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Synthesis of different ZnO-supported metal systems through microemulsion technique and application to catalytic transformation of glycerol to acetol and 1,2-propanediol



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ABSTRACT

Different systems consisting of diverse metals (Au, Pt, Pd, Rh) supported on ZnO (5% by weight) were synthesized through the microemulsion technique (ME) and tested for glycerol hydrogenolysis, the main products being hydroxyacetone (acetol) and 1,2-propanediol (1,2-PDO). The solids synthesized using sodium borohydride as the reducing agent (B series) had smaller particle sizes as compared to the use of hydrazine (H series) which, in turn, resulted in a better catalytic performance. This synthetic method allowed us to obtain similar metal particle sizes (2–4 nm) for Pt, Pd and Rh solids in B series, whereas average gold metal particle was higher (>8 nm) which probably accounts for Au-containing systems being inactive under our experimental conditions. Reactivity order followed the sequence Rh > Pt > Pd. A comparison of the systems synthesized in the present paper through ME technique with those obtained in a previous work through the deposition–precipitation process revealed a higher activity and selectivity to acetol for the former solids which could be related to the presence of surfactant. Moreover, results suggested that metal sites could participate not only in hydrogenation of acetol to 1,2-propanediol but also in the previous dehydration step of glycerol to acetol.

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1. Introduction

Glycerol is a byproduct obtained during production of biodiesel through transesterification of vegetable oils. Approximately 10% weight of the converted feedstock is released as glycerol which makes its possible valorization an interesting issue. One possibility is its catalytic transformation on different metals under hydrogen or inert atmosphere. One of the chemicals produced from glycerol in neutral medium is 1,2-propanediol (PDO) resulting from a dehydration process (leading to hydroxyacetone or acetol) followed by a hydrogenation step. 1,2-PDO can be used as antifreeze, in food industry or as feedstock in the preparation of polyester resins for film and fiber manufacture [1]. As for acetol, it is used as an interesting organic intermediate to produce polyols and acrolein, in food industry to give aroma to food, in textiles or in cosmetic industry as skin tanning agent [2]. Some of the metals used in the transformation of glycerol into 1,2-PDO include Cu [3-5], and noble metals such as Ir [6], Ru [7–9], Rh [10,11], Pd [10,12] or Pt [13,14].

In a previous study [14], different reducible oxides (TiO₂, ZnO, SnO₂ and ZrO₂) were screened as support for platinum and tested for glycerol hydrogenolysis, ZnO being the solid with the highest selectivity to 1,2-PDO. This prompted us to select ZnO as the support for diverse metals (Pt, Rh, Pd and Au) which were incorporated through the deposition-precipitation technique in a nominal content of 5% by weight. All the solids exhibited the best catalytic performance on reduction treatment at 200 °C whereas higher temperatures led to the formation of a metal-Zn alloy which under our experimental conditions was detrimental to activity. Catalytic activity followed the sequence Pt>Rh>Pd>>Au. However, XRD and TEM studies revealed quite different metal particle sizes, for Pt and Rh as compared to Pd and Au (3.1, 3.7, 15 and 12 nm, respectively). Therefore, it was not clear to what extent catalytic results had been influenced by the different metal particle size. In order to cast further light on that, in the present study a new synthesis under similar conditions (same metal precursor, support and metal content) is carried out by the microemulsion technique.

A microemulsion (ME) is a thermodynamically stable colloidal dispersion in which two immiscible liquids (polar and non-polar) form nanosized droplets dispersed in a continuous phase and stabilized by a third component: the surfactant. These nanodroplets



