

2-Propanol dehydration and dehydrogenation on Pt/Al₂O₃ and Pt/Al₂O₃-CeO₂ catalysts

Deshidratación y deshidrogenación de 2-propanol en catalizadores de Pt/Al₂O₃ y Pt/Al₂O₃-CeO₂

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Received: February 8, 2021; Accepted: March 30, 2021

Abstract

A series of Pt-based catalysts were tested in 2-propanol dehydrogenation and dehydration reactions to produce mainly propylene and water plus acetone and hydrogen. Alumina and alumina-ceria catalytic supports (AC) were prepared by the sol-gel method. Pt catalysts were obtained by incipient-wetness impregnation (IWI), and characterized by atomic absorption spectroscopy (AAS), temperature-programmed reduction (TPR), and Fourier transform infrared spectroscopy (FTIR). It was found that the calcined catalysts (PtO_x/AC) increased the dehydration capacity when compared to their respective catalytic supports, both series with no appreciable dehydrogenation products. The reduced catalysts (Pt⁰/AC) showed high dehydrogenation activity in 2-propanol reactions, with high selectivity towards acetone and hydrogen at low temperatures. These catalytic systems present a change in selectivity towards propylene above 230 °C and the loss of activity of Pt-reduced species. This deactivation was related with the bands of asymmetric vibrations of C-H and C-O bonds in the post-reaction material characterized by FTIR, which have been attributed to either carbon deposition or oxygenated intermediates chemisorbed on the Pt surface. Moreover, the temperature range, where Pt⁰ is deactivated, is progressively shifted to higher values as the amount of ceria increases. This is attributed to the fact that ceria modifies the surface interactions of Pt sites with the molecules that cause deactivation. Catalysts were completely regenerated with a mild treatment under a N₂ flow at 500 °C.

Keywords: Pt/Al₂O₃-CeO₂, 2-propanol dehydrogenation, 2-propanol dehydration, Pt deactivation, Pt regeneration.

Resumen

Una serie de catalizadores de Pt se probó en reacciones de deshidrogenación y deshidratación de 2-propanol para producir principalmente propileno y agua más acetona e hidrógeno. Se prepararon soportes catalíticos de alúmina y alúmina-ceria (AC) mediante el método sol-gel. Los catalizadores de Pt se obtuvieron mediante impregnación húmeda incipiente (IWI) y se caracterizaron por espectroscopía de absorción atómica (AAS), reducción a temperatura programada (TPR) y espectroscopía infrarroja (FTIR). Se encontró que los catalizadores calcinados (PtO_x/AC) aumentaron la capacidad de deshidratación en comparación con sus respectivos soportes catalíticos, ambas series sin productos de deshidrogenación apreciables. Los catalizadores reducidos (Pt⁰/AC) mostraron alta actividad de deshidrogenación en reacciones de 2-propanol, con alta selectividad hacia acetona e hidrógeno a bajas temperaturas, presentando un cambio de selectividad hacia el propileno por encima de 230 °C y pérdida de actividad de las especies de Pt reducidas. Esta desactivación se relacionó con bandas de vibraciones asimétricas de los enlaces C-H y C-O en el material caracterizado post-reacción, atribuidas a la deposición de carbono o intermediarios oxigenados quimisorbidos en la superficie de Pt. El rango de temperatura donde el Pt⁰ se desactiva, se desplaza progresivamente a valores más altos a medida que aumenta la cantidad de ceria. Esto se atribuye que la ceria modifica las interacciones superficiales de los sitios Pt con las moléculas que provocan la desactivación. Los catalizadores se regeneraron completamente con un tratamiento a 500 °C en un flujo de N₂.

Palabras clave: Pt/Al₂O₃-CeO₂, deshidrogenación de 2-propanol, deshidratación de 2-propanol, desactivación de Pt, regeneración de Pt.

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Tel. 5558044648

<https://doi.org/10.24275/rmiq/Cat2360>

ISSN:1665-2738, issn-e: 2395-8472

1 Introduction

In the last decades, alcohol decomposition has been used as a catalytic test to determine the acidity and the basicity of novel materials (Rekoske and Barteau, 1997; Aramendía *et al.*, 1994). These reactions have been also employed as competitive-parallel reactions with many useful reaction products (Marek and Hanh, 1932; Wood *et al.*, 1972). Catalytic decomposition of alcohols using either noble metals or metal oxides are receiving attention due to their applicability to obtain both highly-demanded and/or valuable compounds; producing, olefins and water by dehydration and hydrogen and ketones or aldehydes by dehydrogenation (Marek and Hanh, 1932; Ertl *et al.*, 2008; Mayorga *et al.*, 2020). For instance, isopropanol decomposition has been studied with several catalysts, including Pt based catalysts, which have demonstrated high activity and selectivity towards hydrogen production (Karakuş *et al.*, 2013; Mostafa *et al.*, 2009).

