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Synthesis, Characterization and Catalytic Properties of Nanocrystaline Y_2O_3-coated TiO_2 in the Ethanol Dehydration Reaction

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In the present study, TiO_2 nanopowder was partially coated with Y_2O_3 precursors generated by a sol-gel modified route. The system of nanocoated particles formed an ultra thin structure on the TiO_2 surfaces. The modified nanoparticles were characterized by high resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD) analysis, Zeta potential and surface area through N_2 fisisorption measurements. Bioethanol dehydration was used as a probe reaction to investigate the modifications on the nanoparticles surface. The process led to the obtainment of nanoparticles with important surface characteristics and catalytic behavior in the bioethanol dehydration reaction, with improved activity and particular selectivity in comparison to their non-coated analogs. The ethylene production was disfavored and selectivity toward acetaldehyde, hydrogen and ethane increased over modified nanoparticles.

Keywords: *catalysis, surface modifications, titania, coating*

1. Introduction

Metal oxides are a subject of intense research in materials science. These oxides play an important role in heterogeneous catalysis, acting as active phase, promoter or support of solid catalysts. The catalytic properties of solids are highly dependent on their surface features. It is well known that the final structural characteristics of the catalysts are dependent on their preparation methods. In this sense, new synthesis methods, which lead to materials with superior performances, have been reported[1-3]. There is a general consensus that the possibility of preparing oxide particles on a nanoscale level would be very interesting due to its special physical and chemical properties in comparison to those of bulk particles[4-7]. The combination of two materials on a nanometer scale, one acting as the core and the other as the coating, can result in interesting surface modifications that are substantially different from those of the core, thus making the nanocoated particles attractive for several applications, including in catalysis[8-10]. The control of surfaces and the modifications of the structures of the particles can be used to obtain additional information on the catalytic properties and applications of these nanostructured materials.

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Titanium oxide nanoparticles have been previously investigated by our group[11-14]. It is well known that this semiconducting oxide has excellent potential for several applications, due to its high capacity to adsorb gaseous molecules and to promote reactions over its surface[4,11-14]. The present paper focuses on the preparation and characterization of surface-modified TiO_2 nanoparticles, using Y_2O_3 as an insulating oxide, revealing its effects on their catalytic performances in the bioethanol dehydration reaction. Recently, a number of publications report experimental catalytic studies for the aforementioned reaction, discussing the utilization of different catalysts. From the data reported, not only the operational conditions employed, but also the nature of the catalyst used, has been shown to influence the catalytic performance. The ethanol dehydration process has gained increasing attention due to the possibility of obtaining ethylene, which is considered a valuable raw material in the petrochemical industry. Conventionally, ethylene is commercially produced by the thermal cracking of liquefied petroleum gas or naphtha processes, which require high temperatures. In contrast, catalytic dehydration of ethanol to ethylene requires lower temperatures and can offer higher ethylene yields[15-19].

2. Experimental Procedure

2.1. *Sample preparation*

The surface-modified TiO_2 samples were obtained based on the sol-gel modified route, also known as in situ polymerizable complex method[14,20]. The starting materials were yttrium carbonate (Aldrich Co.), titanium oxide (P25; ca. 80% anatase and 20% rutile, Degussa Co.), citric acid (Mallinckrodt) and ethylene glycol (Mallinckrodt). Colloidal dispersions containing 2 g of commercial TiO_2 nanoparticles in 50 mL of deionized water were prepared. The TiO_2 powder was dispersed in water using an ultrasonic probe. An yttrium polymeric precursor water-based solution was used to coat the TiO_2 nanoparticles. A polymeric resin was obtained by quelating a metal ion from the yttrium salt ($Y_2(CO_3)_3$ – Aldrich Co.) with citric acid ($C_6O_7H_8$ – Mallinckrodt), followed by polymerization against ethylene glycol ($C_2H_4(OH)_2$ – Mallinckrodt). The obtained resins were added into colloidal dispersions to obtain dispersions containing 0.4% (TiO_2-Y_2O_3(0.4)); 0.8% (TiO_2-Y_2O_3(0.8)); 1.2% (TiO_2-Y_2O_3(1.2)); 2.4% (TiO_2-Y_2O_3(2.4)) in weight of Y_2O_3 per weight of TiO_2. These dispersions were sonicated for 10 minutes and the aqueous solvent was removed using a rotary evaporator. The resultant solid was pulverized and calcined, in an air atmosphere, at 450 °C for 4 hours. The complexation of yttrium with citric acid and the posterior esterification reaction between metal citrate and ethylene glycol is illustrated in Figure 1[21].

