ISSN 0023-1584, Kinetics and Catalysis, 2008, Vol. 49, No. 4, pp. 574–580. © MAIK “Nauka/Interperiodica” (Russia), 2008.
Published in Russian in Kinetika i Kataliz, 2008, Vol. 49, No. 4, pp. 599–606.

III INTERNATIONAL CONFERENCE
“CATALYSIS: FUNDAMENTALS AND APPLICATIONS”

A Comparative Study of Ir/Ga_2O_3, Pt/Ga_2O_3, and Ru/Ga_2O_3 Catalysts in Selective Hydrogenation of Crotonaldehyde[1]

E. Gebauer-Henke[a], J. Farbotko[a], R. Touroude[b], and J. Rynkowski[a]
[a] *Institute of General and Ecological Chemistry, Technical University of Łódź, Poland*
[b] *LMSPC, UMR 7515 du CNRS, ECPM-ULP, Strasbourg Cedex 2, France*
e-mail: jacryn@.p.lodz.pl

Received October 15, 2007; in final form, January 9, 2008

Abstract—Catalytic performance of gallia-supported iridium catalysts in the reaction of selective hydrogenation of crotonaldehyde in the gas phase was studied and compared to that of platinum and ruthenium catalysts. The best catalytic properties in terms of the selectivity to crotyl alcohol are shown by 5 wt % Pt/α-Ga_2O_3 and 5 wt % Ir/α-Ga_2O_3 catalysts prepared from nonchlorine precursors: $Pt(acac)_2$ and $Ir(acac)_3$, but for the 5 wt % Pt/α-Ga_2O_3 a very high selectivity of 75% at the high conversion (ca. 60%) is observed. A high selectivity of galia-supported iridium and platinum catalysts was explained by the surface reducibility of gallium oxide leading to covering (decoration) of platinum and iridium by gallium suboxides and the promoting effect of gallium.

DOI: 10.1134/S0023158408040186

1. INTRODUCTION

One of challenging tasks in catalytic hydrogenation is selective reduction of the C=C double bond in α,β-unsaturated aldehydes to the desired product, α,β-unsaturated alcohols. In this field monometallic catalysts supported on Al_2O_3 and SiO_2 mostly give the formation of saturated aldehydes [1, 2]. For small molecules like crotonaldehyde, the reaction is almost quantitatively selective to saturated aldehydes. Therefore, it is desirable to find a catalyst that can control the selectivity towards unsaturated alcohol.

The factors affecting activity and selectivity in the hydrogenation of α,β-unsaturated aldehydes have been reviewed in numerous works [2–7]. The most important seems to be the metal particle size and the presence of promoters, such as second metal or alkaline solutions, but also the kind of the support used. Partly reducible supports like TiO_2, Nb_2O_5, Y_2O_3, ZrO_2, ZnO_2, CeO_2, and ZnO appeared to be very promising [4–6].

The most universally used metallic hydrogenation catalysts are supported Pt, Ru, Rh, Os, Ir, Ni, Co, and Pd systems. Platinum-group metals can be ranked according to their selectivity for C=O hydrogenation as follows [7]: Ir > Pt > Ru > Rh.

Such a trend was confirmed by Sokol’skii [8] for crotonaldehyde hydrogenation (Os > Ir > Ru > Rh ≈ Pt ≈ Pd) and by Cordier [9] for cinnamaldehyde hydrogenation (Os > Ir > Pt > Ru > Rh > Pd).

Gallium is mentioned as an effective promoter in the reduction of the carbonyl group in Pt-based catalysts [10]. Englisch et al. [11] show that transitional metals like Ga can be used as promoters in catalysis for selective hydrogenation of α,β-unsaturated aldehydes.

In our previous studies we examined the catalytic performance of Ga_2O_3-supported platinum [12] and ruthenium catalysts [13]. We found that some of them, especially 5 wt % Pt/α-Ga_2O_3, obtained from $Pt(acac)_2$, show very promising activity and selectivity to crotyl alcohol.

In this work we focused our attention on Ir/Ga_2O_3 catalysts and a comparison of the results with those described earlier for Pt/Ga_2O_3 and Ru/Ga_2O_3 systems.