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can be used as nanoreactors to synthesize metal particles in a very narrow particle size range. There are several reviews on the preparation of nanoparticles of noble metals through this technique and their application as catalyst to several processes [15–18]. Basically, some of the crucial parameters to be considered are the type of surfactant (anionic, cationic or non-ionic, the latter normally being less sensitive to temperature), the oil phase (oil-surfactant interaction influences the shape and size of microemulsion) or the concentration of metal solution (normally high concentrations lead to larger final metal particle sizes). The internal structure of the ME is determined by the relative fractions of these three constituents: surfactant, oil and water solution. The ME is only formed for certain ratios of the constituents, outside which a two-phase system is formed. The ratios for which the ME exists depend on the system, nature and polarity of the components, and changing these ratios the size of droplets are controlled and hence the final particle size. Another important point to be considered is the reducing agent which will lead to the formation of metallic particles, the most commonly used being hydrazine (N2H4) and sodium borohydride (NaBH₄). Typically a stoichiometric excess is used in order to ensure the full reduction of precursor salt. Furthermore, such an excess results in smaller metal particle sizes because the nucleation is favored over particle growth [19]. Others parameters influencing the process are temperature, speed of stirring or atmosphere, just to cite some of them.

2. Experimental

2.1. Materials

Synperonic 13/6.5 was a gift from Croda. All the other chemicals (2,2,4-trimethylpentane (99.9%, TMP), hydrazine monohydrate 98%, sodium borohydride 96%, 8 wt% H₂PtCl₆ aqueous solution, HAuCl₄, Pd(NO₃)₂, RhCl₃, ZnO nanopowder, acetone (technical grade), tetrahydrofuran (99.9%, THF), glycerol 99%, 1,2-propanediol 99.5%, 1,3-propanediol 98%, hydroxyacetone (acetol, 95%), ethylene glycol 99.5%, n-propanol 99.5%, acrolein (\geq 95%) and lactic acid \geq 85%) were purchased from Sigma–Aldrich. MilliQ water was used for preparation of the aqueous solutions of metal salts.

2.2. Synthesis of ZnO-supported systems

Fig. 1A summarizes the main steps for the preparation of the catalysts from a water in oil microemulsion (reverse micelle). The total amounts of reagents were calculated in order to obtain a nominal content of 5 wt% metal in 2 g of catalyst.

Under optimized conditions, the composition of microemulsions (ME) was surfactant: synperonic 13/6.5 (28.6 wt%), oil: trimethylpentane (TMP) (66.8 wt%), water: 2 wt% metal precursor salt (4.6 wt%).

As depicted in Fig. 1A, the synthesis began mixing the corresponding amounts of Synperonic 13/6.5 and TMP in a flask. The mixture was kept under vigorous stirring (1000 rpm) and then the water solution of precursor was added dropwise resulting in a transparent solution of microemulsion encapsulating the dissolved metallic precursor. ME was then deoxygenated bubbling N₂ for a couple of minutes and for the rest of the process an inert atmosphere was created with N₂. Afterwards, the reducing agent (NaBH₄ or N₂H₂), in a 1:5 molar ratio (metal: reducing agent) was added as a fresh water solution 10 M (maximum 1 min old). The color of solution changed from yellow (Pt, Pd and Au), red (Rh) to black just with the first drop of reducing agent solution. At that point, the metallic particle had already been formed and stabilized by surfactant. In order to ensure a full reduction of precursor the mixture was kept under stirring for 1 h. The inert atmosphere was then removed and the system was kept stirred one additional hour. The next step was the addition of the support (1.8 g ZnO) directly followed by acetone (50% weight of total ME) as destabilizing agent all at once. The suspension was kept stirring for 2 h for a full destabilization of the ME.

The suspension was then centrifuged (3000 rpm) for 15 min. A good indicative of a successful reduction and destabilization was that after separation of the solid, the liquid was transparent and colorless.

Then the solids were carefully washed with ethanol, acetone, cold water (at room temperature) and hot water (boiling water), three times each with half the weight of acetone employed for destabilization. Finally, the systems were dried for 12 h at 120 °C and when applicable calcined at 300 °C or 500 °C for 16 h (ramp of 1 °C/min) with a flow of synthetic air of 2 L/h.

