Palladium Supported Catalysts

Transition metals, which belong to group VIII, play an important role in heterogeneous catalysis. Palladium has a wide use not only in industrial processes [1-5] but also in basic chemical research [6-12], where it has arguably become the most versatile metal. It is worth pointing out its role in hydrogenation and dehydrogenation reactions [13-16], especially, those concerning the hydrogenation of vegetable oils [17, 18], which does not only represent an important reaction in food industry, but also it focuses our interest because its connection to our research field. On the other hand, active carbon is one of the most used support mainly because of its inertness, low cost, high surface area, easy recovery of metal phase in the spent catalyst and low deactivation [19]. Furthermore, it presented very interesting and motivating results in the study of the catalytic reactivity of ethyl linoleate (see *Chapter 3.5*). Thus, it was fully justified the study of the catalytic behaviour of palladium supported on active carbon in our work.

The catalytic testing with other palladium supported catalysts using other supports, such as, γ-Al$_2$O$_3$ and MgO, was considered to be useful. However, preliminary results showed no interesting results. This fact forced that our effort basically centred on supported catalysts on AC. The effects of different metallic amounts and reduction temperature of the catalysts on the reactivity of di-unsaturated FAEE are presented in the following chapter.

3.6.1 Experimental

The support was previously dried at 120 °C overnight. The precursor salt of palladium, PdCl$_2$, was diluted in MilliQ water. A few drops of HCl conc. were added in order to favour the solution of the salt. The brownish solution was slightly heated up. The supported catalysts were prepared by IWI of the dried active carbon to give a final metal load from 0.6 % to 4.8 % (w/w). After impregnation, they were left to dry at room temperature.

The reduction of palladium was performed in situ under a flow of H$_2$ (5%) in argon. The oven temperature was heated up from 40 °C to 250 °C or to 600 °C with a heating rate of 7 °C/min. The nomenclature for the catalysts will be Pd (metal

load)Support$_{reduction\ temperature}$. In both cases, the catalysts were left under argon for 8 hours to desorbed hydrogen.

The catalytic tests were performed at 240 °C with 0.11 μmol g cat^{-1} s^{-1} using argon as inert carrier with a flow of 0.225 mL/s. The samples were diluted in ethanol before being analysed by GC. The catalysts were characterized by XRD, physisorption of nitrogen, chemisorption of nitrogen and TPR measurements.

3.6.2   Results and Discussion

Characterization of the catalysts

XRD measurements confirmed the presence of the crystalline phase corresponding to metallic palladium. The pattern of Pd(1.2)AC$_{600}$ catalyst is presented in Fig. 3.6.1. The peaks of the pattern of palladium supported catalysts were in good agreement with those of the JCPDS file 046-1043 (dashed lines). The three diffraction peaks at 40.1, 46.6 and 68.1 degrees correspond to the {111}, {200} and {220} planes,
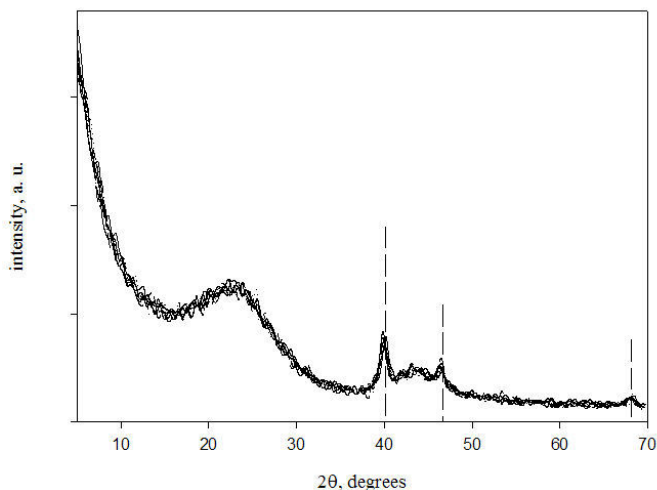

Figure 3.6.1 XRD pattern of Pd(1.2)AC$_{600}$.

respectively, of the Pd face-centered cubic (fcc) crystal structure. Palladium oxides were not detected whether they were not present or the technique could not detect them due to the support signal and/or to the low concentration of the compounds.

