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Dimethyl adipate hydrogenation at presence of Pt based catalysts

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Abstract

Dimethyl adipate hydrogenations catalyzed by Pt/Al_2O_3 and Pt/TiO_2 have been studied. Catalysts were prepared with the conventional impregnation method. Physical–chemical characterization of the catalytic systems was made with the use of different techniques: N_2 and H_2 sorption, scanning electron microscopy (SEM), energy-dispersive electron (EDS) probe X-ray analysis, temperature programmed reduction (TPR) and inductively coupled plasma optics emission spectrometry (ICP-OES). Metals dispersion in the catalysts is directly related to the superficial area of the supports, and partially covered particles (in the case of the TiO_2) can be present. Support modifies the behavior of metals in its surface for different ways: SMSI effect (TiO_2) or acidity (Al_2O_3). The catalyst supported on Al_2O_3 is more active, reaching 52.91% conversion after 10 h of reaction, while at the same period of time, the catalyst supported on TiO_2 converted only 15.56% of the substrate. Methyl caproate, adipic acid mono-methyl ester and caprolactone were obtained as main products by Pt/Al_2O_3 catalyst. These products indicate that carboxylic groups have not been activated enough, leading to formation of significant amount of hydrogenation products different from 1,6-hexanediol (diol). Pt/TiO_2 catalyst obtained methyl caproate, caprolactone, hexane and diol, where hexane formation occurred from methyl caproate. Diol formation occurred after 5 h of reaction and it indicates participation of platinum and TiO_2 as active catalytic sites.

Keywords: Selective hydrogenation; Diol; Pt/TiO_2; Pt/Al_2O_3; Ester hydrogenation

1. Introduction

Diols are widely applied as raw material for the synthesis of polyesters, polyurethanes, varnishes, adhesives, textile auxiliaries, fragrances, pharmaceutics, and recently, for the production of biodegradable polymers [1]. These materials can be obtained from the catalytic hydrogenation of dicarboxylic acids and esters. Catalysts commonly used consist of copper or zinc chromate [2], ruthenium dioxide [3] and rhenium heptoxide [4] under strict reactional conditions.

The 1,6-hexanediol obtained from catalytic hydrogenation of adipic ester is industrialized under reaction conditions where temperature and pressure rates vary from 443 to 513 K and from 150 to 330 atm, respectively. Moreover, the selective production of 1,6-hexanediol is a complex reaction, since various products can be obtained from its respective ester hydrogenation. Under hydrogenation conditions, esters originated from dicarboxylic acids can be transformed into their respective diols, or glycols, according to the equation:

$$\mathrm{ROOC{-}(CH_2)_n{-}COOR} + 4\mathrm{H_2} \Rightarrow \mathrm{HO{-}(CH_2)_{n+2}{-}OH} + 2\mathrm{ROH} \qquad (1)$$

Esters hydrogenation reaction is also called hydrogenolysis because before the atomic hydrogen addition there must be rupture of one of the links C–O or O–R on the ester. Thus, the reaction selectivity depends on the point where the hydrogenolysis occurs, with possible formation of many products, such as alcohols (with diols among them), carboxylic acids, esters, lactones, cyclic ethers and

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hydrocarbons. Therefore, the development of a selective catalytic system suits interest to the production of diol under less severe reactional conditions.

Catalytic hydrogenation reactions of polyfunctional compounds have been object of extensive series of researches, such as: oleic acid hydrogenation on impregnated catalyst Ru-Sn/TiO_2 [5] and on sol–gel Ru–Sn/Al_2O_3 [6], cinnamic aldehyde hydrogenation on Pt–Fe/TiO_2 [7], citral hydrogenation at presence of Rh–Sn/TiO_2 [8], Rh–Sn/SiO_2 [9] and Ru–Sn/TiO_2 [10] and dimethyl adipate hydrogenation by Ru–Sn [11].

