step (2) is the base-catalyzed aldol condensation of acetaldehyde to 2-butenal, and steps (3) and (4) are hydrogenation reactions of 2-butenal, 2-butenol, and/or butanal into 1-butanol. The metal carries out the ethanol dehydrogenation to acetaldehyde, as well as the hydrogenation of reaction intermediates to 1-butanol, while the homogeneous base is responsible for the aldol-condensation step in this Guerbet reaction mechanism.^[10] However, despite the fact that homogeneous catalysts have been widely studied with rather good performance,[11] it is known that the use of basic heterogeneous catalysts is more desirable from a sustainable point of view. In this sense, the solid basic catalysts such as the non-expensive alkaline earth metal oxides and hydroxides are receiving more attention in last years as promising alternatives in base-catalyzed reactions.[12]

Quite a few recent reviews can be found in literature offering a detailed discussion on heterogeneous catalysts employed in this reaction.^[6,13-15] From these reviews, it is generally drawn that, due to the plurality of reactions involved, the use of catalytic systems simultaneously displaying basic, acidic and

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Figure 1. Ethanol condensation mechanism based on the Guerbet reaction. DHG: dehydrogenation, C: aldol-condensation, DH: dehydration, H: hydrogenation.

dehydrogenating/hydrogenating properties is required. Even so, alternatively to the two aldehyde self-aldolization mechanism, a few works employing hydroxyapatite catalysts^[16,17] or MgO^[18] addresses the mechanism as a direct bimolecular condensation of ethanol (proton abstraction mechanism). Note that this reaction mechanism could only be expected in the case of not transition metal-oxide catalysts.

Despite the generally accepted fact that the coupling reaction of alcohols requires a base as a critical component, it is often claimed that appropriate strength of acid-base pairs is also essential. For this reason, many heterogeneous catalytic systems described in the literature and patents for the condensation of ethanol to 1-butanol are mixed oxides, where Lewis acidic metals (such as AI) are incorporated in the MgO structure, often prepared from thermal treatment of hydrotalcites^[19-21] as well as mixed oxides modified with transition metals.^[22-26] Nevertheless, there are other materials free of magnesia that have proven to be active for ethanol Guerbet condensation reaction such as zeolites modified with alkali metals,^[27] transition metals supported on slightly basic alumina^[28,29], Cu on high surface area $Ce_2O^{[30]}$ and modified zirconia with Na.^[31]

Most of these works employing metal oxides describe a twophase process where ethanol is previously evaporated and passed with a carrier gas through a solid fixed bed catalytic system, where high reaction temperatures are required (usually starting from 573 K).^[18,21,22] The dehydrogenation is generally considered the rate determining step explaining the high reaction temperatures of the above mentioned references. For this reason and in order to reduce the reaction temperature, most of the reported catalytic systems combine an alkali metal compound with a reduced transition metal as a hydrogenating/dehydrogenation agent. Some reported examples have been previously mentioned for Cu,^[22] Ni^[28, 29] or Pd.^[24, 25]

Carbon materials, such as high surface area graphites (HSAG) and graphene derived materials,^[32] are widely used as catalyst supports with the aim of improving dispersion of the active phase. Moreover, it has been interestingly reported in literature that the strength of basic sites necessary for aldol condensation reactions can be improved by dispersing the metal oxides onto them.^[33,34] In this sense, carbon materials represent ideal supports for that goal thanks to their inert nature contrary to other inorganic supports that normally have acid/basic sites that can interfere with the catalytic performance giving rise to undesired side reactions. Furthermore, the hydrophobic nature of carbon materials could result advantageous taking into account that water is a byproduct in this condensation reaction.