The evolution of hydrogen in TPR measurements of Pd(0.6)AC and AC is shown in Fig. 3.6.2. The wide peak centred at 620 °C was associated to the support, since it was present in both measurements. This hydrogen consumption may be related to the reduction of surface oxygen groups [20] or to the adsorption on surface sites of the support formed upon the decomposition of oxygen complexes [21]. The
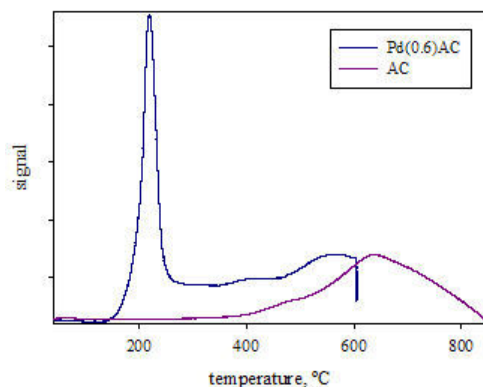

Figure 3.6.2 TPR analyse of Pd(0.6)AC and AC.

defined and narrow peak around 210 °C was not present in TPR measurement of AC; therefore, it was attributed to the reduction of the metallic precursor to metal.

The metal dispersion is related to the interaction between the metal precursor and the support, and, thus, influenced by several factors of the catalyst preparation, such as, the polarity of the solvent, the pH of the impregnating solution, the cationic or anionic nature of the metal precursor, types and amount of surface complexes on the support, etc. [21-23]. In metal supported on active carbon, the dispersion of the metal is apparently related to the surface chemistry of the support, concretely, to the oxygen-containing groups [21, 24]. The dispersion of our catalysts was in all cases around 30 % (Table 3.6.1). For Pd(0.6)AC$_{600}$, the dispersion achieved the highest value (32 %). Those values were relatively high considering the reduction temperature at which the catalysts had been subjected to and comparing them to already reported values [25]. The mobility of the metallic phase through the carbonaceous material, provoked by the decomposition of the less stable oxygen complexes which may act as anchoring centres for palladium species, appeared not to be so important [25]. It is relatively consistent with the results obtained in

Chapter 3.5, where AC showed a surface chemistry mainly based on carbonyl functionality. These carbonyl-containing groups decomposed at higher temperatures (around 900 °C); up to 600 °C, the decomposition of oxygen-containing groups was not so notable, which may be related to the low gasification of the support, and, consequently, a smaller effect of reduction temperature to the metallic dispersion.

Table 3.6.1

Properties of palladium supported catalysts.

Catalyst	% metal (w/w)	S_{BET} (m²/g)	Pd dispersion (%)
Pd(0.6)AC	0.6	1265	30.2
Pd(1.2)AC	1.2	1178	29.3
Pd(2.4)AC	2.4	1154	29.2
Pd(3.5)AC	3.5	1099	28.6
Pd(4.8)AC	4.8	1073	27.8
AC	0	1402	-

Concerning the surface area determined by the BET method, the metal supporting followed by reduction caused a decrease of surface area in all cases in comparison to AC. The specific surface area decreased with the increased of metal loading. This diminution may be related to lower micropore volume [26].

Catalytic Activity

Effect of catalyst weight

The conversion of ethyl linoleate at 240 °C after 2 hours reaction using different amounts of Pd(1.2)AC$_{600}$ is shown in Fig. 3.6.3. Up to 0.5 g no mass transfer problems occur, since the conversion increases lineally with the weight of the catalyst. However, the conversion becomes constant from 0.5 g to 1 g. indicating some difficulties in mass transfer. Therefore, from now on, the amount of used catalyst is going to be ≤ 0.5 g.
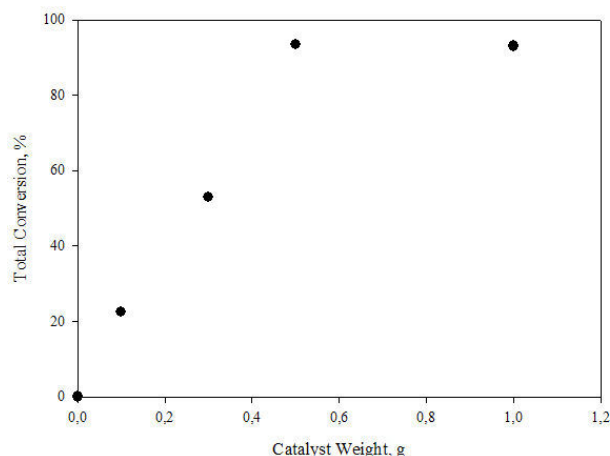
Figure 3.6.3 Total conversion of ethyl linoleate using different catalyst weights.