More recently, second-generation biofuels have received attention due to their multiple applications in biomass-based processes, mainly for clean fuels and raw materials demanded as chemicals (Naik *et al.*, 2009). For instance, C₃-C₄ alcohols have been proposed as an alternative to conventional gasoline and diesel fuels (Agarwal, 2006; Surisetty *et al.*, 2011). International organizations include 2-propanol, 2-methyl-2-propanol and 2-methyl-1-propanol as alternative components of gasoline since they enhance octane number (Elvers, 2008; De Klerk, 2011). On the other hand, bio-alcohols could be produced by the catalytic conversion of glycerol, which is a by-product of biodiesel production. Once large-scale commercial biodiesel production takes place, excess glycerol would become available in large volume (Basu, 2018; Espinel-Ríos and Ruiz-Espinoza, 2019). Hence, catalytic conversion of glycerol to value-added propanols appears as a promising synthetic route, e.g. the selective hydrogenolysis of bio-glycerol to 1-propanol and 2-propanol using bifunctional Pd/MoO₃-Al₂O₃ catalysts (Samudrala and Bhattacharya, 2018). Thus, 2-propanol has a potential utility as solvent, biofuel, gasoline additive and feedstock.

Regarding 2-propanol as feedstock, its decomposition leads to obtain propylene and acetone, which are intermediate chemicals with a very high demand (Moulijn *et al.*, 2001) and also hydrogen, a clean fuel (Rostrup, 2001). In this respect, Mostafa

et al. (2009) conducted a study over the activity and selectivity of Pt-supported catalysts in the decomposition reactions of several alcohols. They reported Pt supported on zirconia in 2-propanol decomposition, showing some activity below 200 °C and an increase in the conversion and dehydrogenation selectivity above 200 °C. However, above 250 °C the catalytic activity abruptly decreases, and they attributed this deactivation to carbon deposition on the catalyst surface.

In a previous work (Pérez-Pastenes *et al.*, 2006), we reported that low amounts of ceria addition in alumina (2 and 5 wt% ceria) modify both textural and structural properties of alumina-ceria oxides using a specific sol-gel procedure. These materials were tested in the 2-propanol reaction and only the transformation of 2-propanol to propylene in the temperature range of 150-250 °C was observed. This was attributed to the presence of acid sites conducting alcohols dehydration following an E1 mechanism (Pérez-Pastenes *et al.*, 2006; Aramendía *et al.*, 1996). Also, a correlation between the 2-propanol reaction rate and the total acidity of alumina-ceria samples calculated by NH₃-TPD was reported. That study showed that the presence of ceria diminishes the activity in 2-propanol dehydration, i.e. as ceria amount increases the reaction rate decreases. More recently, we have found that with this sol-gel method, it is possible to obtain high amounts of 2-D surface ceria even in materials with high ceria loading, that is in the materials with 2 and 5 wt% ceria, all the ceria content is present as surface ceria (Pérez-Pastenes *et al.*, 2017). Alumina-ceria materials provide desirable combined properties, i.e. the high specific surface area of alumina (Knözinger and Ratnasamy, 1978; Zhu *et al.*, 2020), the capability of ceria to store/release oxygen (Trovarelli, 1996; Özkan *et al.*, 2020), the decrease in acidity due to ceria presence in the support and the high thermal stability of supports when ceria-alumina materials form mixed-oxides (Pérez-Pastenes *et al.*, 2006).

Hence, dehydrogenation and dehydration of 2-propanol have promissory applicability in the production of propylene, acetone and hydrogen. Nevertheless, only few studies using Pt catalysts have been reported and none of them using Pt/Al₂O₃-CeO₂. This work is devoted to the study of Pt supported on alumina and alumina-ceria carriers, in order to observe the effect of ceria on the activity and selectivity in the competing dehydration and dehydrogenation reaction system.

2 Materials and methods

2.1 Materials preparation

Alumina-ceria materials were prepared by the following sol-gel technique as previously reported (Pérez-Pastenes *et al.*, 2006): i) aluminum tri-sec-butoxide (Aldrich, 99.99%) was dissolved in 2-propanol (Baker, 99.5%) at 0 °C using a glass vessel, ii) HNO₃ (Aldrich, 69%) diluted in deionized water and Ce(NO₃)₃ (Aldrich, 99%) dissolved in 2-propanol were slowly added into the reactor. The molar ratios of (alkoxide+salt): alcohol:water:acid reactants were 1:65:30:0.2, iii) the obtained sols were aged for 24 hours and subsequently dried in vacuum at room temperature; gels were formed after about 72 hours as white monoliths with no appreciable syneresis, and iv) the dried materials were calcined with an air flow at 700 °C for 8 hours. The samples with 0, 2 and 5 wt. % of ceria in alumina-ceria oxides are identified as samples A, AC2 and AC5, respectively.