Although the Guerbet reaction with longer-chain alcohols has been broadly studied, the ethanol coupling reaction is still a

challenging task owing to the uncontrolled formation of sideproducts due to the high reactivity of the intermediate product acetaldehyde.^[35] Furthermore, finding a selective and stable catalyst in condensation reactions, which are quite significant in the preparation of fuels and chemicals from biomass derivatives, emerges as a great task in heterogeneous catalysis. Magnesium oxides have been extensively explored as reference material for processes involving aldol condensation reactions,^[36,37] however. although there are a few papers describing the use of MgObased materials in the condensation of ethanol, they usually refer to processes at atmospheric pressure and high temperatures.^[14,18,19] Besides, to our knowledge, very little has been published about the effect of addition of transition metals to MgO as well as employing carbon supports in the Guerbet reaction of ethanol in fixed bed reactors. In this work, we have prepared Pd catalysts supported on Mg-based materials. This metal was chosen because of the high selectivities reported for this reaction.^[24,25] Thereafter, the influence in the catalytic activity and selectivity towards 1-butanol has been studied using Pd over composites of Mg-carbon material (HSAG) and comparatively studied with the Pd/Mg.

Results and Discussion

Structural and textural features. The X-ray diffraction patterns of the commercial Mg(OH)₂, the support MgO and the resulting Pd/Mg catalyst are represented in Figure 2. The Mg(OH)₂ diffractogram can be indexed as the hexagonal brucite phase (JCPDS card 084-2164) while the thermal dehydration process at 723 K gave rise to the characteristic periclase structure of MgO (JCPDS card 45-946). The crystallite size of MgO was estimated from line broadening of (200) diffraction peak (20=42.9°) using Scherrer formula, while for Mg(OH)₂ the peak at 2 θ =58.8° corresponding to reflection plane (110) was used to determine the mean size of crystallites. The values are included in Table 1, together with some other parameters related to textural and structural properties. As it was expected, the thermal decomposition of Mg(OH)₂ resulted in the formation of MgO particles of a much smaller size which is in good agreement with other reported observations.[38,39] This was also reflected in the increase in the measured surface area (from 17 m²/g to 105 m²/g, Table 1). The subsequent incorporation of metal NPs to the MgO support caused again some evident changes in the structure and texture of the material (Figure 2, Table 1). The bifunctional Pd/Mg catalyst showed the characteristic peaks of brucite structure of Mg(OH)₂, which confirmed that aqueous impregnation transformed MgO back to Mg(OH)₂ as a consequence of its interaction with water.^[40] Although it can be observed that the main peak at ~43° corresponding to residual MgO was also present in the sample. It should be noted that the conversion of MgO into Mg(OH)₂ during the impregnation procedure to incorporate the metal caused a decrease in the surface area as well as in the pore volume with respect to the starting MgO and this is in agreement with other authors' findings^[39,40] (Table 1). The distinct peaks of the Pd NPs (JCPDS card 001-1201) were detected at 20 of 40.4, 46.8, 68.4 and 82.4°.



Figure 2. XRD pattern of Pd/Mg catalyst. For comparison purposes the patterns of the starting $Mg(OH)_2$ and MgO are also represented.

In Figure 3 the XRD pattern of the Pd/Mg-HSAG catalyst is represented. As can be observed, reflections corresponding to

metallic Pd were detected and the diffractogram confirmed that incorporation of Pd NPs during the synthesis procedure converted the MgO in $Mg(OH)_2$ as was previously observed with the massive Pd/Mg catalyst.



Figure 3. XRD pattern of Pd/Mg-HSAG catalyst. For comparison purposes the patterns of the supports Mg-HSAG and HSAG are also represented.

In Figure 4 the XRD patterns of Pd/Mg and Pd/Mg-HSAG treated and not in helium at 723 K prior to hydrogen reduction at 573 K are shown. As can be observed for both catalysts, the thermal treatment at 723 K after deposition of Pd NPs, decomposed Mg(OH)₂ to MgO as the reflections corresponding to Mg(OH)₂ disappear. The diffraction patterns show sharper palladium peaks after thermal treatment, implying an increase of particle size, which is more evident for the Pd/Mg-HSAG catalyst.