Effect of metal load

Total conversion along reaction time using different metal load supported AC is presented in Fig. 3.6.4. The total conversion value decreased as % of metal load supported on AC decreased. The highest conversion value ($\approx$ 80 %) was achieved by Pd(4.8)AC$_{600}$; while Pd(0)AC showed a lower value around 20 %. A common observation in all cases was the important deactivation. At the beginning of the reaction, all catalysts presented conversion values around 100 %. Plateau state was faster reached by Pd(0)AC than by the rest of supported catalysts. The deactivation of the catalyst was apparently smoothed by the addition of palladium to the catalyst. Then, the effect of palladium emerged to maintain the catalytic activity along the reaction time.

Analogously to AC (see *Chapter 3.5*), four family products were obtained in all cases. The ability of the catalyst to dehydrogenate is given by the obtaining of aromatic FAEE and of FAEE, whose mass spectra show a molecular ion at m/z = 302 (see *Chapter 3.2*). Mono-unsaturated FAEE are the product of the hydrogenation of starting material. The amount of totally saturated FAEE is considered negligible. Finally, another family of reaction products is comprised by isomers of di-unsaturated FAEE. Concerning selectivity towards aromatic FAEE, the catalyst with

the lowest metallic content, 0.6 %, showed a value of 63 %. On the contrary, Pd(4.8)AC$_{600}$ selectivity value was around 10 %. The rest of the catalyst presented values in the range of 20 to 23 %. Regarding the hydrogenation reaction, the opposite trend was showed; that is, Pd(4.8)AC$_{600}$ had the highest value (47 %) and Pd(0.6)AC$_{600}$ had the lowest one (23 %). A possible spill-over effect may be the explanation to balance the hydrogen used to obtain mono-unsaturated FAEE in the case of Pd(4.8)AC$_{600}$. Analogously, the catalysts, whose metallic load was 0 %, 1.2 %, 2.4 % and 3.5 %, had similar selectivity values (30-40 %) towards mono-unsaturated
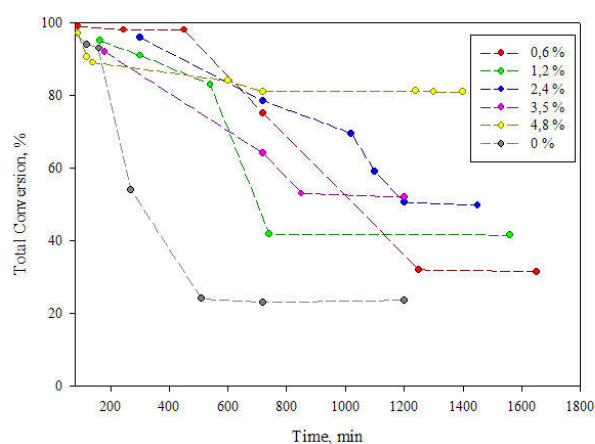

Figure 3.6.4 Total conversion of ethyl linoleate using different metallic-content supported catalysts.