Generally, the hydrogenation of molecules containing the carbonyl group is held at presence of catalysts supported by group VIIIB metals, Ru, Rh, Pd, Os, Ir, Pt, Ni and Co. However, monometallic catalysts are not very effective regarding the selective attack of the carbonyl function [11]. Among those metals, Ru has shown better catalytic performance in reducing the occurrence of undesirable reactions, although none of the systems has led to 1,6-hexanediol formation. These systems selectivity can be modified by inserting a second metal considered inactive in hydrogenation reactions, such as Sn [12]. Ru–Sn/TiO_2 systems have shown to be active, though little selective to the formation of the desirable product, while Ru–Sn/Al_2O_3 systems have presented 22% selectivity diol [11]. In contrast, the use of TiO_2 as support on the cinnamic aldehyde hydrogenation has considerably increased the reaction selectivity to the corresponding alcohol [7].

This paper exploits platinum as active metal, and TiO_2 and Al_2O_3 as supports. Catalysts were obtained with the impregnation method, not only because of its simple handling properties in the preparation process, but also due to the excellent performance presented by these catalysts on the selective hydrogenation of polyfunctional compounds. For instance, Pt-Fe/TiO_2 catalyst used by Silva et al. [10] on the cinnamic aldehyde hydrogenation, the Ru-Sn/TiO_2 catalyst used by Santos and co-workers [5] on the oleic acid, or even catalytic system Rh-Sn/TiO_2 applied by Lobão et al. [8] on the citral hydrogenation.

2. Materials and methods

2.1. Catalysts preparation

Catalysts were prepared with the impregnation method in aqueous suspensions, in order to obtain a catalyst with nominal concentration of 2% in platinum weight. Supports applied here were TiO_2 (Aldrich, >99%, crushed and strained in average fraction of 0.045 mm) and y-Al_2O_3 (Degussa type 213, crushed and strained in average fraction of 0.045 mm), and the precursor salt used here was $Pt(NH_3)_4Cl_2{\cdot}0.68H_2O$ (Aldrich, 98%). Impregnation was done by adding support and solution containing metallic precursor in a rotative evaporator, with bath at 333 K and vacuum for 5 h. Next, samples were dried in oven for 12 h, at temperature of 393 K. Catalysts were then subjected to calcination by treatments for 4 h at 673 K, under flow of 50 mL min^{-1} of synthetic air, and reduction for 2 h at 673 K, under flow of 40 mL min^{-1} of 2% H_2 and 98% N_2 mixture.

2.2. Characterization

A Micrometrics ASAP 2010 device was used to obtain adsorption measures at temperature of 77 K, under pressure rate from 10 to 925 mmHg. Catalysts specific area was obtained by using the Brunauer, Emmett and Teller (BET) method.

Assays of temperature-programmed reduction (TPR) were held on quartz reactor, using 100 mg of catalysts under flow of reductive gas mixture containing 1% hydrogen and 99% helium, at outflow of 25 mL min^{-1}. Analysis temperature was programmed to vary from 298 to 1073 K, with heating rate of 5 K min^{-1}. Throughout the analysis, hydrogen consumption profiles were recorded by using a Balzers Omnistar Quadrupole Mass Spectrometer, model QMS200, in function of temperature.

Scanning electron microscopy (SEM) was done with a Leica-Zeiss LEO 440 microscope, to which a Si(Li) energy dispersive analyst with Be window is attached, model Oxford 7060. Energy-dispersive electron (EDS) probe X-ray analysis was done with element mapping.

Hydrogen sorption was done with samples of 0.4 g of the catalysts. Initially, their surfaces were cleaned by evacuation of the system under flow of He at 393 K. After that, the catalysts had been reduced "in situ" at 673 K for 2 h under flow of H_2 and the system was evacuated under flow of H_2 for 1 h until reaching the sorption temperature (308 K). The sorption measurements were obtained in pressures varying from 10 to 400 mmHg.

2.3. Catalytic tests

Dimethyl adipate hydrogenation was held on a high pressure Parr reactor, made of 316 stainless steel and equipped with mechanical stirring axe with speed setting. Reactions were carried out in liquid phase with 1,4-dioxane as suitable solvent to keep the reaction phase homogeneity. The system was kept at 523 K and 50 atm of H_2 [1], under constant mechanical agitation at speed of 1500 rpm. Agitation speed has been considered by Silva et al. [7] as enough to keep system free from diffusional limitations. Typically, 1.40 g of catalyst, 80 mL of 1,4-dioxane, 7.09 g of dimethyl adipate and 3.6 g of tetradecane (internal standard) were used. Samples were collected for each reaction for 15 h.