Table 1. Textural and structural parameters of supports and catalysts.								
SUPPORTS					CATALYSTS			
Sample	S _{BET} (m²/g)	Pore volume ^[a] (cm ³ /g)	MgO loading ^[b] (wt %)	Crystal size (nm)	Sample	S _{BET} (m²/g)	Pore volume (cm ³ /g)	Mg(OH) ₂ Crystal size ^[c] (nm)
Mg(OH) ₂	17	0.11	-	44 ^[c]	Pd/Mg	41	0.23	17
MgO	105	0.39	-	9.9 ^[d]	Pd/Mg-HSAG	224	0.54	22
Mg-HSAG	234	0.56	45	20 ^[d]	Pd/Mg*	166	-	-
					Pd/Mg-HSAG*	215	-	-

[a] BJH desorption pore volume. [b] Determined from thermogravimetric analysis in air. Crystallite size was determined applying Scherrer formula to [c] peak at $2\Theta = 58.8^{\circ}$ corresponding to Mg(OH)₂, [d] peak at $2\Theta = 42.9^{\circ}$ corresponding to MgO, * After thermal treatment in helium at 723K prior reduction with hydrogen.

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Figure 4. XRD patterns corresponding to A) Pd/Mg and B) Pd/Mg-HSAG catalysts a) thermally treated at 723 K and reduced at 573 K and b) directly reduced at 573 K.

In Figure 5 are represented the TEM images of the Pd catalysts and the corresponding histograms representing the particle size distribution are depicted in Figure 6. TEM micrographs confirmed the formation of metal nanoparticles during the activation process with hydrogen. The Pd catalysts supported over Mg have a Gaussian particle size distribution in which the maximum of the peak coincides with the average Pd particle size. The combination of metal and Mg gave rise to bigger average Pd particle sizes (d=3.5-3.8, Fig.5b and 5d) than that of Pd/HSAG (d=2.6 nm, Fig.5a). It is interesting to note that Pd/HSAG shows non Gaussian particle size distribution and that approximately 45% of the palladium particles has a diameter smaller than 2 nm (Fig.6). Additionally, the TEM study confirms the conclusions drawn from the X-ray study in which palladium peaks of larger intensity were observed for catalysts treated in helium at 723K. This thermal treatment has a remarkable effect on the particle size and its distribution, considering that both catalysts studied lose their Gaussian distribution and suffered an increase in the average particle size, noticing that approximately 15% of the particles have a diameter superior than 9 nm.

Figure 7a) represents the evolution of the differential heat of adsorption of CO_2 with the surface coverage of $Mg(OH)_2$ and MgO. The increase in the CO_2 uptake is accompanied by a continuous decrease in the differential heat from initial values around 125 kJ/mol to ~40 kJ/mol, this last value is attributed to the limit between chemical and physical for CO_2 adsorption.^[41] The differential heats of adsorption indicate the basic strength of the adsorption sites; thus this figure points out to a heterogeneous basic sites strength distribution. Attending to the differences in the strength of the adsorption sites of CO_2 , three

types of basic sites have been established: strong basic sites (Q_{diff}>90 KJ/mol), medium-strength basic sites (90>Q_{diff}>60 KJ/mol) and weak-strength basic sites (Qdiff<60 KJ/mol). The total amount of basic sites and the corresponding percentage of each type for every sample are summarized in Table 2. As reported in Table 2, Mg(OH)₂ and MgO have identical total quantity of basic sites and quite similar strength distribution and heats of adsorption, presumably due to Mg(OH)₂ being degasified at 623K for 10 hours prior to calorimetric measurements, conditions that lead to the formation of MgO as reveled in the XRD patterns (do not shown for the sake of brevity). While exhibiting quite comparable evolution of the differential heat of adsorption to MgO, a decrease in the total amount of basic sites was observed for samples containing Pd (Fig.7b), which may be due to the hydroxylation of MgO surface that takes place during wetness impregnation with the acidic aqueous palladium nitrate solution.^[42] However, the calorimetry study of Pd/Mg and Pd/Mg-HSAG after thermal treatment at 723K (Fig.7c) showed higher heats of adsorption at initial values of surface CO₂ coverage, which implies a considerable strengthening of strong basic sites compared to the other samples and even MgO. Probably this effect is due to metalsupport interaction at high temperatures, as it was previously reported.^[43-47] Particularly, Ueda et al^[43-45] observed that the addition of metals has a remarkable effect in the basic surface of MgO, revealing that the incorporation of metal atoms causes a distortion in the lattice, the expansion of Mg-O bond length and the localization of electron on oxygen atom. As a result, the combination of M-MgO exhibits higher basic properties.