2.2. *Sample characterization*

The structure and morphology of the samples were studied by high resolution transmission electron microscopy (HRTEM - Philips CM 200). The specific surface areas (B.E.T. method) of the samples were determined by N_2 adsorption/desorption isotherms at liquid nitrogen temperature by means of an Autosorb-1C analyzer (Quantachrome Instruments). The zeta potential of the dilute suspensions was measured in a Zeta Potential Meter (Brookhaven Inst. Corp. Zetaplus). Phase identification was carried out by X-ray diffraction (XRD) analysis (D5000,Siemens,Germany) using CuKα radiation.

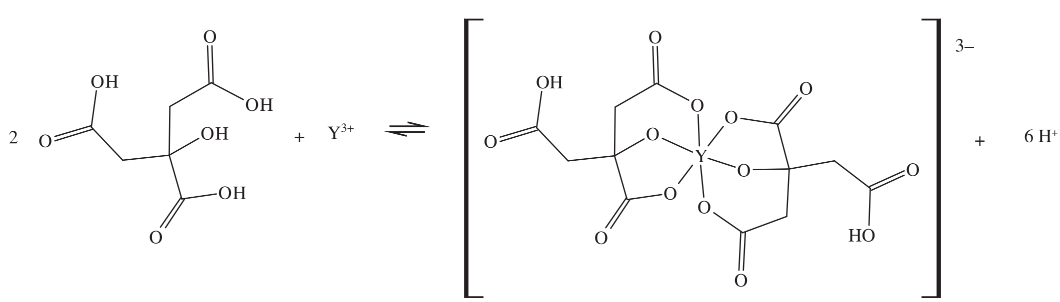
2.3. *Catalytic tests*

Catalytic performance tests were conducted at atmospheric pressure with a quartz fixed-bed reactor (inner diameter 12 mm) fitted in a programmable oven, at 500 °C. The water:ethanol mixture, of known composition, was pumped into a heated chamber (kept at 200 °C) and vaporized. The water-ethanol gas (N_2) stream (30 mL/min) was then fed to the reactor containing 100 mg of the catalyst powder. The reactants and the composition of the reactor effluent were analyzed on line with a gas chromatograph (Shimadzu GC 8A).

3. Results and Discussion

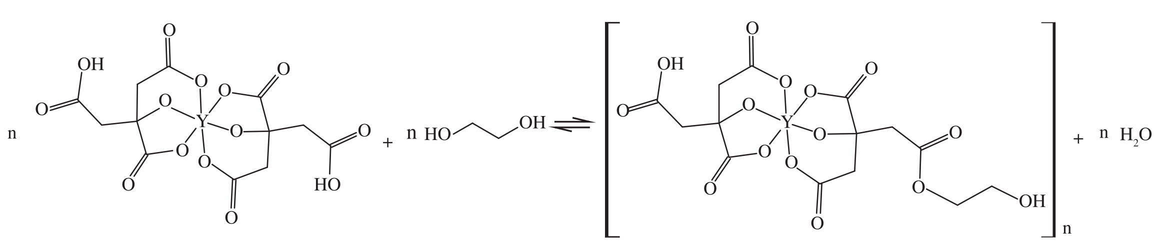
3.1. *Characterization*

The samples were characterized by HRTEM, after the annealing process, in order to understand the effect



$$2\,C_6H_8O_7\,(aq) + Y^{3+}\,(aq) \rightleftharpoons [Y(C_6H_5O_7)_2]^{3-}\,(aq) + 6\,H^+\,(aq)$$

(a)



Polymeric structure

$$n\,[Y(C_6H_5O_7)_2]^{3-}\,(aq) + n\,C_2H_6O_2\,(l) \rightleftharpoons n\,[Y(C_6H_5O_7)(C_8H_9O_8)]^{3-}\,(s) + n\,H_2O$$

(b)

Figure 1. Schematic representation of the metal-citric acid complex and polymeric precursor formation.

