Catal Lett (2008) 123:207–212
DOI 10.1007/s10562-008-9444-2

Ethylene Hydrogenation over Pt/Ga_2O_3/Al_2O_3 Catalysts

**Francisco Domínguez · Gabriela Carruyo · Raisel Andrade ·
Roger Solano · Douglas Rodríguez · Jorge Sánchez ·
Geomar Arteaga**

Received: 23 November 2007 / Accepted: 12 February 2008 / Published online: 6 March 2008

Abstract The effects of gallia addition on the Pt dispersion and the activity for ethylene hydrogenation at 0 °C were studied for Pt-supported catalysts as a function of the reduction temperature (350, 450, and 550 °C). The catalysts contained 0.5 wt.% Pt and were prepared by successive incipient wetness impregnations with $Ga(NO_3)_3$ and H_2PtCl_6 aqueous solutions. CO and H_2 chemisorption data indicated that, the addition of small amount of Ga_2O_3 caused an increase of the Pt dispersion and a decrease of ethylene conversion. Both of them decreased appreciably when Ga_2O_3 addition was increased, particularly, for the case where β-Ga_2O_3 was used as a support. The increase in reduction temperature magnified the negative effects of the gallia addition on dispersion and activity, although the addition of small amount of gallia improved the resistance to metal sintering. Results were interpreted in terms of the presence of reduced Ga species, which can encapsulate Pt particles.

Keywords Pt/Al_2O_3 catalysts · Gallia · Alumina · Ethylene hydrogenation

1 Introduction

The use of catalysts containing gallium in the heterogeneous catalytic processes has increased significantly. The more important applications include dehydrogenation and aromatization of light hydrocarbons [1, 2], methanol synthesis [3], the selective removal of nitrogen oxides [4, 5], and cracking and hydrocracking of cumene [6]. Nakagawa et al. [1] found that Ga_2O_3 was an effective catalyst for the dehydrogenation of ethane to ethene in the presence of carbon dioxide at 650 °C. They proposed that the reaction proceeded on the acid sites of the catalyst, because Ga_2O_3 loaded on a basic support did not exhibit dehydrogenation activity. Michorczyk et al. [2] found similar results for the dehydrogenation of propane to propene over gallium oxide.

Recently, it was reported that the addition of Ga_2O_3 to Al_2O_3 improved the selective removal of NO_x, which was attributed to strong Lewis acid sites: coordinately unsaturated cations, Al^{3+}_{cus} and Ga^{3+}_{cus}, produced as a result of the dehydroxylation of cations in tetrahedral positions [7]. Brønsted acid sites could also be present and they contribute to the acidity of gallia species [8]. Mediavilla et al. showed the presence of extra framework gallium species with a high surface acidity on MFI-type gallosilicates, such as Ga_2O, Ga^+ and Ga^0 formed after thermal treatments [9].

Owing to the partial reduction of gallia dispersed on a support and the modification of alumina acidity by gallia, it is expected that the presence of gallium can also modify the catalytic properties of a supported metal in different ways depending on the treatment conditions [10]. For this reason, the aim of this work was to study the effect of gallia addition on dispersion and activity of Pt/Al_2O_3 catalysts for the ethylene hydrogenation reaction as a function of the reduction temperature. The Pt/Ga_2O_3/Al_2O_3 catalysts were prepared varying the gallia content up to 10 wt.% and, for comparison, a Pt/Ga_2O_3 catalyst was also prepared. CO and H_2 chemisorptions were used to determine Pt dispersion. Ethylene hydrogenation was chosen to evaluate the catalytic properties of these catalysts because this reaction is

F. Domínguez (✉) · G. Carruyo · R. Andrade · R. Solano ·
D. Rodríguez · J. Sánchez · G. Arteaga
Instituto de Superficies y Catálisis, Facultad de Ingeniería,
Universidad del Zulia, Apartado 15251, Maracaibo 4003A,
Venezuela
e-mail: fdominguez@luz.edu.ve

G. Arteaga
e-mail: garteaga2007@yahoo.com

insensitive structure [11, 12] and a very simple probe reaction at low temperatures, occurring basically on the metallic phase and involving few side reactions.