Catalyst nomenclature includes the metal, the support (ZnO), the reducing agent (B or H for sodium borohydride or hydrazine, respectively) and the thermal treatment. Therefore, for instance, 'Pt/ZnO-H unred' denotes the platinum system synthesized through reduction with hydrazine and tested as synthesized (unreduced) whereas 'Pd/ZnO-B calc500 red 200' refers to the palladium solid obtained through reduction with NaBH₄ and submitted to calcination at 500 °C first followed by reduction at 200 °C.

For comparative purposes, the corresponding systems synthesized through the deposition–precipitation method using the same precursor salt, support and nominal metal content (5 wt%) were also tested in this study. Fig. 1B summarizes the main synthetic steps whereas full details on the synthesis and characterization of the catalysts can be found elsewhere [14]. The nomenclature of these systems is M/ZnO dp 200 where M refers to the metal, dp to the synthetic method (deposition–precipitation) and 200 to the reduction temperature ($200 \circ C$).

2.3. Characterization

Elemental analysis of metal-containing samples was performed by the staff at the Central Service for Research Support (SCAI) of the University of Córdoba. It was performed using inductively coupled plasma mass spectrometry (ICP-MS). Measurements were made on a Perkin-Elmer ELAN DRC-e instrument following dissolution of the sample in a 1:3 HNO₃/HCl mixture with a soft heating. Calibration was done by using PE Pure Plus atomic spectroscopy standards, also from Perkin-Elmer.

Surface areas of the solids were determined from nitrogen adsorption-desorption isotherms obtained at liquid nitrogen temperature on a Micromeritics ASAP-2010 instrument, using the Brunnauer–Emmett–Teller (BET) method. All samples were degassed to 0.1 Pa at 120 °C prior to measurement.

Transmission electron microscopy (TEM) images were obtained using a Philips CM-10 microscope. All samples were mounted on 3 mm holey carbon copper grids.

EDX measurements were performed on a JEOL JSM-6300 scanning electron microscope (SEM) equipped with an energydispersive X-ray (EDX) detector. It was operated at an acceleration voltage of 20 keV with a resolution of 65 eV.

X-ray patterns of all M/ZnO-B and M/ZnO-H samples (Fig. 3) were obtained on a Siemens D5005 X-ray diffractometer utilizing Cu K α radiation. A secondary monochromator was used. The metallic particle sizes were estimated by using the Scherrer formula assuming spherical crystallites. X-ray diffractograms of Pd/ZnO-B calcined/reduced at different temperatures (Fig. 8) were recorded on a Siemens D-5000 diffractometer equipped with a DACO-MP automatic control and data acquisition system. The instrument was equipped with a graphite monochromator and used Co K α radiation.



Fig. 1. Schematic representation of the synthetic procedure followed to obtain the different ZnO-supported metal systems through microemulsion technique (A) and deposition–precipitation method (B).

X-ray photoelectron spectroscopy (XPS) data were recorded on 4 mm × 4 mm pellets 0.5 mm thick that were obtained by gently pressing the powdered materials following outgassing to a pressure below about 2×10^{-8} Torr at 150 °C in the instrument pre-chamber to remove chemisorbed volatile species. The main chamber of the Leibold-Heraeus LHS10 spectrometer used, capable of operating down to less than 2×10^{-9} Torr, was equipped with an EA-200MCD hemispherical electron analyser with a dual X-ray source using Mg K α (hv = 1253.6 eV) at 120 W, at 30 mA, with C(1s) as energy reference (284.6 eV).

Surface acidity was determined by thermal programmed desorption (TPD) of pyridine previously adsorbed on the solids monitored by TCD. An amount of 50 mg of sample was placed under a He stream flowing at 10 mL/min in a reactor 10 mm in diameter that was placed inside an oven. The He stream was used to clean the solids by heating to $350 \,^{\circ}$ C at a rate of $10 \,^{\circ}$ C/min and then cooling by thermal inertia to room temperature. At that point, the surface of the solid was saturated with the probe molecule for 30 min. Pyridine was supplied by bubbling the He stream through liquid pyridine at room temperature. After saturation, excess physisorbed probe substance was removed by passing a He stream at 10 mL/min for 1 h. Then, desorption was started by raising the temperature to 400 °C at 10 °C/min and holding the final level for 30 min.