Reaction products quantification was done by using gas chromatography with a Thermo Quest Trace GC 2000 chromatograph having a capillary column HP1 and for internal standard, tetradecane. Identification of the products was previously held in a gas chromatograph attached to a mass spectrometer HP5988 A.

Table 1
BET surface area of supports and catalysts

Solid	S_{BET} ($m^2\ g^{-1}$)
Al_2O_3	198
Pt/Al_2O_3	140
TiO_2	21
Pt/TiO_2	12

3. Results

Nitrogen adsorption isothermals obtained to TiO_2 and Al_2O_3 supports presented themselves as peculiar of macroporous or non-porous material [13]. Superficial area values determined by BET method, shown in Table 1, are very low to TiO_2 support, as well as to Pt/TiO_2 catalyst when compared to solid containing Al_2O_3. Results indicate that material containing TiO_2 is little porous, and the available surface area is related to wide and/or rough pore areas of the particles surface. High surface areas and metallic dispersions in the catalysts lead, generally, to high catalytic activities. However, systems prepared on supports with low surface areas can also lead to interesting results, mainly in selectivity terms. In these cases, special attention must be given to the supports that interact with the metallic phase. Regarding the catalysts preparation, it was observed that Pt catalysts had presented a trend of metal segregation during the stage of calcination, with partial deposition on the walls of the glass reactor. This problem could be prevented controlling the heating rate in values lower than 10 K min^{-1} during the calcination process. To confirm the incorporation of platinum in the catalysts, the metal content was determined by ICP-OES. The results indicate the following Pt percentages in the as synthesized catalysts: Pt/TiO_2 1.44% and Pt/Al_2O_3 1.94%. After calcination, the metallic content was maintained: Pt/TiO_2 1.40% and Pt/Al_2O_3 1.94%.

Profiles of temperature programmed reduction for catalysts containing platinum supported on Al_2O_3 and TiO_2 are illustrated on Fig. 1. It is possible to observe that the reduction profile is slightly different according to the applied support. TPR graph to the Pt/TiO_2 system presents only one peak of hydrogen consumption, around 430 K, which is related to the reduction of Pt^{2+} to Pt^0. For the Pt/Al_2O_3 system, the occurrence of two unresolved peaks between 380 and 450 K can be noticed, similarly to the results presented by Resende et al. [14]. This behavior indicates that a platinum reduction is influenced by different interactions between metallic atoms or between metal and support. An increase on the metal reduction temperature shows that the interaction between active metal and support is more effective, as identified by Subramanian [15].

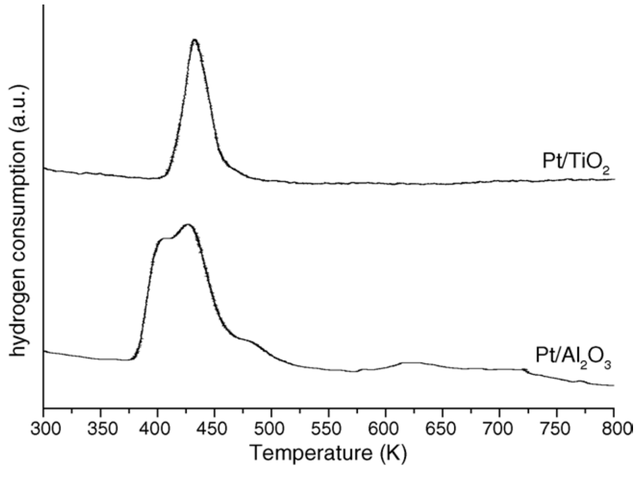


Fig. 1. TPR profiles for Pt supported on Al_2O_3 and TiO_2.