2 Experimental

2.1 Catalyst Preparation

Four supports were used in this study: γ-Al_2O_3 (Rhône Poulénc), 1 wt.% Ga_2O_3/γ-Al_2O_3, 10 wt.% Ga_2O_3/γ-Al_2O_3, and β-Ga_2O_3 (Aldrich), with particle sizes in the range 60–80 mesh. All supports were calcined at 700 °C for 2 h heating at a rate of 10 °C/min. The Ga_2O_3/γ-Al_2O_3 supports were prepared by incipient wetness impregnation of calcined γ-alumina with the adequate amount of an aqueous solution of $Ga(NO_3)_3 \cdot xH_2O$ (99.9%, Aldrich). After impregnation, the wet solids were dried at 70 °C in a rotavapor and then at 120 °C overnight in a furnace, and finally calcined. The Pt supported catalysts were prepared by incipient wetness impregnation of the supports with the appropriate amounts of an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ (40% Pt, Alfa Products) to deposit 0.5 wt.% Pt. The catalyst pastes were dried as explained above.

2.2 Catalysts Characterization

The Pt and Ga_2O_3 contents of the catalysts were determined by energy dispersive X-ray fluorescence (EDXRF) in a Shimadzu EDX-700 HS spectrometer. The composition of the prepared catalysts is given in Table 1.

The measurements of CO and H_2 chemisorptions were carried out by the pulses method at room temperature, using a stainless steel line equipped with a Valco injection valve and a thermal conductivity detector (TCD). The pulse volume was 46 µL. The TCD signal was stabilized in a flow of Ar for the H_2 chemisorption or He for the CO chemisorption. The catalyst sample (100 mg) was charged in a quartz reactor, dried at 120 °C for 2 h in a flow of Ar, then reduced in a flow of H_2 at 350, 450 or 550 °C for 2 h and finally cooled to room temperature in flowing H_2. Before chemisorption, the reactor was flushed out with a flow of Ar or He at the same reduction temperature for 30 min. The flow of the gases was always of 30 cm^3/min. CO (Matheson, >99.6%), H_2 (produced by a Packard 9200 generator provided with a Linde 4A molecular sieve trap), Ar (Praxair, 99.999%) and He (99.999%, Praxair) were used in these experiments.

Table 1 Chemical composition and surface area of the supports and catalysts

Catalyst	Pt	Ga_2O_3	Al_2O_3	S_{BET} (m^2/g) (*)
Al	–	–	99.63	184
1GaAl	–	1.35	99.17	170
13GaAl	–	13.21	86.79	152
Ga	–	99.94	–	19
PtAl	0.39	–	99.61	ND
Pt1GaAl	0.47	1.30	98.23	ND
Pt13GaAl	0.35	13.17	86.48	ND
PtGa	0.39	99.61	–	ND

* Surface areas determined in a previous work (see Ref. [13])

ND: Not determined

2.3 Catalytic Tests

The reaction was carried out at 0 °C, using an ice and water bath with a recirculation pump, and atmospheric pressure under continuous flow conditions in a conventional reaction system made of stainless steel. The catalyst sample (20 mg) was mixed with crushed Pyrex glass (180 mg) in order to avoid hot spots. The drying and reduction treatments were similar to those used in the chemisorption measurements. Before commencing the reaction, the reactor was purged with a flow of Ar for 10 min. The reactor feed was a gaseous mixture of ethylene (99.999%, Praxair), hydrogen and Ar (60 cm^3/min as diluents) with a molar H_2/C_2H_4 ratio of 3 and a total flow rate of 100 cm^3/min. The products were analyzed on line by using a Perkin Elmer Autosystem XL gas chromatograph equipped with an alumina F1 (Anasorb) packed column and a flame ionization detector (FID).

3 Results and Discussion

3.1 Dispersion of Platinum

The values of H/Pt and CO/Pt ratios are shown in Table 2 for the catalysts reduced at 350, 450 and 550 °C. The PtAl catalyst exhibited high values of H/Pt ratio, close to one, indicating that platinum was in a highly dispersed state in this catalyst. An increase of the reduction temperature (from 350 to 550 °C) caused a significant decrease in the H/Pt ratio. This can be associated to a decrease in the Pt dispersion due to a sintering of Pt particles by exposing the catalyst to higher temperatures. Similarly, a strong decrease in the CO/Pt ratio with increasing reduction temperature was observed for the PtAl catalyst, therefore confirming the diminution in dispersion. Compared to H/Pt ratios, the lower values of CO/Pt ratio could indicate that platinum was in a moderate dispersed state in the Pt/Al_2O_3 catalyst. However, the high H/CO ratios (>2) observed for this catalyst suggest that an important portion of adsorbed CO molecules was in the bridged form, where each CO