2. EXPERIMENTAL

Support Preparation

Two gallium oxide supports were used: α-Ga_2O_3 S_{BET} = 48.7 m^2/g, mesoporous, and β-Ga_2O_3 (Aldrich 21506-6, 99.99%, S_{BET} = 2.2 m^2/g, nonporous). α-Ga_2O_3 was prepared in our laboratory by dissolving metallic gallium in concentrated nitric acid (V) followed by precipitation of $Ga(OH)_3$ with NH_3 aq., drying at 120°C, and calcination at 500°C for 3 h in air.

Catalyst Preparation

Ir/Ga_2O_3 catalysts were prepared by a wet impregnation method of two: α- and β-Ga_2O_3, using methanolic solution of iridium acetyl acetate ($Ir(acac)_3$—Aldrich). Methanol was slowly evaporated on a hot plate. The samples were dried at 120°C for 2 h, calcined in air at 200°C for 2 h.

---

[1] This article was submitted by the authors in English.

The composition and BET surface of catalysts are presented in Table 1. The exact amount of iridium was determined by inductively coupled plasma (ICP) method and found to be very close to the nominal one.

Catalytic Tests

Catalytic tests were carried out in a glass reactor, operating at atmospheric pressure. The total gas flow controlled by a flowmeter varied with the changes in the pump rate at the end of the flow line. Pure crotonaldehyde (Fluka), stored in argon, was used as received. A certain quantity (50–250 μl) was drawn up from the bottle using a tight syringe and introduced through a vaccine cap into a reservoir installed on-line and maintained at 0°C: therefore, aldehyde at constant partial pressure (8 Torr) was carried over the catalyst by hydrogen flow (50–60 cm^3/min). Beyond the aldehyde reservoir, the gas line was thermostated at about 60°C to avoid any condensation. The reaction products were drawn off the flow line at different times during the catalytic run and analyzed by gas chromatography at 85°C using a flame ionization detector.

Catalyst samples (5–100 mg) were reduced at the chosen temperature for 1 h and then cooled under H_2 prior to the reaction carried out at a temperature of 80°C.

The reaction activities were calculated using the formula $A = \alpha F/\omega$, where α is the crotonaldehyde conversion [%], F is the flow rate of crotonaldehyde [mol/s], and ω is the weight of platinum [g]. The selectivity to different products, crotyl alcohol, butanal, butanol, and hydrocarbons was calculated as the molar ratio of the selected product to the total amount of products formed. The sensitivity factors are taken as 1.4 for the hydrocarbons and 1 for the other products.

It was checked that both supports alone, α- and β-Ga_2O_3, after H_2 pretreatment up to 300°C, had no activity in crotonaldehyde hydrogenation.

X-Ray Diffraction Measurements

XRD analyses were carried out in Siemens D 5000 (supports) and X'PERT PRO MPD PAN polycrystalline diffractometer (catalysts), using CuK_α radiation. The measurements of catalysts were made in situ in the stream of 5% H_2/Ar in the temperature range 30–700°C, with the heating rate 1 K/min. Patterns were recorded in the scanning mode (2.0 s/step, step size: $2\theta = 0.05°$, 2θ range 30°–80°). The mean crystallite size of Ga_2O_3 samples was related to a pure x-ray broadening by the Scherer formula $D = k\lambda/\beta\cos\theta$. The measured line broadening b was corrected for the instrumental broadening B, using an equation $\beta = \sqrt{B^2 - b^2}$. The particle shape factor k was taken as 0.9. Phase identification was made basing on JCPDS and ICDS files.

Table 1. Catalyst composition

Catalysts	Ir precursors	Ir content, wt %	S_{BET}, m^2/g
α-Ga_2O_3	–	–	48.7
β-Ga_2O_3	–	–	2.2
5 wt % Ir/α-Ga_2O_3	$Ir(acac)_3$	4.92	60.5
5 wt % Ir/β-Ga_2O_3	$Ir(acac)_3$	5.07	3.7

Temperature-Programmed Reduction Measurements

All TPR courses were carried out in Altamira apparatus (Altamira Instruments, United States) using an Ar-H_2 mixture (5 vol % H_2) and a flow rate 50 cm^3/min, and sample weight of 100 mg; the temperature increase was 10 K/min. Prior to the TPR, samples were calcined in air at 200°C for 2 h.