FAEE. Isomerization selectivity augmented along reaction time. In general, the rising possessed a smooth trend, except in the case of Pd(4.8)AC$_{600}$ and Pd(0)AC, where the selectivity value abruptly increased after 2 hours reaction. As a final point referring to selectivity, the tendency to obtain FAEE with m/z = 302 was around 1 % in all cases. The next figure (Fig. 3.6.6) represents the selectivity towards the different reaction products of each catalyst.
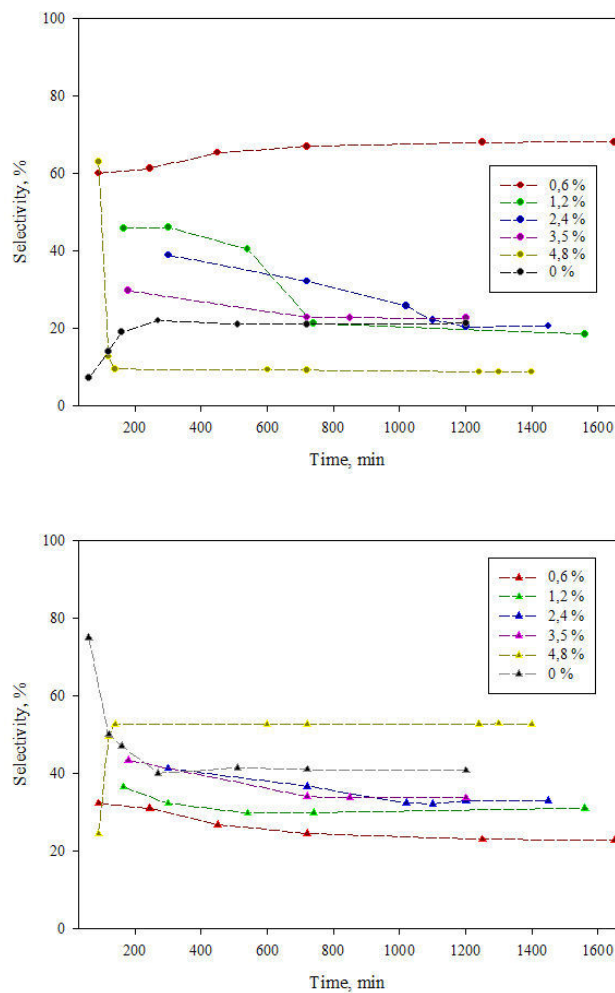