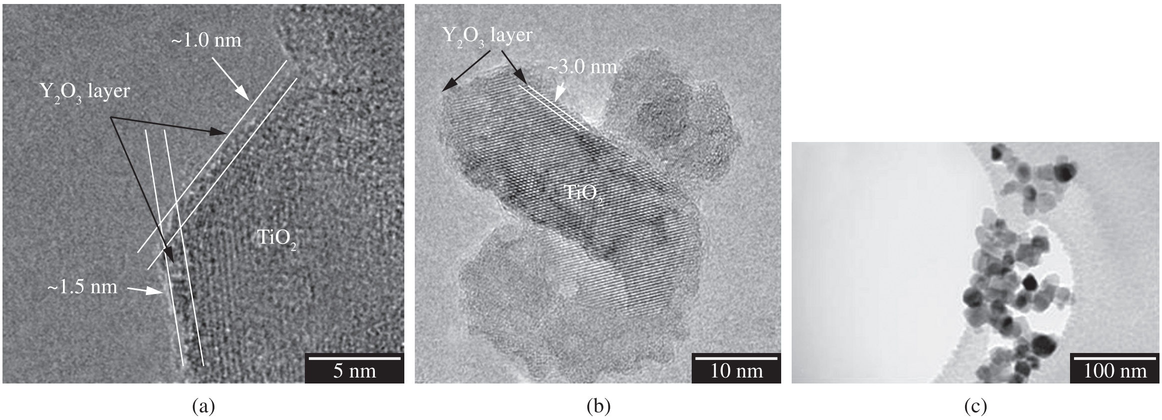


Figure 2. HRTEM images of TiO_2 nanoparticles modified with Y_2O_3: a) TiO_2-Y_2O_3(0.4); b) TiO_2-Y_2O_3(0.8); and c) modified nanoparticles exhibiting a spherical morphology and similar size.

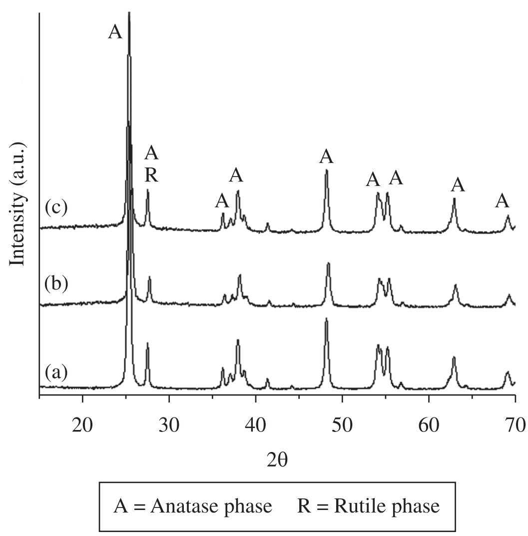


Figure 3. X-ray diffraction patterns for Y_2O_3 coating of TiO_2 nanopowders: a) TiO_2-Y_2O_3(0.4); b) TiO_2-Y_2O_3(1.2); and c) TiO_2-Y_2O_3(2.4).

Table 1. Physical-chemical characterizations of unmodified (TiO_2) and modified (TiO_2-Y_2O_3) nanoparticles.

Samples	$S_{(B.E.T)}$ [a] ($m^2.g^{-1}$)	I.E. [b]
TiO_2	81	2.6
TiO_2-Y_2O_3(0.4)	51	–
TiO_2-Y_2O_3(0.8)	52	–
TiO_2-Y_2O_3(1.2)	51	–
TiO_2-Y_2O_3(2.4)	50	4.6

a = specific surface area, calculated according B.E.T. method. b = isoelectric point, obtained graphically by Zeta potential measurements, for the catalysts.