Pt supported on alumina and alumina-ceria catalysts were prepared by incipient-wetness impregnation (IWI) at room temperature to spread nominal 1% wt Pt. An aqueous solution of H₂PtCl₆ · 6H₂O was used. After impregnation, the materials were dried at 100 °C overnight and then calcined at 500 °C for 4 hours in static air. These catalytic systems are referred as calcined samples. A portion of these calcined material was subjected to a reduction treatment at 500 °C for 2 hours with a 60 cm³/min flow rate of H₂ (Praxair, 99.99%). These are referred as reduced catalytic systems.

2.2 Catalysts characterization

2.2.1 Atomic Absorption Spectroscopy

The net contents of platinum in catalysts were quantitatively determined using Atomic Absorption Spectroscopy (AAS). Catalytic materials were digested in aqueous solution 40 vol.% hydrofluoric acid and then analyzed in a Varian AA-20 equipment. The experiments were performed after calcination of the catalytic materials. The Pt wt.% results for Pt/A, Pt/AC2 and Pt/AC5 were 0.7, 0.6 and 0.8, respectively.

2.2.2 Temperature-programmed reduction

Temperature-Programmed Reduction (TPR) experiments were performed with a RIG-100 ISRI

apparatus equipped with a thermal conductivity detector (TCD). A calcined sample (50 mg) was loaded into a bed of quartz reactor and installed into the oven. The powder samples were treated from 25 to 1000 °C at a heating rate of 10 °C/min in a flow of 10 vol % H₂ in Ar (99.99%, Infra). Total gas flow rate was 60 cm³/min.

2.2.3 FTIR Spectroscopy

Fourier transform infrared (FTIR) spectra were recorded between 400 cm⁻¹ and 4000 cm⁻¹ at room temperature on a Perkin Elmer Paragon 1000 spectrometer using self-supporting KBr disks and 16 scans/s. 1 mg of sample was mixed with 200 mg of KBr.

2.2.4 Catalytic reaction tests

2-propanol decomposition was carried out in a continuous differential reactor, with 50 mg of catalyst, using a nitrogen stream (120 cm³/min) saturated with 2-propanol at room temperature. The catalytic materials were ground and sieved at 80-100 U.S. mesh, in order to rule out internal diffusion mass transfer resistances. Prior to the reaction, the sample was treated for 1 hour with a 60 cm³/min flow rate of N₂ (Praxair, 99.99%) at 500 °C and then cooled down to room temperature in nitrogen flow. Measurements were obtained at intervals of 10 °C after reaching steady state in the range of 150-250 °C. A Gow Mac Gas chromatograph model 750 with FID and a 6 ft (1.82 m) Porapak Q column was used to analyze the reaction products.

3 Results and discussion

3.1 Temperature-programmed reduction

TPR profiles for Pt/A, Pt/AC2 and Pt/AC5 are presented in Fig. 1. Regarding Pt/A sample, it shows three bands of H₂ consumption: a main peak at 280 °C, a shoulder of this process around 390 °C, and a very small peak around 150-160 °C. Different TPR profiles of alumina -supported platinum materials have been reported (Rogemond *et al.*, 1997; Shyu *et al.*, 1989; Prestvik *et al.*, 1998; Pitchon *et al.*, 1996; Chen *et al.*, 1994; Malet and Caballero, 1988; Lieske *et al.*, 1983).

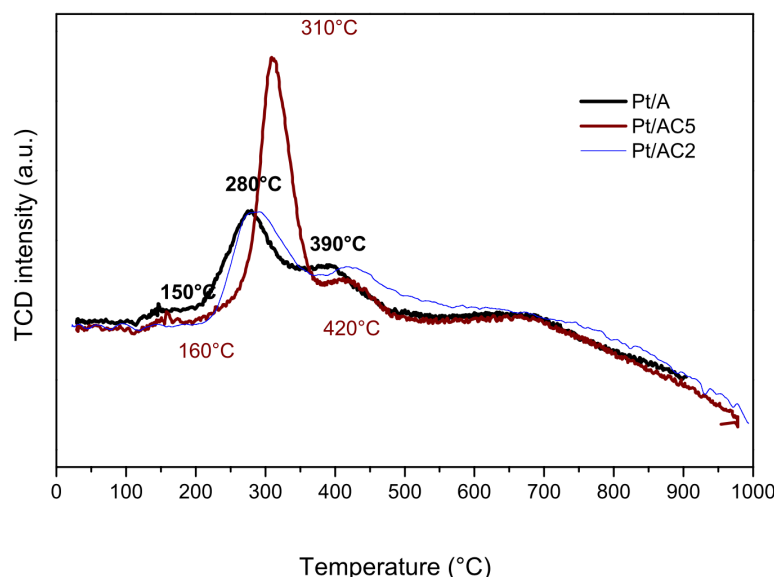


Fig. 1. TPR profiles of Pt/A, Pt/AC2 and Pt/AC5 samples.