2.4. Catalytic tests

Hydrogenolysis of glycerol was conducted in a Berghof HR-100 stainless steel high-pressure autoclave equipped with a 75 mL PTFE vessel and a magnetic stirrer. Under standard conditions, 20 mL of a 1.36 M solution of glycerol in water and 50 mg of catalyst were introduced in the vessel. Reactor was then purged with hydrogen and temperature (180 °C) and hydrogen pressure (6 bar) adjusted. The stirring rate was 1200 rpm. After 15 h of reaction, stirring was stopped and the vessel cooled in an ice bath. The catalyst was spindried and the liquid passed through a filter of PTFE 0.45 μ m. Then it was analyzed by GC-FID (Agilent Technologies 7890, with a Supelco 25357 NukoITM capillary column). Quantification was carried out through the corresponding calibration curves.

3. Results and discussion

As indicated in Section 2, the optimized composition of ME system was surfactant: Synperonic13/6.5 (28.6%), oil: trimethylpentane (66.8%), water: 2 wt% of precursor salt (4.6%). In order to find such a composition, different experiments were performed. It is important to point out that the relative fraction of the constituents of ME is a key feature to control the size of micelles and thus the final



Fig. 2. TEM micrographs of the different microemulsions after the addition of sodium borohydride.

metal particle size. With a view to optimize the process, different mixtures of surfactant and oil at room temperature were prepared. Then an aqueous solution of 1% and 2% weight (wt) of precursor was added dropwise in order to know the solubility limit. Determination of this limit is easy because the microemulsions are isotropic and transparent, and when they destabilize the transparent solution turns into a cloudy system. These experiments determined the region of relative fractions of constituents to form stable reverse micelles. Finally in order to simplify the process, the same system of microemulsion was applied to synthesize all catalysts once ensured that ME was stable for all metal precursors. Also in order to minimize the environmental impact, the system of choice was that in which less amount of surfactant and oil was required.

Fig. 2 shows the TEM micrographs of microemulsions of metallic particles (precursor reduced using NaBH₄). As can be seen, at this point the synthetic method ensured metal particles in the 2-4 nm range. Support (ZnO) was then added and microemulsions were destabilized using acetone. The solid was centrifuged and washed to obtain the different M/ZnO systems (M = Pt, Pd, Rh and Au). Some features concerning characterization of the systems are depicted in Table 1. Surface areas of all the systems are in the $15-17 \text{ m}^2/\text{g}$ range, quite similar to that of the support, ZnO (15 m²/g). Moreover, a comparison of metal nominal contents (5 wt%) with the values determined by ICP-MS evidences that the synthesis of metal particles through ME technique led to a low incorporation of rhodium (0.3%), a higher incorporation of platinum (1.2 and 2.9% for Pt/ZnO-B and Pt/ZnO-H, respectively) and the almost quantitative incorporation of palladium (4.4 and 4.5% for Pd/ZnO-B and Pd/ZnO-H, respectively). It is possible that the washing process of the solids resulted in the partial dissolution of the metals. In fact, ICP-MS monitoring of the washing process of Pt/ZnO-B solid confirmed that there was a progressive loss of platinum, especially during washing with cold water (that step accounts for ca. 53% Pt loss). However, subsequent treatment with hot water did not lead to any further loss thus confirming that the noble metal remained stabilized thereafter on the catalyst surface. Consequently, no significant metal leaching was observed during catalytic studies.