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Figure 5. TEM images of a) Pd/HSAG, b) Pd/Mg, c) Pd/Mg-HSAG, d) Pd/Mg*, e) Pd/Mg-HSAG* catalysts. *Thermally treated in helium at 723K prior reduction with hydrogen.



Figure 6. Particle size distribution of Pd determined from TEM micrographs of the different catalysts.

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Figure 7. Differential heats of CO2 adsorption vs. coverage at 323 K. a) Mg(OH)2 and MgO b) Pd bifunctional catalysts c) Pd bifunctional catalysts* Thermally treated in helium at 723K prior reduction with hydrogen.

	Total	Ba	ution		
0 la	µmol CO ₂ /g	% Strong	% Medium-	% Weak- strength (60>Q _{diff} >40 kJ/mol)	
Sample	(Q _{diff} > 40	sites	strength		
	kJ/mol)	(Qdiff>90 kJ/mol)	(90>Qdiff>00 kJ/mol)		
Mg(OH) ₂	487	51	38	11	
MgO	488	58	32	10	
Pd/Mg	374	47	41	12	
Pd/Mg-HSAG	295	47	38	15	
Pd/Mg*	411	61	29	10	
Pd/Mg-HSAG*	214	68	22	10	

Catalytic tests. First of all, a blank experiment without catalyst showed no ethanol conversion after 6h at 503 K, which indicated the reaction can barely take place in absence of a catalyst. Table 3 summarizes the catalytic parameters obtained with the support Mg-HSAG, as well as with the studied bifunctional catalysts reduced at 573 K and those samples previously treated in helium at 723K. In general, the main products detected were 1-butanol (ButOH), acetaldehyde (Ac), diethyl ether (DEE), carbon monoxide and methane. Other products such as acetone and 1,1-diethoxy ethane, ethyl acetate, 2-butanone, diethoxy butane, butanal, 2-butenal, 2-butanol, 2-ethyl-1-butanol, 1hexanol, 1-octanol, 2-ethyl-1-hexanol were observed in low quantities. The detection of 1,1-diethoxy ethane, ethyl acetate and other higher alcohols (>C4), is in agreement with other author reports for the continuous condensation of ethanol.[17,48-51]

Table 3. Catalytic activity and product selectivities obtained at 503 K and 50 bar after 24 h on stream.									
Comple	Average particle	Conv. (%)	()						
Sample	size (nm)		ButOH	Ac	DEE	CO	CH ₄	Acetone	Others ^[a]
Mg-HSAG	- 7	0.5	0	8	73	-	-	0	19
Pd/HSAG	2.6	4.5	0	2	37	10	14	30	7
Pd/Mg	3.5	17	34	13	27	4	5	0.0	17
Pd/Mg-HSAG	3.8	19	41	15	25	5	6	0.9	7
Pd/Mg*	5.9	22	43	13	1	6	7	1	29
Pd/Mg-HSAG*	6.4	17	54	13	< 1	4	6	<1	22

Ac - Acetaldehvde, DEE - Diethyl ether, ButOH - 1-Butanol, [a] Other products also detected in low quantities; 1.1-diethoxy ethane, ethyl acetate, 1-Hexanol, 2butanona, diethoxy butane, 1-octanol, butanal, 2-butenal, 2-butenol, 2-butanol, 2-ethyl-1-butanol, 1-octanol, 2-ethyl-1-hexanol. * After thermal treatment in helium at 723K prior reduction with hydrogen.