On one hand, some studies have reported a single peak Pt reduction profile observed at different temperatures: a) at 320 °C, attributed by Rogemond *et al.* (1997) to the reduction of PtO or PtO₂ species, where Pt²⁺ (PtO) was validated with XPS analysis and; b) at 130 °C, attributed by Shyu *et al.* (1989) to the reduction of dispersed Pt on alumina (PtO₂-Al₂O₃ complex), using high load of Pt (10 wt%). On the other hand, the most standard TPR profile for this catalytic system is reported with two consumption bands: i) Prestvik *et al.* (1998) found two reduction peaks at 300 and 400 °C, both attributed to the reduction of Pt⁺⁴ species; ii) Pitchon *et al.* (1996) reported two peaks at 150 and 270 °C, which both were attributed to the reduction of PtO₂ particles and PtO dispersed species, respectively; iii) Chen *et al.* (1994) reported a similar TPR profile as that reported by Prestvik *et al.*, with reduction at 300 and 435 °C, using (0.5wt.%) Pt/Al₂O₃ catalyst; iv) Malet and Caballero (1988) reported two consumption bands corresponding to the reduction of Pt⁺⁴ to Pt⁰ species at 300 and 450 °C for materials obtained with chloride precursor; for free-chloride materials, they reported that the reduction was from Pt⁺² to Pt⁰ with two peaks at 280 and 430 °C. Regarding the materials with chloride precursor, Lieske *et al.* (1983) found by DRS UV-Vis the formation of platinum chlorides species after calcination, from the impregnation of H₂PtCl₆ on alumina surface: species of (Pt^{VI}(OH)_xCl_y)_s resulting from oxidation at 300 °C and (Pt^{VI}O_xCl_y)_s species

from oxidation at 500 °C. For these surface complexes, the temperature peaks of main reduction in TPR profiles were 260 and 290 °C, respectively. In general, Pt/Al₂O₃ samples calcined at 500 °C are reported with a main peak reduction ~ 300 °C with a shoulder ~ 450 °C. Thus, Pt/A sample as shown here has the following reduction processes: A) traces of reduction at 150 °C, attributed to reduction of PtO₂ particles with a poor interaction with alumina, B) main peak at 280 °C related to the reduction of (PtIVO_xCl_y)_s species and, C) a “shoulder” at 390 °C, attributed to the reduction of Pt species in high interaction with the support.

Ceria-based materials also show three reduction processes but with a shift in the temperature peaks in comparison to the Pt/A sample. For instance, in Pt/AC5 sample the temperature peaks of reduction were at 160 °C, 310 °C and 420 °C for first, main and shoulder reduction processes, which represent shifts of 10 °C, 30 °C and 30 °C with respect to Pt/A sample, respectively. Reduction of Pt/AC2 sample presents a trend similar to that of Pt/AC5, with a TCD intensity of the reduction peaks between those of Pt/A and Pt/AC5. The total reduction of species in all samples ca. 490 °C, indicating that all species are reduced at the conditions used in this work. It is noticeable the difference in H₂ consumption for the second peak between Pt/A and Pt/AC5 samples, being much higher for the latter. This effect is attributed to the simultaneous reduction of PtO_x and CeO₂ species,

which is in agreement with previous observations reported in the literature (Trovarelli, 1996; Rogemond *et al.*, 1997). Whereas Pt/AC systems present main reduction around 300 °C as described before, ceria-alumina oxides with 2 and 5% wt. % ceria (catalytic supports), obtained by our research group, show one hydrogen consumption peak within 500-530 °C, which was attributed to surface ceria reduction. i.e. agglomerated ceria particles reduction, that occurs at higher temperatures, was not detected (Pérez-Pastenes *et al.*, 2017). TPR profiles of Pt/AC also suggest that all added ceria is highly dispersed in alumina. Thus, platinum and cerium species interact in such a way that they are reduced simultaneously with a peak at 310 °C, decreasing more significantly the temperature at which reduction of ceria species occurs. Regarding the “shoulder”, attributed to the reduction of Pt species with high support interaction as described before, it is observed not only an increase in the reduction temperature but also a diminution of intensity of the peak as the ceria content is increased. This effect could be explained as follows: Pt species interact with both alumina and ceria. Pt species interact preferentially with ceria and reduced conjointly (Trovarelli, 1996). Nonetheless, a lower amount of Pt species interact with alumina diminishing the intensity of the peak but increasing the temperature of this reduction process as the amount of Pt decreases, in agreement with Chen *et al.* (1994).

3.2 2-propanol decomposition

All calcined catalysts in this work (PtO_x/AC) presented complete selectivity towards 2-propanol dehydration. Table 1 shows the comparison in 2-propanol dehydration activity between catalytic supports and calcined Pt catalytic systems. As shown in this table, the presence of PtO_x surface species increase the rate of propylene formation while the activation energy slightly decreases. As occurs in catalytic supports, the measurements indicate that activity diminishes when ceria is present. The activity decreases as the ceria content increases from 2 to 5%. Temperature range was selected in order to keep differential regime ($x < 10\%$) between 120-200 °C.

Regarding 2-propanol decomposition on catalytic supports, in a previous work (Pérez-Pastenes *et al.*, 2006) the properties of ceria-doped-alumina were compared using two methods of preparation: (1) slow addition of cerium salt during alumina sol formation in acidic medium, and (2) direct mixing of aluminum alkoxide before sol formation in an alkaline medium.