of nanocoating on the titania particle surface, which can be confirmed by the images of the partially coated TiO_2, shown in Figure 2. All the modified nanoparticles exhibit a spherical morphology and similar size, despite agglomerate formation (Figure 2c). Such images reveal the formation of irregular islands on the TiO_2 surfaces, which consist of a crystalline core of TiO_2 surrounded by an amorphous coating of ultra thin thickness of Y_2O_3 (0.4 and 0.8% mass of Y_2O_3, shown in Figure 2a,b, respectively). The thickness of the thin coating layer on the TiO_2 particles was related to the Y_2O_3 concentration of the nanocoating. The thickness of the coating is at a range that goes from 1.0 to 3.0 nm. These observations are corroborated by the HRTEM analysis of the TiO_2-Y_2O_3 samples. The crystal structure of the nanocomposites based on the nanocoating of the Y_2O_3 additive on TiO_2 and the respective XRD patterns are shown in Figure 3. In this pattern the peaks can be only ascribed to the tetragonal anatase phase of crystalline TiO_2, however, the reflection peak at $2\theta = 27°$ can also be assigned to rutile phase, indicating the mixture constitutes phases. No diffraction peaks related to the yttrium oxide phase were observed in the nanocoated TiO_2 samples, respectively. A similar finding has been previously reported by Gonçalves et al.[22] for ZrO_2 powder coated with low concentrations of Al_2O_3. Additional information on the textural properties, specific surface area values, of the partially nanocoated TiO_2 samples is summarized in Table 1. The pure TiO_2 sample presented the highest specific surface area, 81 $m^2.g^{-1}$. For the surface-modified samples, specific surface area values were very similar. The comparison shows that the heat treatment employed in the surface modification process resulted in a similar surface area decrease, approximately 37% for all modified nanoparticles, when compared with unmodified nanoparticles. The isoelectric values (graphically obtained by Zeta potential measurements) are compiled in Table 1. We can see that the addition of different amounts of insulating yttrium oxide on the TiO_2 nanoparticles gave different isoelectric point values, indicating that the surface chemical composition changed and an increase of Y_2O_3 concentration on the surface may be assumed[14].

3.2. *Catalytic performances*

In order to investigate the catalytic behavior of the samples, the ethanol dehydration reaction was carried out.

In addition, this process could be used as a probe reaction to evaluate the modifications on the nanoparticles surface. During catalytic dehydration of ethanol, intramolecular dehydration of ethanol to ethylene (Equation 1) and intermolecular dehydration to diethyl-ether (Equation 2) can occur in parallel. At lower temperatures, diethyl-ether is produced in significant quantities, while at higher temperatures ethylene is the major product[16].

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad (1)$$

$$2C_2H_5OH \rightarrow C_2H_5O\ C_2H_5 + H_2O \quad (2)$$

It was observed, from the product distribution shown in Figure 4, that the steam reforming reaction of ethanol (Equation 3) over the catalysts was negligible under the operational conditions employed. This is possibly due to the presence of water in the feed[23].

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \quad (3)$$

However, it can be seen that hydrogen, ethylene and acetaldehyde were the only products detected during the process over the unmodified TiO_2 catalyst (Figure 4a). Dehydration of ethanol, which occurs to an appreciable extent producing ethylene, seems to occur as the main reaction. A slight amount of acetaldehyde was also detected, at the beginning of the test, indicating that ethanol dehydrogenation to acetaldehyde (Equation 4) was promoted. However, during the last 150 minutes, dehydration of ethanol became the predominant reaction. According Zhang et al.[16] ethanol dehydrogenation to produce acetaldehyde can also occur as a side reaction at higher reaction temperatures.

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \quad (4)$$

The ethanol conversion decreased from 43 to 10% after 250 minutes on stream with a significant difference in the product distribution. The coke formation from ethylene polymerization (Equation 5) may be considered as the main reason for the catalyst deactivation observed in this case. The carbon deposited after the catalytic test was visually detected but not measured and characterized in this work.

$$C_2H_4 \rightarrow \text{coke} \quad (5)$$

In spite of the relatively low specific surface area presented, the TiO_2-Y_2O_3(2.4) catalyst achieved significant ethanol conversion values. A layer of yttrium oxide coating can increase the amount of adsorbing centers on the particle surface, which can improve and provide more active sites for further reactions. The modified catalyst presented a distinct behavior (Figure 4b), displaying a higher degree of selectivity toward CH_3CHO and H_2 with lower formation of C_2H_4, indicating that the dehydrogenation reaction of ethanol was favored. Thus, a combination of catalytic properties could be observed on the surface, indicating that this particular catalyst has the ability for dehydration of ethanol and also some capacity for dehydrogenation of ethanol. The incorporation of Y_2O_3, an oxide with alkaline characteristics, into the TiO_2 led to an increase in the acetaldehyde selectivity, favoring the dehydrogenation of ethanol. It is well known that the basic and acidic properties of the oxide catalysts are essential parameters directly affecting the primary selectivity for acetaldehyde or ethylene. Basic sites are predominant in the ethanol dehydrogenation to acetaldehyde, whereas ethylene would be produced with an essential role of the acidic sites of the oxides[23]. Therefore, a basic oxide, such as yttrium oxide, introduced in the TiO_2 matrix promotes the basicity of the surface. The lower ethylene selectivity observed over the modified catalyst corroborates this fact. The surface modifications, due to coating process, change some properties of the titanium oxide, such as the