X-ray diffractograms of the systems are depicted in Fig. 3 and mean particle sizes, as determined from Scherrer equation are indicated in Table 1. From Fig. 3 and Table 1 it is clearly evident that the use of sodium borohydride as the reducing agent (B series) led to smaller metal particles as compared to the utilization of hydrazine (H series). Furthermore, hydrazine was not able to reduce rhodium which was clearly evident during the synthetic method, since unlike the other cases no change in the color of the microemulsion of RhCl₃ was observed when hydrazine was added. Finally, in all cases, and particularly for H series, destabilization of ME with acetone resulted in an increase in metal particle size which was especially dramatic in the case of gold. This testifies to the importance of the different steps (and in particular of ME destabilization) in the synthesis of metal nanoparticles through microemulsion. In order to try to obtain smaller gold metal particle sizes, different modifications were applied to the destabilization step, including the substitution of acetone by THF as the



Fig. 3. X-ray diffractograms of the different systems. Symbols indicate the signal corresponding to the metal: Au (circle), Pd (square) and Pt (triangle).

Table 1

Some features concerning characterization of the different ZnO-supported metal systems.

Catalyst ^a	Metal/ZnO weight%				BET surface ^b (m ² /g)	Mean particle size (nm)	
	Nominal	ICP-MS	EDAX	XPS		TEM	XRD ^c
Pt/ZnO-H	5	2.9	3.4	1.2	15	5.3	5.5
Pt/ZnO-H calc300			2.9	1.3	15	-	-
Pt/ZnOH calc500			-	1.3	15	-	-
Pt/ZnO-B			0.8	0.8	16	2.2	NS
Pt/ZnO-B calc300	5	1.2	0.6	0.6	16	-	-
Pt/ZnO-B calc500			-	0.7	16	-	-
Pt/ZnO dp 200	5	5.2	-	5.3	19	3.1	NS
Pd/ZnO-H			4.1	4.6	15	9.0	6.8
Pd/ZnO-H calc 300	5	4.5	2.8	-	15	-	12.2
Pd/ZnO-H calc 500			3.5	-	15	-	17.7
Pd/ZnO-B			5.3	3.6	16	3.0	NS
Pd/ZnO-B calc 300	5	4.4	4.8	3.4	16	-	7.4
Pd/ZnO-B calc 500			5.7	3.4	16	-	14.2
Pd/ZnO dp 200	5	4.1	-	0.9	17	-	15.0
Rh/ZnO-B	5	0.3	0.6	0.4	16	2.1	NS
Rh/ZnO-B calc 300			0.4	0.4	16	-	-
Rh/ZnO-B calc 500			-	0.3	16	-	-
Rh/ZnO dp 200	5	2.4	-	3.2	25	3.7	-

^a Rh/ZnO-H does not exist since hydrazine was not able to reduce Rh.

^b The support (ZnO) has a surface area of $15 \text{ m}^2 \text{ g}^{-1}$.

^c The measurement of particle sizes of calcined Pd samples corresponded to the peak of PdO at 2θ 39.9°. NS denotes that no signal of the metal was observed by XRD. Au/ZnO-B, Au/ZnO-H and Au/ZnO dp 200 exhibited average particle sizes of 19, 22 and 12 nm, respectively and were inactive for glycerol conversion under our experimental conditions. Therefore, no further characterization was performed.

destabilization agent and the modification of the order of addition of such an agent and ME. All in all, the smaller particle sizes (8 nm) were obtained when ME was added dropwise into a suspension of the support of acetone under vigorous stirring.

TEM micrographs of the different solids after destabilization, filtration and calcination confirmed XRD results. Therefore, B series (Fig. 4 and Table 1) presented metal particle sizes in the 2–4 nm range, the exception being gold in which case bigger particles were obtained. It is also interesting to note the relatively low particle size interval obtained by ME synthetic method (see inset of Fig. 4 for Pt/ZnO-B).