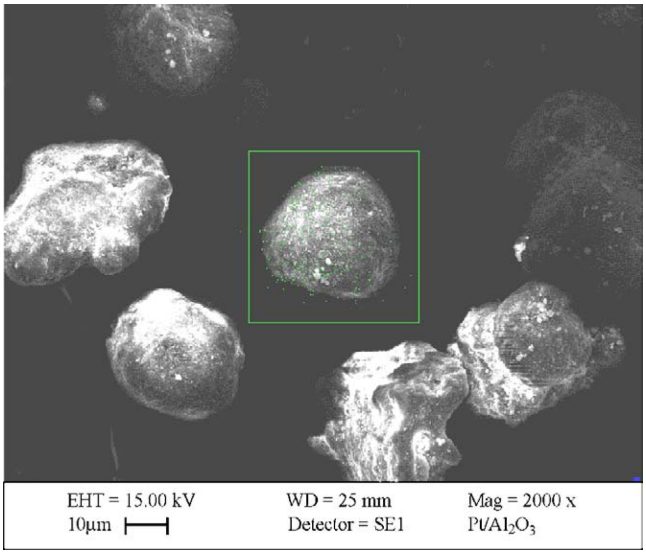


Fig. 2. Micrography of Pt supported on Al_2O_3.

Catalysts micrographies are presented on Figs. 2 and 3. TiO_2 micrography discloses the existence of crystallites that form accumulations without any definite structure. The formation of these accumulations must be contributing for the observed low surface area in this support. In the case of

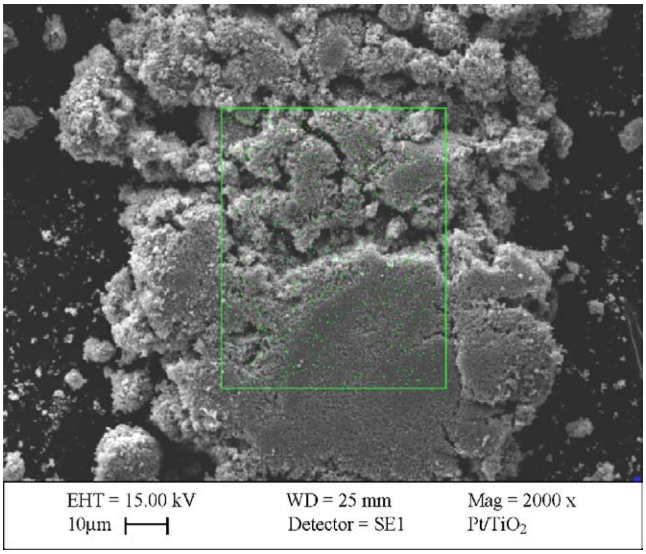


Fig. 3. Micrography of Pt supported on TiO_2.

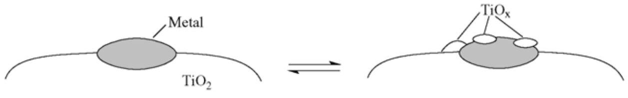


Fig. 4. Decoration effect of TiO$_x$ on metallic particles.

alumina, these accumulations are not observed. The metals deposited on the supports had apparently not modified the particles morphology. Metal dispersion on supports was assessed by EDS analysis. The micrographies indicated that platinum is highly dispersed on supports surface, as no areas with high concentration of that metal have been observed. Hydrogen sorption experiments showed that Pt dispersion on the TiO_2 support was lower than 5%, while it reaches values as high as 68% on the Al_2O_3 support. We can relate the dispersion values to the supports surface area, being that the lowest dispersion is observed in the catalyst supported in TiO_2, whose surface area is reduced. Meanwhile, the surface of the Pt/TiO_2 catalyst increased up to 7500 times (micrography not shown in this article) did not indicate the presence of so great crystallites. These results can be related to the effect of strong metal-support interaction (SMSI). It is known that, when submitted to high temperatures, TiO_2 in contact with the active phase can partially be reduced, producing species normally identified as TiO_x [16]. The mobility of such species allows their migration on metallic particles surface, recovering them in an effect called ‘‘decoration’’ (Fig. 4).