ToF-SIMS Measurements

The ToF-SIMS investigations were performed in the static mode using an ION–TOF instrument (TOF SIMS IV) equipped with a 25 kV pulsed $^{69}Ga^+$ primary ion gun. To obtain the plain surface of catalysts, powder samples were tableted before the measurements. For each sample five spectra were collected (from different areas) in order to determine the distribution of Ir on the support.

FTIR Measurements

FTIR experiments were carried out at a Shimadzu 8501 spectrometer using a quartz cell fitted with NaCl windows and an external furnace. Catalyst samples of 80 mg were prepared in the form of discs 25 mm in diameter. After the reduction in hydrogen at 300°C, the cell was evacuated for 30 min at room temperature. Pulses of CO or crotonaldehyde were introduced at 25°C, and spectra were recorded.

3. RESULTS AND DISCUSSION

The diffractogram of the support prepared by us shows the characteristic lines at 2θ = 33.8°, 36.0°, 40.3°, 41.4°, 50.3°, 55.1°, 63.4°, and 64.8°, which are, in fact, identical to those given in ICSD file (00-006-0503) and the literature [14] proving that we are dealing with α-Ga_2O_3. Likewise, the commercial β-Ga_2O_3 shows characteristic lines, according to ICDS file (01-076-0573). The mean crystallite size of α-Ga_2O_3 and β-Ga_2O_3 was estimated based on the broadening of XRD lines using the Scherer formula, and it was equal to about 16 and 22 nm, respectively.

XRD measurements of both catalysts were made in situ in a reductive atmosphere in the temperature range 30–700°C. Such a procedure allows us to follow a

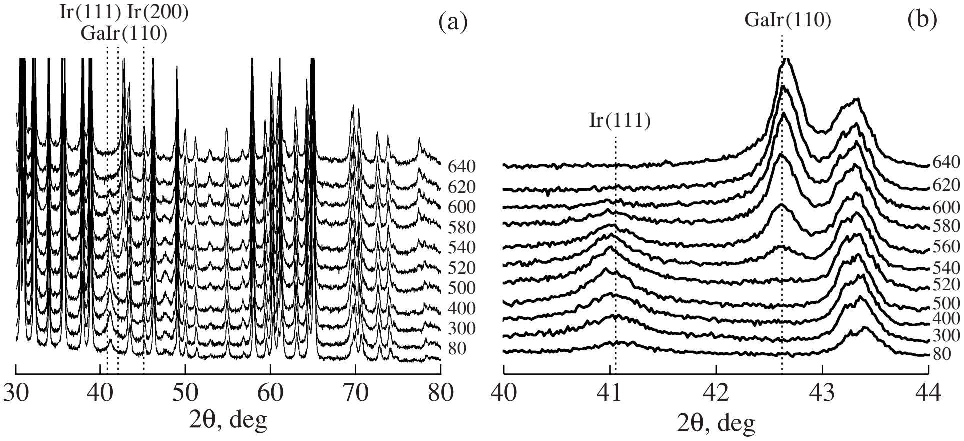

Fig. 1. XRD patterns of 5 wt % Ir/β-Ga_2O_3.

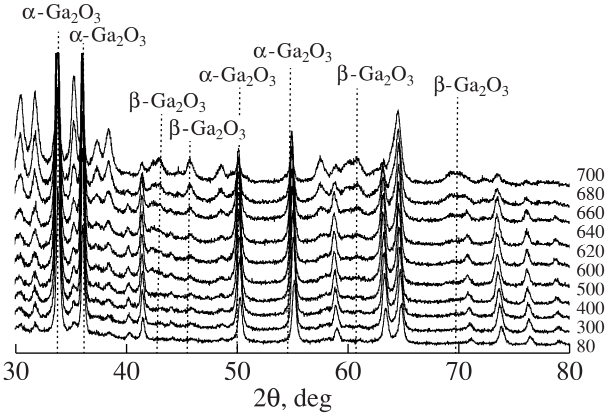

Fig. 2. XRD patterns of 5 wt % Ir/α-Ga_2O_3.