Table 1. Activity measurements of 2-propanol reaction in catalytic supports and calcined catalytic systems. Conversion (X_A) and reaction rate ($-r_A$) are given at 200 °C. All of these catalytic systems produce only propylene and water. Data corresponding to catalytic supports were reported elsewhere (Pérez-Pastenes *et al.*, 2006).

Sample	E_A (kcal/mol)	% X_A	$-r_A \cdot 10^3$ (mol/s·g cat)
PtO _x /A	33.6	13.91	1.29
PtO _x /AC2	35.0	7.50	0.63
PtO _x /AC5	38.0	6.07	0.52
A	36.5	9.2	0.83
AC2	37.5	5.5	0.45
AC5	42.5	1.4	0.12

That study showed that ceria is better dispersed in the first method than in the second. Using the first method, by increasing ceria content (ranging from 0, 2 and 5 wt% CeO₂) led to a decrease in the surface area, acidity and pore volume of the ceria-doped-alumina support. These observations were ascribed to the corresponding increase in a penta-coordinated aluminum content, with increase in the amount of ceria incorporated, conducting to a decrease in the activity of 2-propanol dehydration. In particular for alumina, it has been shown that the values of E_A are similar to those reported in the literature (Escobar *et al.*, 2015; Gosh *et al.*, 2019). For instance, the corresponding E_A for the sample calcined at 973 K, Escobar *et al.* (2015) report a value ca. 40 kcal/mol, whereas in our case correspond to 36.5. These differences might be due to the preparation conditions in each case.

According to the literature, Pt-reduced catalysts favor the selectivity of 2-propanol decomposition towards dehydrogenation (Rioux and Vannice, 2005; Martynenko *et al.*, 2020). The results of this work are in agreement with the literature, since reduced catalysts presented two competitive reactions: dehydration, thus forming propene and water; and dehydrogenation, which produces acetone and hydrogen. This is due to the presence of metallic sites (Pt⁰) and acid sites of Al₂O₃-CeO₂ with the capability to dehydrogenate and dehydrate, respectively. Figure 2 shows that, at temperatures below 200 °C, Pt/A catalyst is highly selective (more than 80%) to acetone and hydrogen. Above this temperature, the selectivity towards propene and water increases progressively, and at about 230 °C, the selectivity is abruptly switched, being higher for dehydration until it reaches the point where acetone and hydrogen almost disappear at about 280 °C.

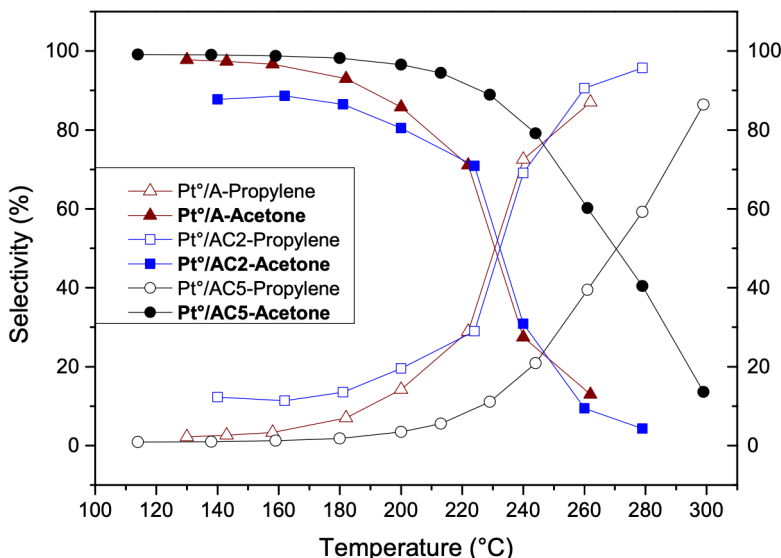


Fig. 2. Selectivity in 2-propanol reactions for Pt⁰/A, Pt⁰/AC2, and Pt⁰/AC5 catalysts. Product selectivity was calculated as (moles of product i)/(moles of product i + moles of product j).

Regarding ceria-based materials, the presence of ceria in the catalysts modifies: a) the initial selectivity, being almost 100% to acetone and hydrogen for Pt/AC2 and Pt/AC5, while for Pt/A is about 88%; b) the temperature at which selectivity changes, being around 270 °C for Pt/AC5, while for Pt/A is 230 °C.