Hydrogenation reactions were held in liquid phase, where the catalyst effect was evaluated for the Pt metal supported on TiO_2 and Al_2O_3. The global activity shown by these catalytic systems was considered in association with dimethyl adipate total consumption on the reaction. Fig. 5 shows dimethyl adipate concentration in function of time, considering 10 h as reactional period for Pt/Al_2O_3 and 15 h for Pt/TiO_2. The experimental errors are ±2%.

A previous evaluation showed that in the catalyst absence, the substrate consumption occurs in the first hour of reaction and corresponds to a conversion of only 3.6%. The main generated products were methyl caproate, hexane and oxepane. The supports are also inactive, except for a small activity of alumina, attributed to its weak acid properties (Lewis acidity).

Results showed that the catalyst supported on Al_2O_3 is more active, reaching 52.91% conversion after 10 h of reaction, while for the same period of time, the catalyst supported on TiO_2 converted only 15.56% of the substrate. Nonetheless, regarding the obtained hydrogenation products, catalysts show extremely distinctive behavior. Products accounted after 10 h of reaction for Pt/Al_2O_3 and 15 h of reaction for Pt/TiO_2 are indicated on Table 2.

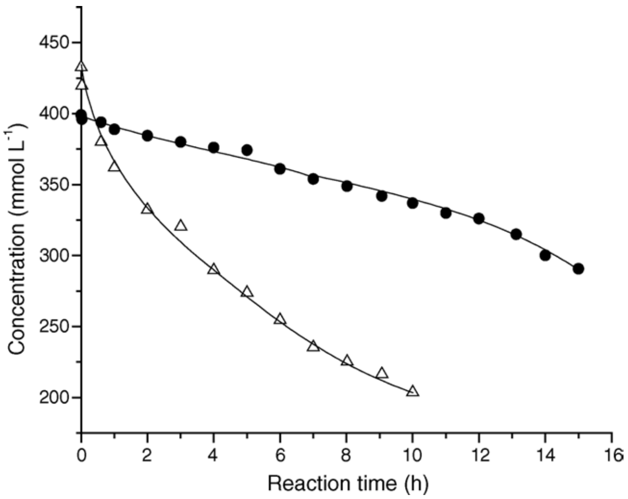


Fig. 5. Dimethyl adipate concentration in function of time to catalysts Pt/Al_2O_3 (△) and Pt/TiO_2 (●).

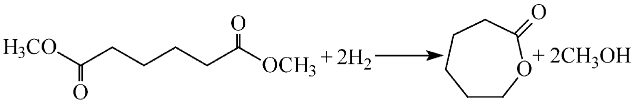
Dimethyl adipate catalytic hydrogenation can result in many products, such as lactones, cyclic ethers, monoesters, carboxylic alcohols, carboxylic acids and hydrocarbons. However, some compounds were not identified due to lack of commercial standards available to calibration. Methanol, hexane, 1-hexanol, caprolactone and 1,6-hexanediol were quantified by calibration curves constructed from standard solutions. Considering the similarity between caprolactone and oxepane, the calibration curve of caprolactone was used for the quantification of both compounds. In a similar way, methyl caproate and adipic acid monomethyl ester had been quantified through the calibration curve of dimethyl adipate. Beyond these products, we had the formation of some compounds that could not be identified by the mass spectrometer analysis. Then, by convenience, these products have been called as ‘‘others’’. The concentration of ‘‘others’’ was gotten by the difference between the initial substrate concentration in the reactor and the sum of the products quantified in the reaction (it is the amount that lacks to close the mass balance).

Pt/Al_2O_3 catalyst was the most active on adipate hydrogenation, forming mainly monomethyl ester (maximum 21.0 mmol L^{-1}), deriving from the hydrogenolysis of an ester O–CH_3 group. Formation of great amount of methyl caproate (11.4 mmol L^{-1}) is also observed and it results from the total hydrogenolysis of one of the substrate –

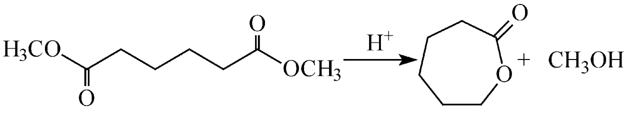
Table 2
Products obtained from dimethyl adipate hydrogenation catalyzed by Pt supported on TiO_2 and Al_2O_3