Figure 8. Conversion and 1-butanol selectivity through 24 hours of reaction. * After thermal treatment in helium at 723K prior reduction with hydrogen.

The bifuncional catalyst proved to be very stable during 24 hours of reaction in terms of conversion and selectivity (Fig. 8) So, after the maximum in conversion is reached at hour 2-3 the catalysts suffer a slight deactivation but after 10 h the reaction achieves the steady state conditions.

The presence of the main reaction products can be explained by the different reaction pathways represented in Fig. 9. Briefly, acetaldehyde is the primary dehydrogenation (R1) product which can undergo subsequent condensation reactions: reacting with another two ethanol molecules giving rise to 1,1-diethoxy ethane (R2) or with another acetaldehyde molecule yielding 3hydroxybutanal (R3), which readily dehydrates to 2-butenal (R4). According to literature, the first condensation is the acidcatalyzed acetylation reaction^[52] while the second one is the base-catalyzed aldol condensation.^[1,40,53] Subsequent hydrogenations of 2-butenal give rise to the desired product 1butanol (R5-6).

1-butanol can also react with unreacted ethanol to form C6 alcohols like 1-hexanol^[15] whose presence in our product stream is higher as the higher the selectivity of 1-butanol is. So Pd/Mg, Pd/Mg-HSAG, Pd/Mg* and Pd/Mg-HSAG* samples shows correspondently 2, 4, 4 and 5% hexanol selectivities, respectively, whereas the corresponding 1-butanol selectivities are 34, 41, 43 and 54% (Table 3).

Diethyl ether is the product of the acid-catalyzed direct ethanol dehydration (R7)^[28,53,54] while methane and carbon monoxide are obtained by metal-catalyzed acetaldehyde decarbonylation (R8).^[55] The presence of Mg in the Pd catalysts reduces considerably the formation of diethyl ether, methane and carbon monoxide, as can be seen in Table 3, presumably because the acid sites of the HSAG support are covered by Mg. Moreover, the selectivity of diethyl ether drops remarkably with Pd catalysts thermally treated in helium at 723 K prior to hydrogen reduction (Table 3), which is in agreement with the XRD and calorimetry studies where it is observed that the interaction of Pd and MgO at this temperature involve a strengthening of the basic sites. Thus the MgO covering the HSAG acid sites has an important role in the decrease of acetone formation. This undesired

product can be obtained via i) decarbonylation and dehydrogenation of 3-hydroxybutanal (R9), which also leads to carbon monoxide and hydrogen formation, and ii) ketonization of acetic acid (R10), product of ethyl acetate hydrolysis.^[53] The former of these two routes is unlikely taking place, as dehydration of 3-hydroxybutanal should predominate. The second route is plausible since carbon dioxide (the other product of acetic acid ketonization) is detected, while acetic acid could not be seen due to the low sensibility of the FID detector. The acetone formation is favored in the Pd-HSAG catalyst, whereas the presence of Mg in Pd/Mg-HSAG reduces considerably this by-product (Table 3).

The first step in the Guerbet route mechanism is dehydrogenation. According to literature, [^{19,20,56]} dehydrogenation of ethanol to acetaldehyde over metal oxides takes place over basic medium-strength Mg²⁺-O²⁻ pairs, which are predominant in MgO with respect to Mg(OH)₂. Aldol condensation of adsorbed acetaldehyde is faster than dehydrogenation^[31,57] and also implies acid-base pairs as well as high quantity of basic sites.^[19] The presence of trace amounts of 2-butenal, crotyl alcohol and butanal among the reaction products suggests that with our catalysts the reaction pathway follows the Guerbet route.