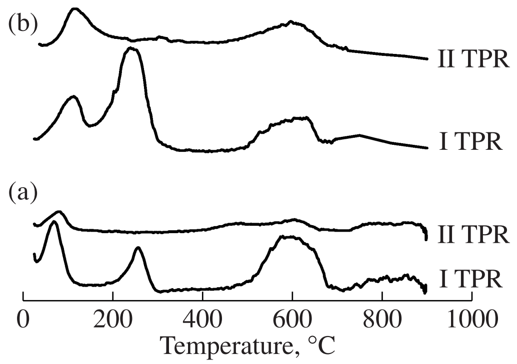

Fig. 3. TPR profiles for (a) 5 wt % Ir/β-Ga_2O_3 and (b) 5 wt % Ir/α-Ga_2O_3.

phase transformation of supports and the active phase. Figure 1 presents a diffractogram of the 5 wt % Ir/β-Ga_2O_3 catalyst. Lines characteristic for β-Ga_2O_3 predominate. There are no lines coming from IrO_2, which suggests that $Ir(acac)_3$ undergoes decomposition to metallic iridium during the calcination at 200°C and/or that iridium oxide is reduced to iridium already at room temperature. One can observe lines of metallic iridium at 2θ about 40.7° and 47.3° corresponding to the (111) and (200) planes. An enlargement in the 2θ range 40°–44° is shown in Fig. 1b to follow a transformation of iridium with the increase of temperature. The intensity of lines characteristic for Ir increases up to a temperature about 540°C, probably reflecting the sintering of metal. At the temperature 540°C, lines at $2\theta = 42.5°$ and 77.8° arise corresponding to the iridium–gallium alloy IrGa, the planes (110) and (211), respectively. Further increase of temperature leads to the gradual deterioration of Ir lines. At the temperatures above 600°C, the complete conversion of Ir in the IrGa alloy is observed.

Diffractograms of the catalyst 5 wt % Ir/α-Ga_2O_3 are presented in Fig. 2. In fact, there are no lines for any iridium-containing phases. We can observed a partial transformation of α polymorphic form to the most stable one—β in the temperature range above 600°C, which is in agreement with the literature [15]. Because, as we show later, the catalytic performance of both catalysts is similar, we suppose that the character of active phase behavior is also close to that discussed above but due to the much higher specific area of β-Ga_2O_3 compared to α-Ga_2O_3, iridium and iridium-containing phases are more dispersed and are not visible by XRD.

TPR profiles for both investigated catalysts are shown in Fig. 3. In our previous paper [12], we checked that pure supports do not undergo the reduction until 900°C.

The TPR profiles for both catalysts are very similar; the only differences are connected with a slight shift of hydrogen consumption maxima and the intensity of the individual TPR peaks. One can distinguish three ranges of reduction: 20–90, 180–280, and 520–650°C. The appropriate maxims are at about 70, 260, and 580°C. The first peak can be connected with further reduction of iridium, after partially decomposition of $Ir(acac)_3$