Table 2 Chemisorption data of the catalysts

Catalyst	350 °C			450 °C			550 °C		
	H/Pt	CO/Pt	H/CO	H/Pt	CO/Pt	H/CO	H/Pt	CO/Pt	H/CO
PtAl	1.10	0.51	2.2	0.88	0.39	2.3	0.77	0.28	2.8
Pt1GaAl	1.08	0.60	1.8	1.06	0.50	2.1	1.00	0.36	2.8
Pt13GaAl	0.56	0.23	2.4	0.25	0.13	1.9	0.09_5	0.05_4	1.8
PtGa	0.14	0.03_9	3.5	0.08_8	0.02_0	4.4	0.05_9	0.01_1	5.4

molecule occupies two surface Pt atoms [13], and that, in consequence, platinum was highly dispersed, not as isolated atoms, but as two-dimensional particles (mats) or clusters.

The addition of gallia also affected the Pt dispersion as shown by the values of the H/Pt and CO/Pt ratios. The addition of 1.3 wt.% Ga_2O_3 (Pt1GaAl catalyst) caused an increase in the values of these ratios and, a slight decrease in the CO/Pt ratio when the reduction temperature increased. The H/Pt ratio did not change with the reduction temperature. The addition of a higher amount of Ga_2O_3 (Pt13GaAl) or supporting the platinum on gallia (PtGa catalyst) led to an enormous decrease in such ratios. These results indicate that the previous deposition of a small amount of gallia (1.3%) on the alumina surface promoted the Pt dispersion and produced a significant resistance of Pt particles to the sintering.

The promotion of the Pt dispersion can be due to an enhancement of the acidity properties of the catalyst surface, favoring the adsorption of $PtCl_6^{2-}$ anions during the impregnation of support with the H_2PtCl_6 solution. The resistance of metal particles to sintering can be associated to a stronger retention of Cl anions on the support surface. It is known that the presence of chlorides induces high Pt dispersions [14]. However, the absence of a promotion effect of gallia on dispersion was observed when the gallia content was increased to 13 wt.% or platinum was supported on gallia and, instead, this oxide produced a decrease in the dispersion similar to that reported in a previous work [15].

For the two catalysts with the higher contents of gallia, the diminutions in both H/Pt and CO/Pt ratios were larger when the catalysts were reduced at 550 °C. These results are in agreement with those reported by Jablonski et al. [10], who found that the $PtGa/Al_2O_3$ catalysts showed a slight decrease in the chemisorption capacity after reduction at 300 °C and a significant decrease after reduction at 500 °C. However, the decreases in such ratios were also significant for the lower reduction temperature (350 °C), about 49% and 87% in the H/Pt ratio and 55% and 92% in the CO/Pt ratio for the Pt13GaAl and PtGa catalysts, respectively, compared to the values of these ratios in the PtAl catalyst. Therefore, this decrease in dispersion associated to the addition of gallia can attribute to an intimate contact between Pt particles and partially reduced gallium species formed during the reduction treatment, where these species could encapsulate or block Pt particles [10, 16–18].

Melo et al. [16] studied by electronic paramagnetic resonance (EPR) two Pt catalysts (0.5%Pt/H[Ga]ZSM5 and 0.5%Pt/H[Al]ZSM5) reduced at 500 °C, and suggested that in the first catalyst Pt was passivated due to its interactions with Ga_2O and GaO^+ species formed during reduction. Zheng et al. [19] studied by XPS the hydrogen reduction of β-gallia at 500 °C and observed a new peak at 19.6 eV attributed to the presence of Ga_2O species. They reported that the amount of Ga^{3+} reduced to Ga^+ was about 2.5 mol% of the total amount of Ga_2O_3.

The reduction of gallia has been represented by the following reactions [16, 20]:

$$Ga_2O_3 + 2H_2 \rightarrow Ga_2O + 2H_2O \quad (1)$$

$$Ga_2O + H_2 \rightarrow 2Ga + H_2O \quad (2)$$

The present chemisorption results and those reported in the literature suggest that the reduction of β-gallia could occur under the conditions used in this work. In our previous work [15], it was found by TPR that gallia was reduced and interacted with Pt particles. The extremely high H/CO ratios, which increased from 3.5 to 5.4 with increasing reduction temperature for PtGa catalyst, indicate that an encapsulation of Pt particles by reduced Ga species affected in different degrees the accessibility of these adsorbates (CO and H_2) into the Pt surface. This effect was more pronounced for CO molecules than for H_2 molecules, in concordance with their molecular sizes. Other catalytic systems, such as Ir/TiO_2 catalysts, have presented the encapsulation of the metal particles by the support after high temperature reduction [21]. Additionally, other authors have found that electronic modifications of Pt sites by Ga could occur in a minor extension when the catalysts were reduced at higher temperatures (773 K) [10]. We do not rule out this explanation.