As can be seen in Table 3, Mg-HSAG showed negligible conversion meanwhile Pd-HSAG exhibited no selectivity to 1butanol. Based on the catalytic tests, the metal/Mg combination is compulsory to obtain good 1-butanol yields. The incorporation of Pd to Mg highly improved the catalytic performance in the condensation of ethanol, because transition metals have better dehydrogenation properties than metal oxides.^[58] Comparison of Pd/Mg catalyst with that supported over HSAG (Pd/Mg-HSAG) reveals that for a very similar conversion (17% and 19%, respectively) the latter gives a higher selectivity towards 1butanol production 34% and 41%, respectively (Table 3). The differences in the catalytic performance between Pd/Mg and Pd/Mg-HSAG can not be ascribed to different basicity properties determined by CO₂ chemisorption as both catalysts have similar percentage of strong surface basic sites (47%). Moreover, the average Pd particle size of the two samples is very close, 3.5

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nm and 3.8 nm for Pd/Mg and Pd/Mg-HSAG, respectively. Therefore, we can speculate about some additional effect of the graphite support which has not been identify by the characterization techniques used but is observed in the increased catalytic selectivity towards 1-butanol. Likely the graphite support makes possible to maximize the interaction between Pd atoms and the strong basic sites of the MgO originating cooperative sites for the tandem reaction. In addition,

the Pd/Mg-HSAG catalyst shows a 2-butenal selectivity of 3% while the selectivity with Pd/Mg is 1%, confirming the greater tendency of Pd/Mg-HSAG to catalyze reactions that require coupled Pd atoms and stronger basic surface sites, since 2-butenal is the product of the base catalyzed aldol condensation of acetaldehyde, and an intermediate in the formation of 1-butanol.



Figure 9. Reaction scheme proposed for ethanol condensation reaction in the liquid phase.^[23]

Catalyst treated in helium at 723 K, in particular Pd/Mg-HSAG, exhibited the best catalytic behavior in terms of 1-butanol selectivity, which coincides with the tendency observed in Table 2 where these catalysts showed higher amount of strong basic

sites than their counterparts. The selectivity towards 1-butanol increased from 34% with Pd/Mg up to 43% after thermal treatment with helium (Table 3). This effect is even more remarkable with Pd/Mg-HSAG, in which 1-butanol selectivity

increases from 41% up to 54%, and it is in accordance with other results reported in bibliography using Ni–MgAlO catalysts^[59] that exhibit conversion and selectivity of 19 and 55%, respectively. In order to rationalize these findings, the type and quantity of active sites involved in the reaction must be analyzed. Concerning basic sites, it is worth mentioning that quite similar basic strength distribution was found in both catalysts after thermal treatment as revealed the Q_{diff} profiles (Fig.5c), suggesting that both catalysts preserve the nature of active sites (same strength of basic sites) for aldol-condensation step. However, the total quantity of strong basic sites measured as CO₂ chemisorbed was 42% lower in Pd/Mg-HSAG than in Pd/Mg after treatment with helium (Table 2) at 723 K.

Based on the microscopy results and catalytic tests, Pd particle size is not critic to achieve Pd-Mg bifunctionality, but it possibly has an effect in ethanol conversion. As it has already been mentioned, it is often claimed dehydrogenation of ethanol to acetaldehvde is the limit step in Guerbet reactions, so this would explain the differences between the Pd catalysts. TEM images (Fig. 5) show quite comparable average particle size for Pd/Mg and Pd/Mg-HSAG catalysts as well as fairly similar particle size distributions (Fig. 6) and ethanol conversion results (Table 3). Nevertheless, the catalyst treated at 723 K showed higher average particle size than their counterparts and considerably different conversion values: Pd/Mg* has lower particle size (5.9 nm) than Pd/Mg-HSAG* (6.4 nm), whereas ethanol conversion is higher for the former (22%) than the latter (19%). On the other hand, it should be remarked that our Pd catalysts are able to dehydrogenated ethanol at relativekly lower reaction temperatures, 503 K, than in the case of non-metallic catalysts. for instance hydroxyapatite, which work minimum at 573K.[60]



Figure 10. Site time yield (%) for bifunctional catalyst after 24 hours of reaction. *After thermal treatment in helium at 723K prior reduction with hydrogen.