The systems were then tested for glycerol hydrogenolysis. Results expressed as mol of glycerol converted per mol of metal and selectivity to 1,2-PDO after 15 h are summarized in Figs. 5 and 6. For comparative purposes, catalytic performance of the corresponding system synthesized through the deposition–precipitation method and reduced at 200 °C (M/ZnO dp 200) is also included. As can be seen, data for Rh/ZnO-H and Au/ZnO-B and Au/ZnO-H are absent. In the first case, as explained above, hydrazine was unable to reduce rhodium particles whereas gold systems were inactive for the reaction, probably as a result of their big particle size (above 8 nm).

Conversion of glycerol into 1,2 or 1,3-propanediol on bifunctional catalysts has been described to occur via dehydration followed by hydrogenation. Depending on the hydroxyl group in glycerol involved in the dehydrogenation (either primary or secondary), 1,2-PDO or 1,3-PDO are obtained, respectively (Scheme 1). Moreover, some other liquid (e.g. ethylene glycol, 1-propanol) and gaseous (e.g. methane, ethane and propane) by-products could be obtained [14]. In our case, under standard conditions (15 h of reaction, 180 °C, 6 bar H₂) all catalysts yielded acetol or 1,2-PDO mainly,



Fig. 4. TEM micrographs of the different M/ZnO-B solids.



Fig. 5. (A) Catalytic transformation of glycerol on Rh/ZnO-B solid (A) results for t=15 h. (B) Kinetic profile for Rh/ZnO-B uncalc 200. Reaction conditions: 50 mg catalysts, 5 mL 1.36 M water solution of glycerol. 180 °C and 6 bar of initial hydrogen pressure.

accounting for ca. 100% selectivity (Figs. 5 and 6) which confirms the dehydration through primary OH. For longer reaction times (i.e. conversions over ca. 20%), some other by-products were obtained though still 1,2-PDO and acetol accounted for over 90% selectivity (Fig. 5B).

The formation of dehydration products in water environment has already been described not only for glycerol transformation into acrolein or acetol [20] but also for some other processes (e.g. dehydration of fructose to 5-hydroxymethylfurfural (HMF)) [21]. There is some controversy in the literature concerning the nature



Fig. 6. Catalytic transformation of glycerol on several Pt and Pd solids. Reaction conditions: 50 mg catalysts, 20 mL 1.36 M water solution of glycerol. 180 °C and 6 bar of initial hydrogen pressure.



Scheme 1. Transformation routes of glycerol into 1,2-PDO or 1,3-PDO through an initial dehydration step.

of the active sites responsible for acetol formation. On the one hand, most of the papers report that dehydration of glycerol to acetol occurs on acid sites [10] although some other works describe the acetol formation on basic sites by a dehydrogenation process followed by dehydration and enolization [22]. In addition, redox properties of metal oxide catalysts could also influence the performance of those solids in the gas-phase dehydration of glycerol [23,24]. Subsequent hydrogenation of acetol on the metal catalysts gives 1,2-propanediol. Kim et al. [25] studying the gas-phase dehydration of glycerol over silica-alumina catalysts concluded that acrolein was formed on Brønsted acid sites whereas acetol vield was proportional to the concentration of Lewis acid sites. However, in batch processes and in an aqueous environment, Brønsted acid sites will be responsible for both acrolein and acetol production [26]. Moreover, a study of glycerol dehydration based on quantum mechanical calculations reported that neutral glycerol showed a high barrier to dehydration whereas protonated glycerol exhibited a much lower barrier for dehydration to acetol [27]. Density functional calculations indicate that glycerol dehydrates to either acetol or acrolein through alkoxide species formed by competitive adsorption of the primary or secondary glycerol OH groups, respectively (Scheme 1). The stronger adsorption mode of glycerol through the secondary OH group was responsible for the higher selectivity to acrole in at moderated temperatures [26]. On the other hand, some other authors conclude that the metal could be involved in the dehydration of glycerol to acetol. Sato et al. [28] found that dehydration of glycerol in gas phase occurred via Cu-alkoxide species formed by the release of an OH radical from the primary OH group. Similarly, Bienholz et al. [29] prepared a set of different silica supported copper catalysts and found a linear relationship between the specific copper surface and the catalytic activity not only in the hydrogenation of acetol to 1.2-PDO but also in the dehydration of glycerol to acetol thus suggesting that both processes occurred at the copper surface. The influence of the metal in the dehydration step has been suggested for some other metals (e.g. Pt [30]). Nevertheless, Wang and Liu [31] working with Cu–ZnO catalysts in the batch conversion of glycerol to 1,2-PDO found that the dehydration step to acetol was carried out on the ZnO acidic surface and the subsequent hydrogenation of acetol to 1,2-PDO takes place in the Cu domains. Furthermore, the activation energy for acetol hydrogenation is about 30 kJ lower than that of glycerol dehydration [32] and therefore dehydration step determines the overall