Figure 3.6.5 Selectivity values vs. reaction time using different palladium-load catalysts (--●-- aromatic FAEE, --▲-- mono-unsaturated FAEE, --■-- di-unsaturated FAEE and --×-- FAEE with m/z = 302). (continued)
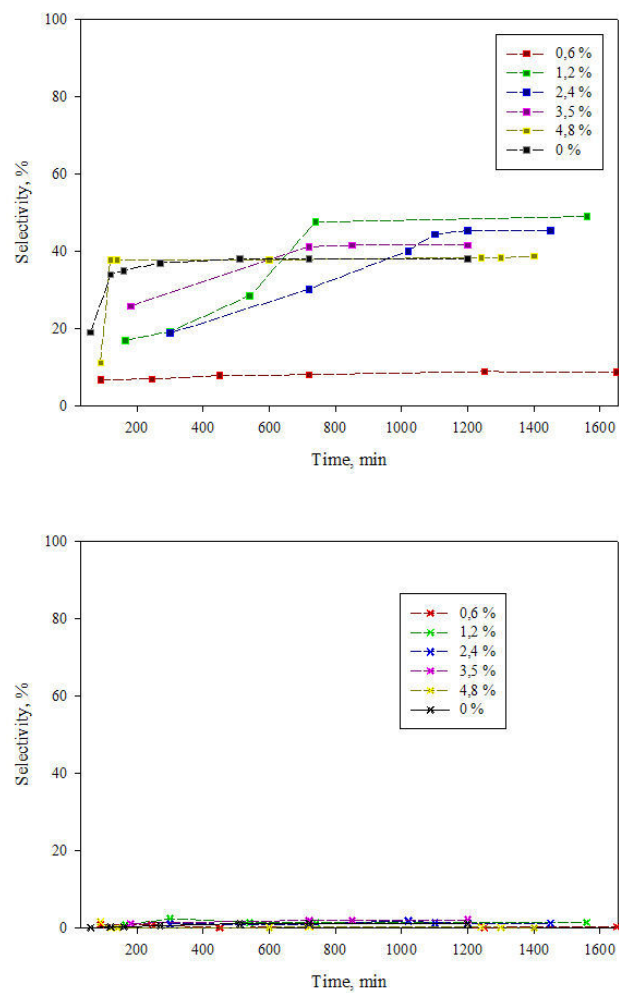
Figure 3.6.5 Selectivity values vs. reaction time using different palladium-load catalysts (--●-- aromatic FAEE, --▲-- mono-unsaturated FAEE, --■-- di-unsaturated FAEE and --×-- FAEE with m/z = 302).
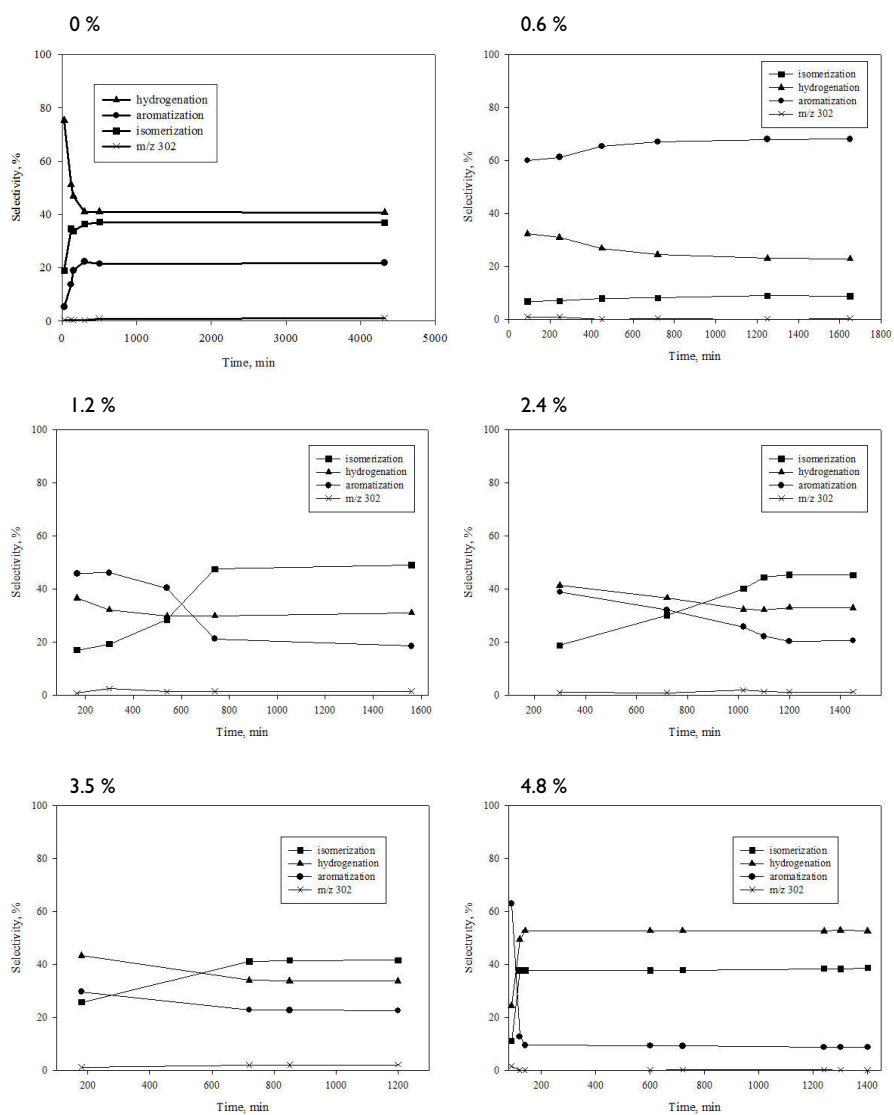
Figure 3.6.6 Selectivity values vs. reaction time using different palladium-load catalysts.