This work studies two general forms of platinum species: oxidized and reduced. On one hand, Pt⁰ metallic phase platinum has the capability to hydrogenate or dehydrogenate depending on the reaction conditions (Cotton and Wilkinson, 2013; Valdez *et al.*, 2012; Sexton *et al.*, 1982). In the conditions used in this study, 2-propanol was decomposed mainly to acetone and hydrogen when Pt⁰ catalysts were tested. The latter is in agreement with Kon *et al.* (2013), who report the following mechanism for oxidant-free dehydrogenation of alcohols using Pt/Al₂O₃ catalysts: (1) reaction of an alcohol with Lewis acid-base pair site of alumina yields an alkoxide, (2) C-H dissociation of the alkoxide by Pt⁰ site to form Pt-H and a ketone, (3) protolysis of Pt-H by a neighboring proton to release H₂. On the other hand, oxidized platinum does not have this dehydrogenating capability; instead, PtO_x species increase the activity of 2-propanol dehydration, diminish the activation energies and increase the reaction rates, when compared with their respective catalytic supports. In the case of the supports, it is observed that the addition of ceria

to alumina decreases the catalytic activity for 2-propanol dehydration due to a diminution of the catalyst acidity (Pérez-Pastenes *et al.*, 2006). In this sense, the presence of PtO_x seems to increase the 2-propanol dehydration due to an increase in acidity, as has been reported for the case of NiO supported on sulfated zirconia (Barrales *et al.*, 2011).

A synergistic effect is observed when platinum and cerium reduced species act together in 2-propanol transformations, increasing the selectivity towards acetone (and hydrogen) production. This result is related to the TPR results, in which it is observed an increase of the peak corresponding to the reduction of platinum and ceria species, with a concomitant decrease of the peak attributed to the reduction of platinum species in higher interaction with alumina. It seems that platinum interacting with ceria favors the dehydrogenation reaction and this effect is correlated with the amount of platinum-ceria observed by TPR. Besides, the influence of the addition of ceria into alumina on the diminution of propylene selectivity has been reported (Pérez-Pastenes *et al.*, 2006). This effect also contributes to increase the selectivity toward dehydrogenation route.

3.3 FTIR spectra

The differences between alumina sol-gel and alumina modified with ceria by FTIR analysis are observed in Figure 3.

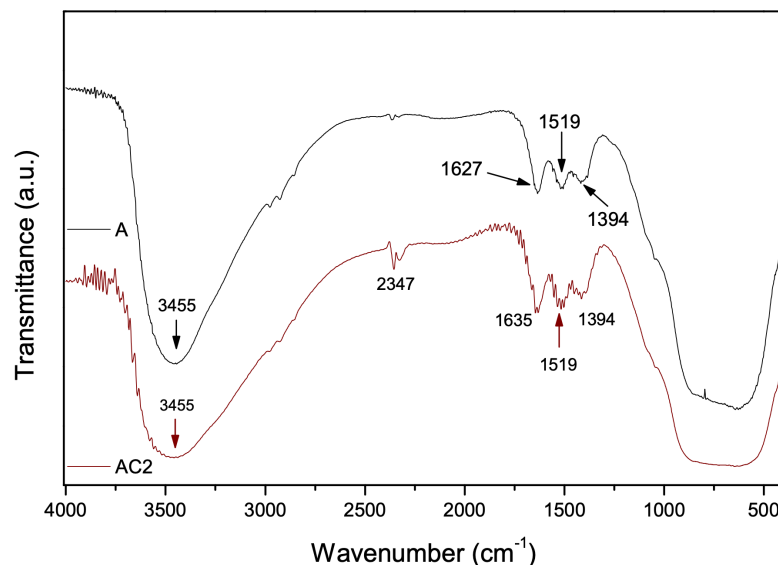


Fig. 3. FTIR spectra of catalytic supports A and AC2.

Sample A presents a band widening around 3455 cm^{-1} attributed to the stretching vibrations of OH groups; while bands around 1627 cm^{-1} , are generated due to vibrations of undissociated water molecules. There are stretching vibrations of Al-OH bonds detected at around 1519 cm^{-1} , and also, at 1394 cm^{-1} a band is observed corresponding to -H asymmetric bending in CH_2 and CH_3 groups (Fritea *et al.*, 2017). The signals corresponding to Al-O bond vibrations were not detected since the low energy spectrum was not well defined. In addition, small bands at approximately 2970 and 2857 cm^{-1} related to $-\text{CH}_3$ degenerated stretching mode and $-\text{CH}_2$ stretching symmetrical vibrations, respectively, are observed. Those signals could be related to organic remains residua from aluminum alkoxide precursor used during sol-gel synthesis (Escobar *et al.*, 2016).