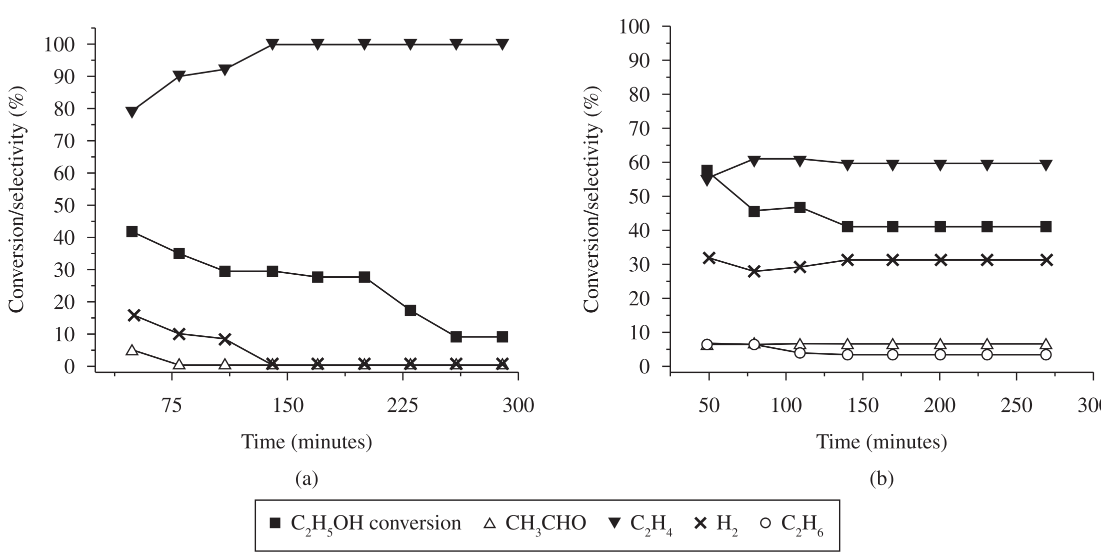


Figure 4. Catalytic performances in the dehydration of ethanol over: a) TiO_2 pure sample; and b) Y_2O_3 coated TiO_2 (TiO_2-Y_2O_3(2.4)).

isoelectric point. The isoelectric point of pure TiO_2 can be shifted to basic pH values via the introduction of a basic surface oxide (Y_2O_3). Thus, the basic characteristics of the rare earth oxide may favor some catalytic aspects such as the increase in the basicity of the surface[24,25]. In the present study, the quantitative determination of basic and acidic sites and its influence on the catalytic behavior was not reported. However, this study is under way and it will be subject of a future report. Even so, the occurrence of an ethanol decomposition reaction (Equation 6) can not be ruled out due to the high hydrogen selectivity value observed.

$$C_2H_5OH \rightarrow 2H_2 + 2C + H_2O \quad (6)$$

The conversion of ethanol using the TiO_2-Y_2O_3(2.4) catalyst was higher than for the TiO_2 catalyst, and this catalyst kept a satisfactory ethanol conversion level until the end of the test, indicating the positive effect of Y_2O_3 incorporation, in spite of the lower specific surface area of this sample compared to the pure TiO_2. The very low concentration of ethane detected at the beginning of the test can be ascribed to the occurrence of ethylene hydrogenation (Equation 7)[26]. These observations are indicative of a moderate modification of the material surface due to the Y_2O_3 incorporation.

$$C_2H_4 + H_2 \rightarrow C_2H_6 \quad (7)$$

4. Conclusion

In this work, we obtained surface-modified TiO_2 nanoparticles, using Y_2O_3 as an insulating oxide, by a sol-gel modified route. The observed structures showed that the proposed method is effective to the modification of TiO_2 surface, despite the irregular distribution of the insulating oxide. These surface modifications changed some properties of the powder, such as the isoelectric point, specific surface area and catalytic activity that were monitored through catalytic tests in ethanol dehydration reaction. It was found that the pure catalyst (TiO_2) were very selective toward ethylene, which is a valuable raw material in the petrochemical industry. On the other hand, the modified catalyst TiO_2-Y_2O_3(2.4) presented an improved activity and particular selectivity in comparison to their non-coated analogs. The ethylene production was disfavored and selectivity toward acetaldehyde, hydrogen and ethane increased over modified nanoparticles. This behavior may be related to the modification of the surface chemical composition due to the coating process.

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