Effect of reduction temperature

A parameter susceptible to be altered was the reduction temperature of the catalyst. As shown in Fig. 3.6.2, the reduction of the metal was achieved at temperatures lower than 300 °C temperature. Thi s temperature may have an important effect on the dispersion of the metal because of the sintering effect caused by gasification of active carbon, migration of particles and sintering. The total conversion of ethyl linoleate when using Pd(0.6)AC$_{250}$ are showed in Fig. 3.6.7. Surprisingly, very alike total conversion curves were obtained indicating that reduction temperature did not affect the reactivity of the catalyst in that case. In comparison to high temperature-reduced catalyst, isomerization appeared to become more important, while the obtaining of aromatic FAEE had smaller
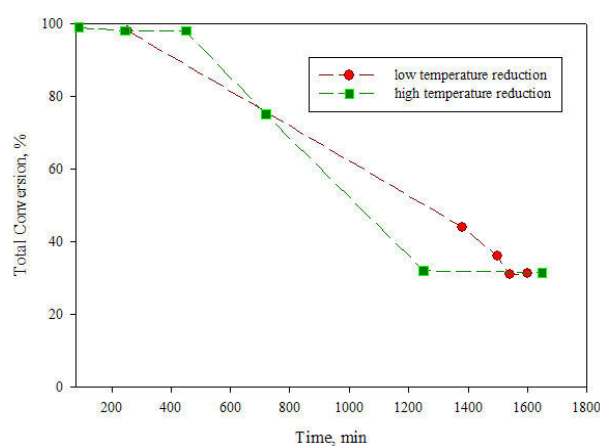

Figure 3.6.7 Total conversion of ethyl linoleate using Pd(0.6)AC
reduced at low (250 C) and high (600 C)

significance. Mono-unsaturated FAEE and FAEE with m/z = 302 selectivity were both alike to those obtained before (Fig. 3.6.8).

The results obtained with Pd(0.6)AC$_{600}$ came out to be quite attractive. Nevertheless, the rest of the supported catalysts did not bring too different results to those obtained with AC. The addition of palladium had only notorious results with the lower metallic content. Then, the difference among catalytic behaviour may be attributed either to alteration of the support rather than to palladium itself or to a promoter role of palladium.
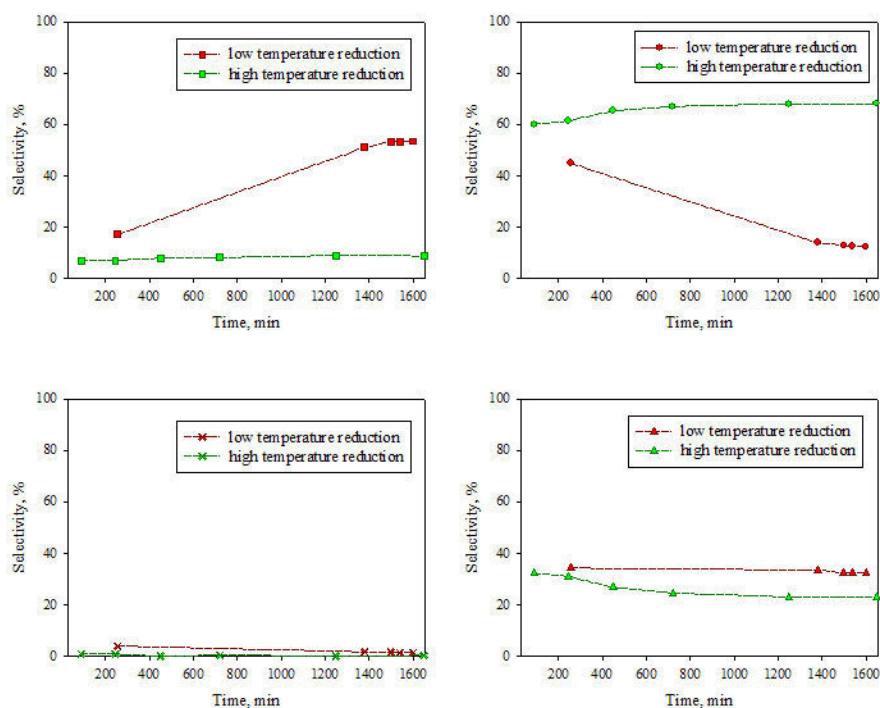
Figure 3.6.8 Selectivity values vs. reaction time using catalysts reduced at low (250 °C) and high (600 °C) temperature (--●-- aromatic FAEE, --▲-- mono-unsaturated FAEE, --■-- di-unsaturated FAEE and --×-- FAEE with m/z = 302).

3.6.3   Conclusions

The addition of palladium affected to the total conversion in the following sense: the more metal was present, the higher total conversion was showed. Regarding the selectivity towards aromatic FAEE, Pd(0.6)AC$_{600}$ presented the highest value. On the contrary, the lowest value was showed by Pd(4.8)AC$_{600}$. For hydrogenation selectivity, the trend was the opposite. The rest of the catalysts, whose metal loads were in between, presented similar catalytic behaviour towards hydrogenation and aromatization as the support itself. Isomerization occurred in the same range for all catalysts, except for Pd(0.6)AC$_{600}$. With such observations, it was difficult to conclude a relation between palladium content and reactivity.