3.2 Catalytic Activity

Figures 1, 2 and 3 show the values of ethylene conversions as a function of the reaction time for the catalysts reduced at 350, 450 and 550 °C, respectively. It is observed in these figures that the two catalysts with the lower gallia contents,

Fig. 1 Ethylene conversion as a function of reaction time for the catalysts reduced at 350 °C

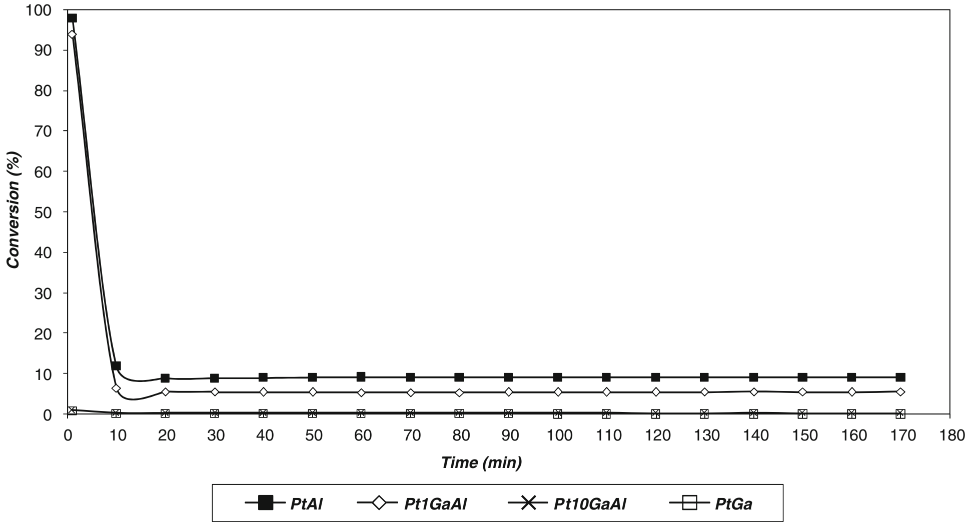


Fig. 2 Ethylene conversion as a function of reaction time for the catalysts reduced at 450 °C

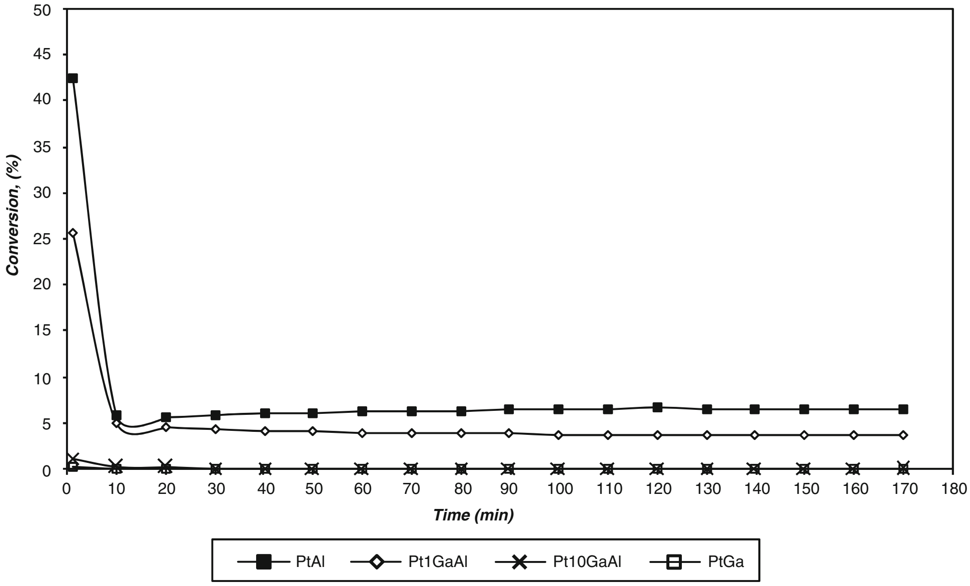
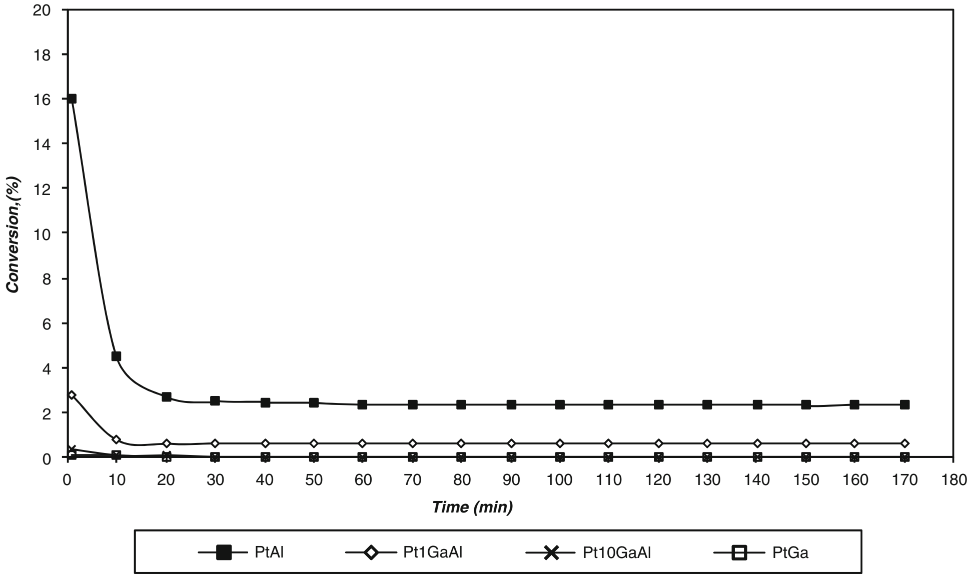