Sample AC2 presents similar FTIR spectra to alumina. The main difference is the presence of a signal at 2347 cm^{-1} , which is attributed to C-O bond vibrations of adsorbed CO_2 , indicating the existence of basic sites (Escobar *et al.* 2020), which are related with the presence of ceria. As in the case of alumina, the low energy spectrum was also not well defined. Albeit the samples were analyzed after calcination at $700\text{ }^\circ\text{C}$, OH groups are detected, which is attributed mainly to the capability of alumina sol-gel to capture moisture from the environment. Figures 4 and 5 show the FTIR analysis of samples Pt/A (Fig 4), and samples: fresh Pt/AC2 (Fig 5a) and Pt/AC2 after a reaction test (Fig 5b). It is observed that a spectrum of Pt-supported

catalyst presents similar vibrational bands to their respective supports, with some additional vibrations. Sample Pt/A presents a weak signal at 1060 cm^{-1} corresponding to Al-O bond vibrations; peaks at 815 and 670 cm^{-1} also appear and are attributed to Al-O bond vibrations of Al ions in tetrahedral symmetry. Regarding ceria-based catalysts, Pt/AC2, presents the same signals described for Pt/A but also a vibration at 2360 cm^{-1} , corresponding to C-O bond vibrations, as is shown in Fig. 5. The related bands of OH groups decrease compared with their corresponding support. The spectrum at low energies also presents the same signals as those observed in Pt/A, i.e. the Al-O bond vibrations. For the Pt/AC2 sample analyzed after 2-propanol reaction test, it is noticeable the reduction in the signal intensity corresponding to C-O bond vibrations, in comparison with the same fresh catalyst. In addition, two weak bands at 2926 and 2852 cm^{-1} were observed; these are attributed to asymmetric vibrations of C-H bonds.

Thus, in 2-propanol decomposition, the reduced materials present high selectivity toward hydrogen and acetone before reaching the temperature range of $240\text{--}280\text{ }^\circ\text{C}$; but near this interval a notable change of selectivity to propylene occurs, in which the materials containing ceria retard this effect to higher temperatures. To explain the latter, the following needs to be considered: 1. Due to the presence of oxygenated molecules in the stream, the oxidation of Pt with oxygen species delivered as the temperature is increased might be considered.

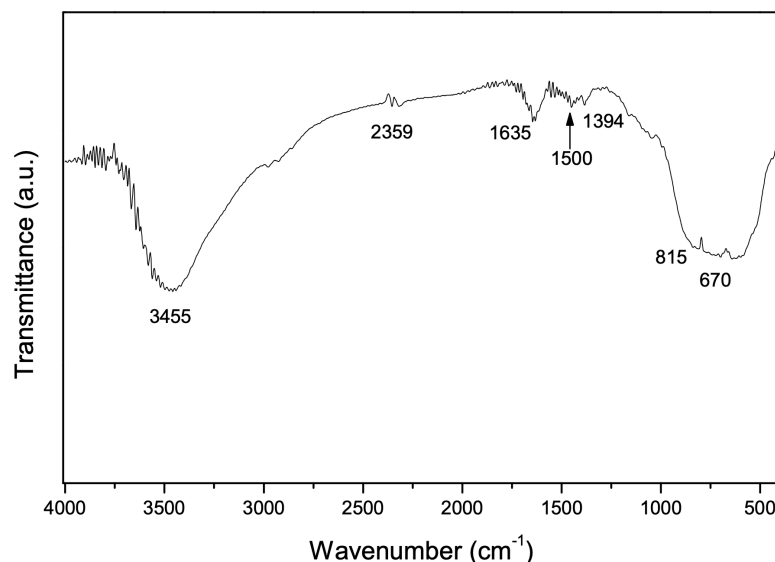


Fig. 4. FTIR spectrum of Pt/A sample: fresh reduced catalyst.

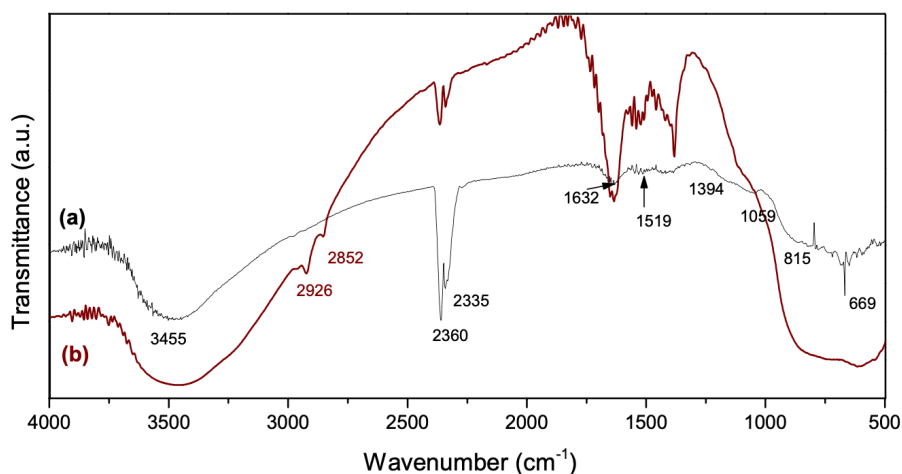


Fig. 5. FTIR spectrum of Pt/AC2 reduced sample: a) fresh catalyst, and b) catalyst after being used in the 2-propanol decomposition.