glycerol conversion while hydrogenation by Cu is responsible for the final selectivity to 1,2-PDO [31,32].

In our study, different preliminary experiments were conducted in order to ensure that M/ZnO solids catalyzed the formation of both acetol and 1,2-PDO. First of all, a blank experiment (1.36 M glycerol, no catalyst) showed that glycerol was stable under reaction conditions. Pure ZnO was then tested as the catalyst and again glycerol was not transformed evidencing that, even though transformation of glycerol into acetol is a simple dehydration process, ZnO cannot catalyze the process under our experimental conditions. Finally, a 1.36 M solution of acetol in water was submitted to the reaction conditions and acetol did not rehydrate. These results seems to support the hypothesis of metal sites participating in both dehydration to acetol and subsequent hydrogenation to 1,2-PDO or, at least, that incorporation of the metal to the ZnO creates a new population of acid sites able to dehydrate the glycerol to acetol.

In order to cast further light on the nature of active sites responsible for formation of acetol, acidity of several systems was determined by thermal programmed desorption (TPD) of preadsorbed pyridine (Fig. 7). As can be seen, the support (ZnO) did not exhibit any peak which could account for its inactivity in



Fig. 7. TPD profile of pre-adsorbed pyridine for some of the Pt-based solids.



Fig. 8. (A) Chemical structure of the surfactant (Synperonic 13/6.5). (B) TG analysis of Pd/ZnO-B and relative percentage of carbon associated to C—O species (from C1s signal by XPS). (C) X-ray diffractograms of Pd/ZnO-B under different thermal treatments.

the process. On the contrary, Pt/ZnO systems synthesized through deposition–precipitation technique, exhibited well-defined pyridine desorption peaks which evidences the existence of acid sites which in turn could result in their observed activity. Those acid sites could originate from the platinum precursor (chloroplatinic acid) [33]. In fact, a comparison of Pt/ZnO dp unred and Pt/ZnO dp 200 systems shows the loss of the peak appearing at higher temperature (ca. $300 \,^{\circ}$ C) in the latter which could be due to the release of chloride during reduction pretreatment as HCl.

Interestingly, despite the fact that Pt/ZnO solids obtained through microemulsion technique did not exhibit any pyridine peak, they were active in glycerol conversion. This could be supportive of the above-mentioned role of metal sites in dehydration of glycerol to acetol. Nevertheless, the possibility of some influence of remaining surfactant or even the existence of low-acidity active sites (not titrated with pyridine) cannot be ruled out.

Results achieved for platinum (Pt/ZnO-B and Pt/ZnO-H), palladium (Pd/ZnO-B and Pd/ZnO-H) and rhodium (Rh/ZnO-B) solids are summarized in Figs. 5 and 6. In all cases B series led to better catalytic results as compared to H series. The lower metal particle sizes (as evidenced by XRD and TEM, see Table 1) in the former case can account for that. Focusing on B series, reactivity order follows the sequence Rh > Pt > Pd. In our previous study on systems synthesized through the deposition–precipitation method [14], palladium was also found to be the least active system though its greater particle size as compared to that of Rh and Pt (22 nm and 3–4 nm, respectively) could explain such catalytic results. In the present work ME technique allowed us to better control metal particle sizes (2–4 nm for all Pt, Pd and Rh in M/ZnO-B series) which confirms that under our experimental conditions Pd is less active.