Figure 10 shows STY (%) for Pd-Mg catalysts based on the number of strong basic sites per gram. Considerable increase of this parameter is observed when catalysts are supported over HSAG and for those treated in helium at 723K in comparison with their counterparts. These tendencies are in consonance with 1-butanol selectivity results, which have great dependence with the catalyst strong basic sites distribution.

Conclusions

The synthesis of 1-butanol from ethanol through the acetaldehyde condensation has been studied in a fixed-bed gas continuous reactor using bifunctional heterogeneous systems based on Pd nanoparticles and magnesium oxide, which incorporated basic properties, supported or not on high surface area graphite. Pd/Mg catalysts supported on graphite were the most selective to 1-butanol, while the thermal treatment in helium at 723 K played an important role on the selectivity of the catalysts for the Guerbet condensation reaction of ethanol. Characterization of the active sites by microcalotrimetry of CO₂ chemisorption (depicting basic sites provided by MgO) and TEM analysis (reveling dehydrogenating/hydrogenating properties related to Pd particle size) allowed us to explain the differences displayed in the catalytic performance. Catalysts treated in helium at 723 K exhibited the best catalytic behavior in terms of 1-butanol selectivity, in particular Pd/Mg-HSAG* material, whose amount of strong basic sites is the highest among the catalysts studied, whereas its larger Pd particle sizes have a slightly negative impact in ethanol conversion. As the condensation of ethanol to 1-butanol is a tandem reaction, ethanol conversion is not only dependent on the size of Pd particles, but also on the efficiency of aldol condensation and hydrogenation over stronger MgO basic sites. Thus the compromise between both parameters in the catalysts, after adequate thermal treatment, gives rise to higher 1-butanol yields.

Experimental Section

Synthesis of the bifunctional catalysts

Preparation of the supports. The support MgO was obtained by calcination at 723 K of a commercial Mg(OH)₂ (Fluka, S_{BET}=17 m²/g). The Mg-carbon materials were prepared by a deposition-precipitation method. The carbon support (HSAG) was suspended by constant stirring in a solution containing the necessary quantity of nitrate magnesium precursor (Mg(NO₃)₂·6H₂O, Sigma Aldrich) to incorporate a 50 wt% of final MgO loading to the support. The pH was adjusted to 11 with NaOH and the final solution was kept stirring for 1 h. After that, the resulting material was centrifuged several times, and dried at 383 K. Thereafter it was treated in a horizontal furnace using a N₂ flow with a heating rate of 5 K/min until 873 K, giving rise to the support Mg-HSAG. **Deposition of metallic Pd nanoparticles on the supports.** The incorporation of metallic palladium nanoparticles (NPs) was done by the wetness impregnation technique using an aqueous solution of $Pd(NO_3)_2 \cdot 2H_2O$ (Sigma Aldrich) with the adequate concentration to incorporate a metal loading of 5 wt% on the support (MgO or Mg-HSAG). The resulting materials were dried in air at 383 K overnight. Finally, the samples were treated at 573K for 1 h under flowing hydrogen (20 mL_{STP}/min).

Catalysts characterization

Structural properties of the supports and the catalysts were determined by X-ray diffraction (XRD), using a Polycristal X'Pert Pro PANalytical diffractometer with Ni-filtered Cu/K radiation (λ = 1.54 Å) operating at 45 kV and 40 mA. For each sample, Bragg's angles between 4° and 90° were scanned at a rate of 0.04°/s.

Values of specific surface area (S_{BET}) and average volume diameter of the supports as well as those of the catalysts were determined by N₂ adsorption-desorption isotherms at 77K in an automatic volumetric adsorption apparatus (Micromeritics ASAP 2010). Prior to nitrogen adsorption, the samples were outgassed for 5 h at 423 K.