2. The selectivity changes from acetone to propylene could be attributed to mechanistic effects in the reaction. For instance, Gallardo-Amores *et al.* (1999) found the 2-propanol oxidation (with presence of oxygen in stream) on Mn_3O_4 produces almost entirely acetone up to 240 °C, with traces of acetaldehyde, acetic acid and propylene; but above this temperature the high acetone selectivity abruptly decreases to zero, while CO_2 yield increases above 95% at 260 °C. They also report this change in selectivity by using Mn-TiO_2 in the same reaction, decreasing acetone yield from 100% to almost

zero, with the concomitant increasing of propylene production. They attributed both results to the reaction mechanism change. 3. As mentioned before, some researchers attributed the loss of activity in alcohols dehydrogenation to deactivation by coke deposition on platinum active sites (Mostafa *et al.*, 2009). 4. Some authors consider the deactivation of reduced platinum due to the chemisorption of oxygenated compounds. Mavrikakis and Barteau (1998) report the reaction sequence for alcohols decomposition by using catalyst based on platinum group metals, involving the formation of an intermediate alkoxide linked to

the surface. This is formed by hydrogen removal of hydroxyl groups followed by the subtraction of α -H conducting to an intermediate aldehyde linked to the surface either to the carbon and oxygen of carbonyl group or just to an oxygen atom, assigned as η^2 (C,O) conformation and as η^1 (O) conformation, respectively. Thus, it is possible that at least one of these oxygenated species might be adsorbed on platinum sites.

To elucidate among these four propositions, further experiments were performed: i) Reduced catalysts were used in 2-propanol reaction experiments at temperatures above 300 °C, corroborating that dehydrogenation did not occur. Propylene was the only product detected. Afterwards, each catalyst was cooled under the same feed flow at 200 °C, temperature at which catalysts were supposed to be active for dehydrogenation. However, at this and lower temperatures catalysts were active to produce mainly propylene with traces of acetone, i.e. the dehydrogenation capability was lost. ii) After the experiment just described, the catalysts were treated at 500 °C with a N₂ flow (30 cm³/min) for 1 hour. Then, catalysts were tested at the same conditions of 2-propanol reactions observing almost the same initial activity, recovering about 95% of dehydrogenation capacity.

With these new results, considerations 1) and 2) can be discarded. Since no reducing stream was used to reactivate the catalysts, oxidation-reduction of platinum species is no longer considered. Also, based on the results of experiment i) in which the dehydrogenation activity was not recovered the explanation based on a change in mechanism is no longer considered. Both experiments are in agreement with explanations of deactivation by superficial carbon formation and also with adsorbed oxygenated species, assuming that either coke or oxygenated intermediates could be removed with N₂ post-treatment. According to this, it is possible to remove certain kind of carbon molecules deposited at the described conditions, although the chemical composition remains unclear.

Regarding FTIR results (Figure 5), the two bands at 2926 and 2852 cm⁻¹, attributed to asymmetric vibrations of C-H bonds correspond to organic species adsorbed on the catalyst as described before, and are more intense in the sample after reaction test. These signals are related to 2-propanol, propylene and other compounds present in the reaction, but it is not possible to discard between carbon deposition and chemisorbed species. Thus, further experiments will be carried out to elucidate the compounds

involved. Finally, the fact that ceria-based catalysts retard the loss of dehydrogenation capacity to higher temperatures could be explained for the last two possibilities. If it were for coke formation and this coke results from propylene, the presence of ceria diminishes the activity to propylene formation [see Table 1], and also it is well known ceria-containing materials inhibit coke formation (Trovarelli, 1996; Vagia and Lemonidou, 2009). If it were for chemisorbed species blocking Pt sites, it is possible that ceria interacts with the intermediaries because of its affinity with oxygenated molecules, retarding the temperature of dehydrogenation activity loss.

Conclusions

This work deals with the influence of ceria in platinum supported on alumina and alumina-ceria employed in the decomposition of 2-propanol. Pt/Al₂O₃ and Pt/Al₂O₃-CeO₂ catalysts were used in calcined and reduced states. Two competing reactions were observed: the dehydrogenation and dehydration of 2-propanol. It is possible to conclude the following:

- Regarding calcined catalysts, the oxidized platinum presented a favorable effect in the reaction rates of 2-propanol dehydration by diminishing the activation energies, promoting an increase in the catalytic activity when compared to their respective catalytic supports.
- Reduced catalysts produce propylene and acetone from 2-propanol, with a high selectivity towards alcohol dehydrogenation at low temperatures (120-240 °C). As the temperature is increased, between 230-270 °C, an abrupt change in selectivity occurs, with propylene as the main product.
- The selectivity change observed is influenced by ceria content. As ceria content is increased the shift temperature increases. This effect could be attributed to ceria has the capacity to store/release oxygen and promote a strong interaction with the platinum, which modifies the adsorption/removal of the oxygenated/carbon compounds involved in the reaction.

Acknowledgements

We thank to CONACyT and PRODEP (project No. 511-6/19-8453, through the program Fortalecimiento de Cuerpos Académicos) for the financial support of this work. H. Pérez-Pastenes gratefully acknowledges CONACyT the grant for his sabbatical stay at Universidad Autónoma Metropolitana-Iztapalapa.

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