Fig. 3 Ethylene conversion as a function of reaction time for the catalysts reduced at 550 °C



particularly PtAl, showed high initial conversions accompanied by a strong catalyst deactivation in the first 10 min of reaction time and then an almost constant conversion. On the contrary, the catalysts with the higher gallia contents (Pt13GaAl and PtGa catalysts) presented very low conversions and a less pronounced deactivation. The strong deactivation of the PtAl and Pt1GaAl catalysts can be attributed to the coke deposition on the actives sites of the Pt surface [15].

Table 3 show the values of the initial ethylene conversions, measured at 1 min of reaction time, as a function of the reduction temperature for the low gallia content (PtAl and Pt1GaAl) and high gallia content (Pt13GaAl and PtGa) catalysts, respectively. All catalysts exhibited a strong decrease in the initial conversion with the increase in the reduction temperature. This agrees with the chemisorption data, which indicated a diminution in the Pt dispersion when the reduction temperature was increased.

On the other hand, the addition of Ga_2O_3 caused a decrease in the initial ethylene conversion: a slight diminution for Pt1GaAl catalyst and a very strong decrease for Pt13GaAl and PtGa catalysts (Table 3). Comparing the effects of the addition of Ga_2O_3 on the initial conversion and dispersion, different tendencies and intensities in these changes were observed. For example, due to the addition of 1.3% Ga_2O_3 (Pt1GaAl catalyst), the Pt dispersion increased (30% for the highest reduction temperature), contrasting with the decrease in the initial conversion (82% for the same reduction temperature). Similar results were presented by Melo et al. [17], who found that the activity of the 1 wt.% Pt/H[Al]ZSM5 catalyst for toluene hydrogenation was 12 times higher than that of the 1 wt.% Pt/H[Ga]ZSM5 catalyst, which had gallium incorporated in the zeolitic structure, whereas the Pt dispersion of the former was 1.6 times lower than that of the latter. This can be due to the Ga migration toward the surface of Pt particles, which should favor electronic and/or geometrical interactions between Pt particles and Ga species; resulting in the passivation of Pt metallic centers for the hydrogenation reactions [17]. When the dose of Ga_2O_3 was increased to 13% (Pt13GaAl catalyst), for any reduction temperature, the initial conversion decreased almost 100 times, while the dispersion diminished to the half. For the case where Pt was supported on pure Ga_2O_3 (PtGa catalyst), the initial conversion decreased from 120 to 250 times, following the increase in reduction temperature, whereas the dispersion fell 10 times, as compared to that of the Pt/Al_2O_3 catalyst.