Low temperature reduction implied no changes in the conversion of ethyl linoleate. However, it did favour the obtaining of di-unsaturated FAEE isomers accounting for a diminution of aromatic FAEE.

References

[1] R. B. Anderson, K. C. Stein, J. J. Feenan, L. E. J. Hofer, Ind. Eng. Chem. 53 (1961) 809.

[2] W. K. Lam, L. Lloyd, Oil Gas 27 (1972) 66.

[3] R. A. Dalla Betta, K. Tsurumi, Shoji, US Patent 5258349 (1993).

[4] S. Morikawa, S. Samejima, M. Yoshitake, N. Tatematsu, Jpn Patent 3-099026 (1991).

[5] J. Moore, J. O'Kell, EU Patent 508660 (1992).

[6] G. C. Bond, P. B. Wells, Adv. Catal. 15 (1964) 91.

[7] T. Mallat, A. Baiker, Catal. Today 19 (1994) 247.

[8] M. L. Derrien, Stud. Surf. Sci. Catal. 27 (1986) 613.

[9] A. Trovarelli, Catal. Rev.-Sci. Eng. 38 (1996) 439.

[10] C. F. Cullis, B. M. Willatt, J. Catal. 83 (1982) 267.

[11] J. H. Kang, E. W. Shin, W. J. Kim, J. D. Park, S. H. Moon, J. Catal. 208 (2002) 310.

[12] H. U. Blaser, A. Indolese, A. Schnyder, H. Steiner, M. Studer, J. Mol. Catal. A: Chem. 173 (2001) 3.

[13] P. N. Rylander, in: Hydrogenation Methods, Bench top Edition, Academic Press, New York, 1990, pp. 29–158. ISBN 0-126-05366-9

[14] Houben-Weyl, in: Methoden der Organischen Chemie, Reduktionen I, Vierte Auflage, Band IV/1c, Georg Thieme Verlag, Stuttgart, 1980, pp. 145–543. ISBN 3-13-2009-040

[15] M. Freifelder, in: Practical Catalytic Hydrogenation, Wiley/Interscience, New York, 1971, pp. 127–449. ISBN 0-471-27800-9

[16] D. Teschner, A. Pestryakova, E. Kleimenov, M. Hävecker, H. Bluhma, H. Sauer, A. Knop-Gericke, R. Schlögl, J. Catal. 230 (2005) 195.

[17] M. B. Fernández, G. M. Tonetto, G. H. Crapiste, M. L. Ferreira, D. E. Damiani, J. Mol. Catal. A: Chem. 237 (2005) 67.

[18] C. M. Piqueras, M. B. Fernández, G. M. Tonetto, S. Bottini, D. E. Damiani, Catal. Comm. 7 (2006) 344.

[19] E. Auer, A. Freund, J. Pietsch, T. Tacke, Appl. Catal. A 173 (1998) 259.

[20] D. J. Suh, T. J. Park, S. K. Ihm, Carbon 31 (1993) 427.

[21] A. Sepúlveda-Escribano, F. Coloma, F. Rodríguez-Reinoso, Appl. Catal. A 173 (1998) 247.

[22] F. Coloma, A. Sepúlveda-Escribano, J. L. G. Fierro, F. Rodríguez-Reinoso, Langmuir 10 (1994) 750.

[23] C. Prado-Burguete, A. Linares-Solano, F. Rodríguez-Reinoso, C. Salinas-Martínez de Lecea, J. Catal. 115 (1989) 98.

[24] A. Dandekar, R. T. K. Baker M. A. Vannice, J. Catal. 183 (1999) 131.

[25] A. L. Dantas Ramos, P. da Silva Alves, D. A. G. Aranda, M. Schmal, Appl. Catal. A 277 (2004) 71.

[26] M. Snåre, I. Kubičková, P. Mäki-Arvela, K. Eränen, D. Yu. Murzin, Ind. Eng. Chem. Res. 45 (2006) 5708.