Catalyst	Adipate conversion (%)	Concentrations (mmol L^{-1})							
		Diol	Hexane	Capro-lactone	Methyl Caproate	Monomethyl Ester	Oxepane	1-Hexanol	Others
Pt/TiO_2	19.03	1.39	7.99	5.79	0.00	–	–	–	48.65
Pt/Al_2O_3	52.91	–	–	6.21	11.30	21.01	3.75	0.56	132.63

$OOCH_3$ groups. Caprolactone production reaches 6.5 mmol L^{-1}, and it may have been formed from two different ways: hydrogenation (2) or intermolecular esterification (3) of dimethyl adipate.

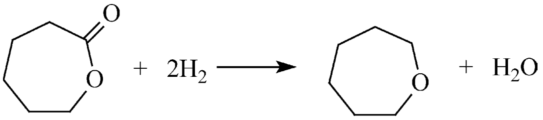


(2)

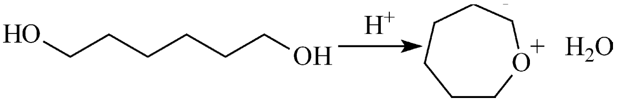


(3)

The presence of acid sites seems to favor the cyclic derivatives formation, as pointed out by Aurox et al. [17], which can indicate support contribution to the formation of caprolactone and oxepane, in terms of Al_2O_3, while on the TiO_2 supported system, the first one was only identified in low concentration. It is also important to consider that the oxepane formation may occur because of the caprolactone hydrogenation (4) or the hexanediol dehydration (5), which would be more likely due to Al_2O_3 acid properties identified by Badlani and Wachs [18].

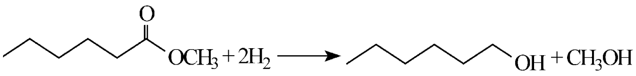


(4)



(5)

Besides that, the resulting lactone amount increases up to around 7 h of reaction and, after that, it is basically constant. Oxepane, on the other hand, shows gradual concentration increase throughout the complete reaction, where it is not possible to observe any relation between its formation and a decrease on the lactone concentration. Formation of 1-hexanol was observed in very small amounts (0.6 mmol L^{-1}). This product may derive from methyl caproate hydrogenation (6) or from 1,6 hexanediol (7). Methyl caproate concentration increases continuously with time, and no reduction related to 1-hexanol formation is observed. However, since the ester concentration is a lot higher than that of alcohol (21.0 and 0.6 mmol L^{-1}, respectively), it is not possible to exclude such possibility.



(6)

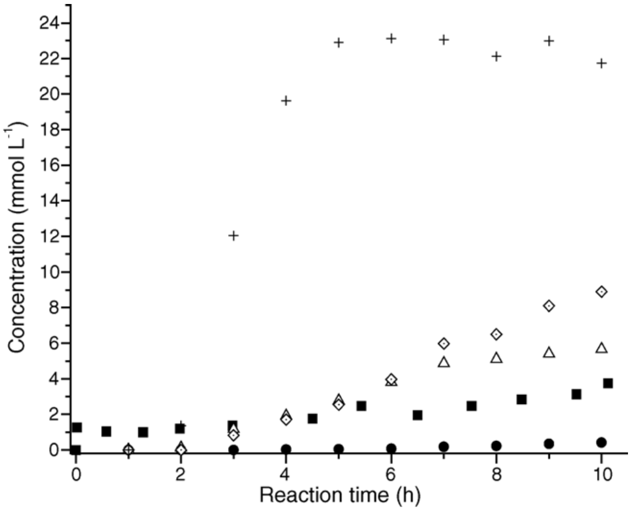
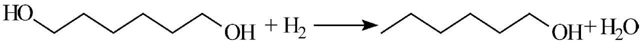
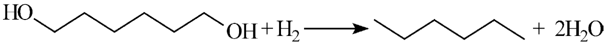


Fig. 6. Products obtained with catalyst Pt/Al_2O_3: (●) hexanol, (△) caprolactone, (■) oxepane, (◇) methyl caproate, (+) monomethyl ester, (*) diol and (▲) hexane.