Table 3 Effect of the reduction temperature on the initial ethylene conversion

Catalyst	350 °C	450 °C	550 °C
PtAl	97.8	42.6	16.0
Pt1GaAl	93.9	25.6	2.8
Pt13GaAl	1.1	1.1	0.3
PtGa	0.8	0.3	0.1

These results also imply that the coverage of Pt particles by reduced Ga species, such as Ga_2O and GaO^+ [16–20, 22], hindered the ethylene hydrogenation. The higher the reduction temperature, the higher the amounts of these species that can be formed and, therefore, the higher the influence on catalytic activity can be observed. The greater effect of gallia addition and reduction temperature on the initial activity than on the Pt dispersion can be explained in terms of the differences in size between the molecules used for chemisorption (H_2 and CO) and the molecule used for reaction (C_2H_4).

These results indicate that the platinum particles dispersed on the surface of gallia-containing catalysts are less active for hydrogenation reactions, confirming that electronic and/or geometrical platinum–gallium interactions affect negatively the catalytic activity of the metallic function.

4 Conclusions

The addition of a small amount of gallia (about 1 wt.%) to the support of a Pt/Al_2O_3 catalyst promoted the Pt dispersion, whereas large gallia additions (>10 wt.%, including the case where β-Ga_2O_3 was used as a support) caused a strong decrease in dispersion. This was modified in the following order: Pt1GaAl > PtAl >> Pt13GaAl >> PtGa. The dispersion also decreased with the increment in reduction temperature, though a low gallia content favored a high resistance of platinum to sintering. The Pt/Al_2O_3 catalyst showed the highest conversions of ethylene to ethane. The initial ethylene conversion decreased when the reduction temperature and gallia content were increased. The addition of 13 wt. % Ga_2O_3 affected considerably more the conversion than the dispersion. The effects of gallia addition on dispersion and activity could be ascribed to the encapsulating of Pt particles by partially reduced gallia.

Acknowledgments The authors thank CONDES (Project VAC-CC-0869-04) and FONACIT (Project S1-2002000289) for financial support

References

1. Michorczyk P, Ogonowski J (2003) Appl Catal A: Gen 251:425
2. Nakagawa K, Kajita Ch, Ide Y, Okamura M, Kato S, Kasuya H, Ikenaga N, Kobayashi T, Susuki T (2000) Catal Lett 64:215

3. Collins S, Baltanás M, Bonivardi A (2005) Appl Catal A: Gen 295:126
4. Haneda M, Joubert E, Ménézoa J, Duprez D, Barbier J, Bion N, Daturi M, Saussey J, Lavalley J, Hamada H (2001) J Mol Catal A 175:179
5. Chen L, Horiuchi T, Mori T (1999) Catal Lett 60:237
6. Olorunyolemi T, Kydd R (1996) J Catal 158:583
7. Pushkar Y, Sinitsky A, Parenago O, Kharlanov A, Lunina E (2000) Appl Surf Sci 167:69
8. Rodríguez M, Otero C (2003) Mater Lett 57:2292
9. Mediavilla M, Melo L, Diaz Y, Brito J, Albornoz A, Solano R (2007) Micropor Mesopor Mater 102:86
10. Jablonski EL, Castro AA, Scelza OA, de Miguel SR (1999) Appl Catal A 183:189
11. Rioux RM, Komor R, Song H, Hoefelmeyer JD, Grass M, Niesz K, Yang P, Somorjai GA (2008) J Catal 254:1
12. Dorling TA, Eastlake MJ, Moss RL (1969) J Catal 14:23
13. De la Cruz C, Sheppard N (1994) Spectrochim Acta 50:271
14. Anderson J, Mordente M, Rochester CJ (1989) J Chem Soc, Faraday Trans 1 85:2983
15. Domínguez F, Sánchez J, Arteaga G, Choren E (2005) J Mol Catal A 228:319
16. Melo L, Llanos A, Mediavilla M, Moronta D (2002) J Mol Catal A 177:281
17. Melo L, Díaz Y, Mediavilla M, Albornoz A, Brito J (2004) Catal Lett 97:105
18. Díaz Y, Melo L, Mediavilla M, Albornoz A, Brito J (2005) J Mol Catal A 227:7
19. Zheng B, Hua W, Yue Y, Gao Z (2005) J Catal 232:143
20. Fricke R, Kosslick H, Lischke G, Richter M (2000) Chem Rev 100:2303
21. Tauster SJ, Fung SC (1978) J Catal 55:29
22. Cao YC, Jiang XZ (2005) J Mol Catal Vol 242:119