To obtain information on the particle size and distribution of metal NPs on the different supports, the catalysts were subjected to a detailed transmission electron microscopy (TEM) study. TEM micrographs were obtained on a JEOL JEM-2100F microscope at 200 kV. The samples were ground and ultrasonically suspended in ethanol before deposition over a copper grid with carbon coated layers. The mean diameter (d) of Pd particles was calculated based on a minimum of 300 particles, using the following equation where n_i is the number of particles with diameter d:

$$d = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

The amount and strength of the basic sites were determined by CO_2 adsorption using a volumetric equipment described in detail in a previous work.^[61] Successive doses of CO_2 were introduced into the system at 323 K to titrate the surface of the catalysts until a final pressure of 7 Torr was reached. Prior to the measurements, aliquots (200 mg) of the materials were pretreated for 10 hours under vacuum at 623 K and outgassed overnight. The differential heats of adsorption (Q_{diff}) were obtained as the ratio between the exothermic integrated values of each pulse and the adsorbed amount of CO_2 .

Catalytic reaction

The reactions were performed in a fixed bed reactor operated in gas phase at 503 K and 50 bar using a stream of helium and ethanol. Catalysts (0.5 g) were reduced in-situ with hydrogen at 573 K for 1 h before reaction. In order to study the influence of calcination temperature, two additional experiments were carried out with catalysts Pd/Mg and Pd/Mg-HSAG, therefore they were also treated in helium at 723 K for 1 h prior reduction with hydrogen. For all experiments, helium flow rate during reaction was 50 mL_{STP}/min and ethanol flow rate was adjusted to 0.02

mL/min with a HPLC-pump. Condensed products were collected and analyzed by gas chromatography (GC) while gas products were analyzed by on-line GC. The analysis of the collected reaction products was carried out with a gas chromatograph (Bruker Scion 436) equipped with a FID detector and configured with a capilar column BR-Swax. The temperature program for GC separation was hold at 50°C for 1 minute, ramp to 150°C at 15°C/min and hold at 150°C for 3.61 min (total=12 min). The analysis of gaseous products was carried out with two gas cromatographs (Varian CP 3380) equipped with FID and TCD detectors and configured with a capilar column SupelQ Plot and 60/80 Carboxen-1000 column, respectively. The temperature program for GC-FID separation was ramp from 35 to 51°C at 2°C/min and hold at 51°C for 1 min, then ramp to 200°C at 16°C/min and hold at 200°C for 7 min (total = 25 min). For the GC-TCD, the temperature program was hold at 50°C for 3 minutes, ramp to 150 at 5°C/min and then to 225 at 20 °C/min (total = 26.75 min). Calibration of the possible reaction products was done with commercial standards. After 24 hours of reaction time, the ethanol conversion X_{EtOH} is calculated using the following equation:

$$Y_{EtOH} (\%) = \frac{\sum_{i} n_{i} mol_{i}}{2mol'_{EtOH} + \sum_{i} n_{i} mol_{i}} \cdot 100$$

Where n_i is the number of carbon atoms of the product *i*, mol_i is the number of mol of the product *i*, and mol_{EtOH} is the number of mol of unreacted ethanol.

The selectivity to a specific product was defined as follows:

$$S_i(\%) = \frac{n_i mol_i}{\Sigma_i n_i mol_i} \cdot 100$$

The carbon balance (C%), which resulted higher than 90%, was defined as:

$$C(\%) = \frac{\Sigma_i n_i mol_i + 2mol'_{EtOH}}{2mol_{EtOH}} \cdot 100$$

In addition, site time yield STY (%) of butanol was defined as:

$$STY(\%) = \frac{\mu mol ButOH}{\mu mol CO_2/g} (> 90 \frac{KJ}{mol}) \cdot 100$$

Where µmol ButOH/h·g is the number of 1-butanol produced per hour and per gram of catalyst, and µmol CO₂/g (> 90 KJ/mol) is the number of µmol CO₂ absorbed per gram of catalyst with heat of adsorption superior than 90 KJ/mol, which correspond to the strong basic sites.

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Keywords: bioethanol • biobutanol • basic sites • bifunctional catalyst • metal nanoparticle

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