Focusing on B-series, the best catalytic results for each metal corresponds to Pt/ZnO-B calc300 unred (510 mol glycerol/mol of metal, 87% selectivity to acetol), Pd/ZnO-B calc500 unred (279 mol glycerol/mol of metal, 51% selectivity acetol) and Rh/ZnO-B uncalc red 200 (800 mol glycerol/mol of metal, 91% selectivity to acetol). In the first case, catalytic activity is quite close to that of the corresponding DP counterpart (Pt/ZnO dp 200, 538 mol glycerol/mol Rh) whereas in the other two cases, synthesis through the ME method led to a significant improvement in activity (see Figs. 5A and 6). Furthermore, ME systems are comparatively more selective to acetol than their DP counterparts. If we assume a separate function of catalyst components (acidic and metallic) this would mean that in ME systems the metallic function is lower than in DP catalysts in which acetol is readily hydrogenated to 1,2-PDO. Some remaining surfactant in the surrounding of metallic particles could be the

reason for the low hydrogenating activity of the ME systems. Moreover, interestingly, despite the fact that as-synthesized M/ZnO-B systems consist of metal particles in the zero oxidation state, their optimum catalytic performance is achieved upon thermal pretreatment (calcination and/or reduction) normally at ca. 200-300 °C. In order to cast further light on the reason for that, different characterization studies were carried out. Fig. 8 shows the results for Pd/ZnO-B system. First, a thermogravimetric study (TG) of the system revealed that the solid exhibited a weight loss of ca. 22% upon calcination at temperatures up to 400 °C. This is probably due to decomposition of remaining surfactant. In fact, an XPS study of Pd/ZnO-B as synthesized and calcined at 300 °C and 500 °C in the C1s region (not shown) revealed the progressive decrease in the signal at 286.6 eV assigned to C-O species in alcohol and ether groups [34]. More interestingly, an XRD study of the system showed that smaller metal particles were obtained upon reduction for uncalcined systems as compared to previously calcined ones suggesting that the remaining surfactant prevents to a certain extent sintering of metal particles. Therefore, thermal treatment has two opposite effects on catalytic performance of M/ZnO-B solids. On the one hand, as temperature rises less surfactant remains which should be positive since metal particles are more accessible. On the other, thermal treatment results in an increase in particle size and appearance of strong metal-support interaction (SMSI) effect (at ca. 400 °C) which is detrimental to activity. It seems that there is an optimum temperature (ca. 200-300 °C) for which a compromise is reached.

4. Conclusions

ME technique is an adequate method to control metal particle size though it requires optimization of several parameters. The method allowed us to synthesize Pt, Pd and Rh systems with similar metal particle sizes (2–4 nm, B-series). NaBH₄ used as reducing agent gave smaller particle sizes than hydrazine thus accounting for the better catalytic performance in glycerol transformation to acetol and 1,2-PDO of B-series. Systems obtained through ME technique contained particles in the metal state though thermal treatment to temperatures in the 200–300 °C range led to an improvement of catalytic performance. As temperature rises there are two opposite effects. On the one hand, surfactant is removed which is positive to activity. On the other, progressive loss of surfactant favors sintering of metal particles and at 400 °C a metal-Zn alloy is formed both being detrimental to activity. In this sense, a compromise between both trends seems to be reached at temperatures of 200–300 °C. Reactivity order followed the sequence Rh > Pt > Pd and ME systems were found to be comparatively more selective to acetol than DP solids. This could be due to some remaining surfactant in the surroundings of metallic particles thus limiting their hydrogenation activity. Moreover, metal seems to participate both in dehydration of glycerol to acetol and the subsequent reduction to 1,2-PDO.

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