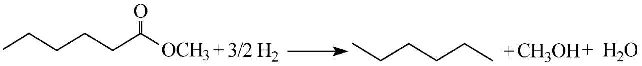


(7)

Reaction with Pt/TiO_2 originated smaller diversity of products, among which, 1,6-hexanediol (maximum 1.6 mmol L^{-1}). It was also possible to detect significant hexane amount (maximum 8.0 mmol L^{-1}), which may be formed by the hydrogenation of 1,6-hexanediol itself (8), or of methyl caproate (9).



(8)



(9)

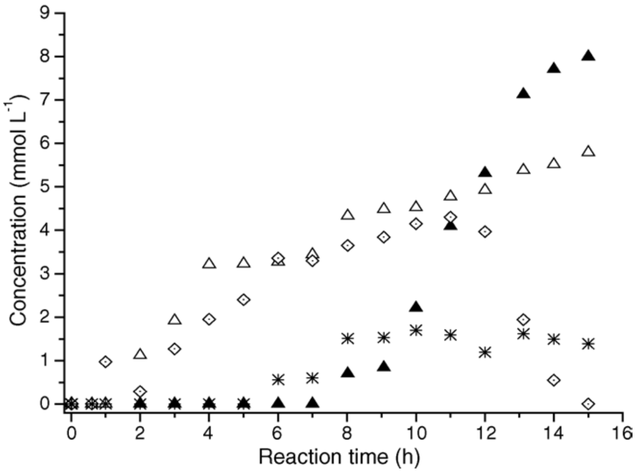


Fig. 7. Products obtained with catalyst Pt/TiO_2 (caption identical to the one on Fig. 6).

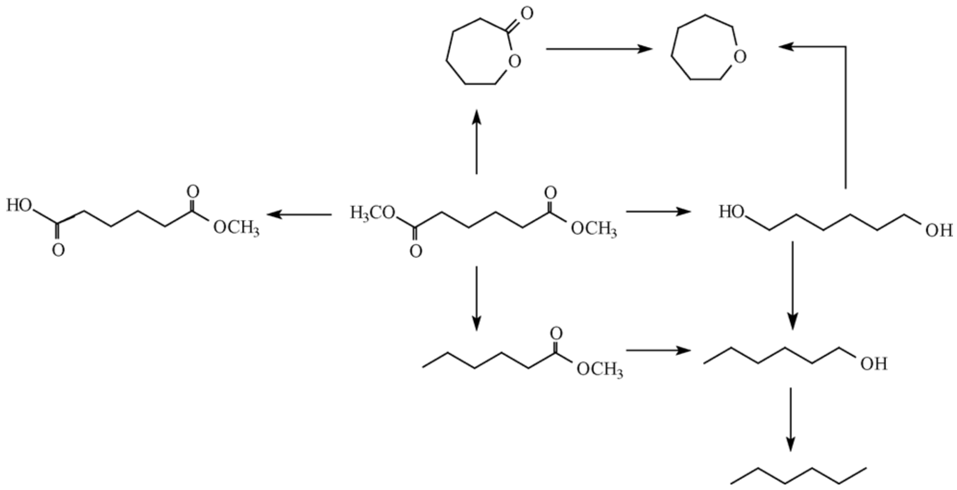


Fig. 8. Dimethyl adipate hydrogenation reactional scheme.

The second option seems to be more likely, according to data from the kinetic study, discussed below.

A kinetic study has indicated results illustrated on Fig. 6, for Pt/Al_2O_3 catalyst and on Fig. 7 for Pt/TiO_2 catalyst. In both cases, it is possible to observe an induction period of about 2 h.

Dimethyl adipate hydrogenation occurs in a series of parallel and consecutive reactions and it may offer various products, according to Fig. 8. In a first stage, monomethyl ester or methyl 6-hydroxy-hexanoate can be formed. The second compound (not present on the figure) can originate several products, among which methyl caproate, hexanol, hexane, caprolactone, oxepane and diol have been identified. Since the first reactional stage of the methyl 6-hydroxy-hexanoate formation is very fast [1], its conversion to subsequent products was taken as catalytic activity measure on tested systems. For Pt/Al_2O_3, methyl caproate and adipic acid monomethyl ester were formed preferably to alcohols. Carboxylic group left on molecules is more stabilized by the conjugated system than the hydroxyl group and, therefore, it is less susceptible to hydrogenation. For Pt/TiO_2, methyl caproate formation is crescent with up to 11 h of reaction. After that period, a decrease occurs on its concentration, at the same time as hexane concentration increases, confirming its formation in succeeding stages. After 15 h of reaction, initially formed methyl caproate is totally consumed, while hexane concentration reaches its maximum. Diol formation can only be observed after 5 h of reaction and it keeps stable up to the end. This behavior indicates that it goes through an induction period necessary to obtain selective catalytic sites on this system. Similar behavior was observed by Mendes et al. [5] on carbonyl hydrogenation in other organic substrates.

Studies done by Toba et al. [1] have indicated that the hydrogenation process must occur in three distinct stages: (1) carboxylic group activation; (2) molecular hydrogen activation; (3) active hydrogen migration to activated carboxylic group.

Titania supported metallic catalyst was selective to diol, while alumina supported catalyst, not only did not produce diol, but it also originated large amount of undesirable products. Both the hydrogenation process activity and selectivity are extremely dependent on the oxide used for support. Once both metal and support are separately inactive [19], a synergic effect is clearly observed occurring after the metal deposition on the support. This process may be favoring the formation of new active sites by means of interaction of metallic crystallites with the oxide surface, or promoting the presence of more than one different active site, necessary for higher hydrogenation activity and selectivity. The first possibility could be attributable to strong metal-support interactions (SMSI), which have been identified on systems consisting of noble metals dispersed on TiO_2 [20,21]. The second option is related to the fact that both the metallic atoms active sites and those of the support can be effective part of the reaction, which would include metallic atoms hydrogen migration to substrate molecules adsorbed on the oxide surface. This increase on supported metals activity is associated to the existence of metallic cations on the support surface, formed throughout the hydrogen activation process [22]. These cations interact with carbonyl oxygen of adipate molecule, promoting hydrogenation according to system illustrated on Fig. 9, modified from Mendes et al. [5].

However, Toba et al. [1] have demonstrated that the carboxyl group activation by the support is not effective, which leads to the formation of mono-carboxylic acids. Activation is not favored unless a second metal, such as Sn, is used, which has also been confirmed by Mendes et al. [5]. In addition, the large amount of acid sites on Al_2O_3 surface

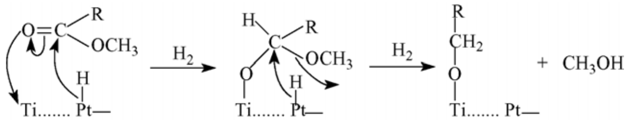


Fig. 9. Carboxyl group hydrogenation by titania supported metallic catalyst system.

may be adding to formation of undesirable products, which were not identified by the chromatographic analysis applied on this paper (‘‘others’’, on Table 2).

4. Conclusion

Pt/Al_2O_3 use as a catalyst on dimethyl adipate hydrogenation allowed obtaining methyl caproate and adipic acid monomethyl ester acid as main products. Dimethyl adipate total concentration was 52.91% after 10 h of reaction. Support acidity has favored formation of cyclic derivatives and, in the case of Al_2O_3, 1,6-hexanediol dehydration. Following reduction reactions can also be hindering diol recovery, promoting 1-hexanol and hexane formations.

Diol is formed only after 5 h of reaction, indicating that in the induction period, selective catalytic sites for this conversion are formed, probably related to the combined contribution of support and active metal.

Pt/TiO_2 catalyst promoted formation of the desirable product, 1,6-hexanediol, besides generating smaller amount of sub-products. These results indicate that Pt/TiO_2 is a potential catalyst for 1,6-hexanediol production. The system optimization could be done by the incorporation of additives as Sn, Fe or others, which favor the activation of carbonyl groups.

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