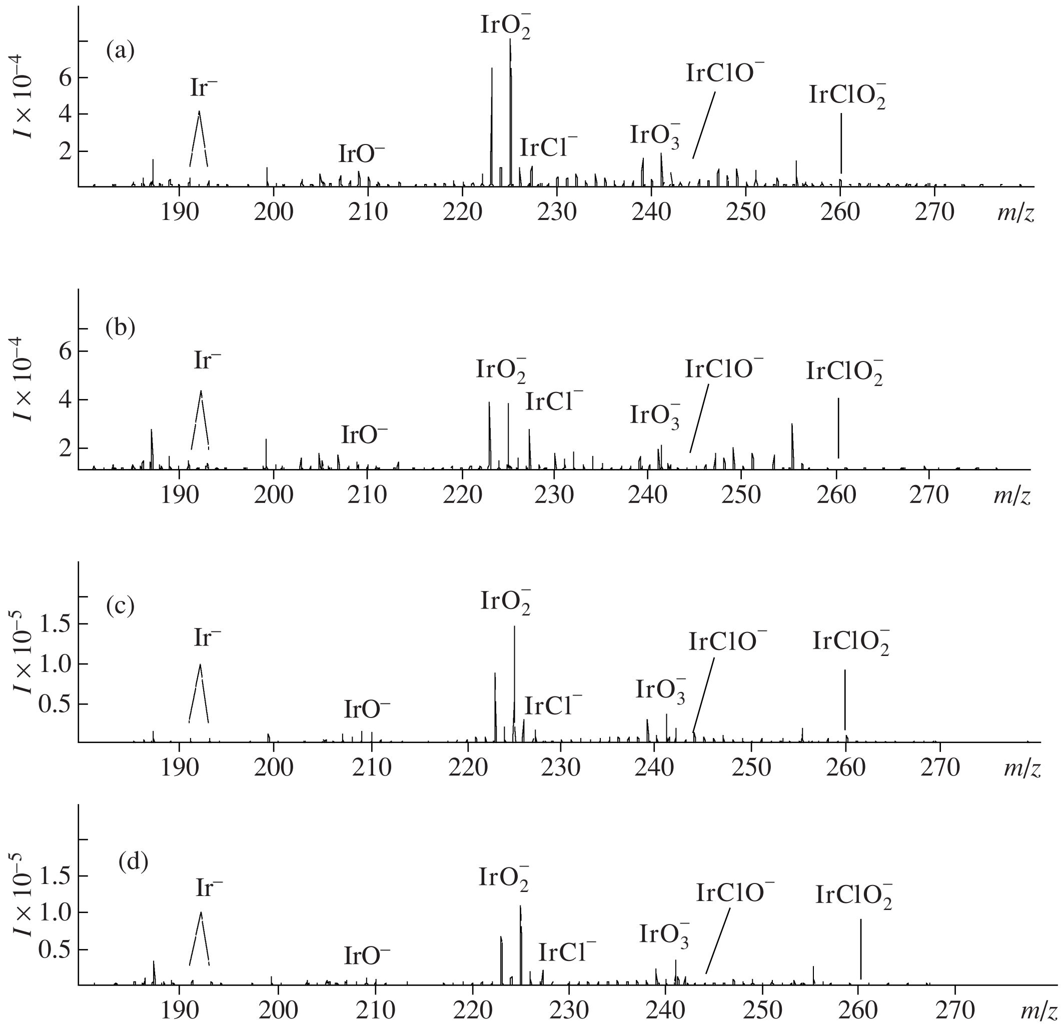

Fig. 4. TOF-SIMS spectra of 5 wt % Ir/α-Ga_2O_3 after reduction at (a) 200 and (b) 800°C and 5 wt % Ir/β-Ga_2O_3 (c) 200 and (d) 800°C.

during calcination at 200°C and/or its reduction at room temperature, which is in agreement with the literature [16–18]. The second one can be ascribed to the surface reduction of gallium oxide promoted in the presence of iridium, leading to the "decorating" of iridium crystallites by a thin layer of gallium oxide. The last one we attribute to the formation of the IrGa alloy. One can note that TPR results are in a very good accordance with conclusions coming from XRD. The more pronounced surface reduction of gallia in the case of 5 wt % Ir/α-Ga_2O_3 can be rationalized by a better dispersion of Ir on a more developed surface of α-Ga_2O_3. The second TPR were carried out after reoxidation of the catalysts at the temperature 200°C. Only a small part of iridium is reoxidized in such conditions.

TOF-SIMS spectra are presented in Fig. 4. Measurements were carried out for the catalysts reduced at 200 and 800°C. Catalysts reduced at 200°C show an optimum catalytic performance, whereas those reduced at 800°C are inactive.

The spectra for both catalysts after reduction at 200°C are very similar. Peaks corresponding to IrO^-, IrO_2^-, IrO_3^-, $IrCl^-$, $IrClO^-$, and $IrClO_2^-$ can be observed. However the $^{193}Ir^-/^{71}GaO^-$ intensity ratios for both catalysts are different and equal to 0.079 and 0.151 for 5 wt % Ir/α-Ga_2O_3 and 5 wt % Ir/β-Ga_2O_3, respectively. The predomination of the $^{71}GaO^-$ ion seems to confirm the supposition suggested earlier about decoration of iridium particles by a layer of partially reduced oxide. This effect is more pronounced for the 5 wt % Ir/α-Ga_2O_3, which is convincing, taking into consideration the much higher surface area of α-Ga_2O_3 than β-Ga_2O_3.

For catalysts reduced at 800°C, one can observe a decrease of intensity of ions coming from the metallic phase, which is connected with formation of GaIr alloy proved before by in situ XRD investigations.

Table 2. Adsorption bands on FTIR spectra for 5 wt % Ir/α-Ga_2O_3 and 5 wt % Ir/β-Ga_2O_3

Catalysts	Wave number, cm^{-1}									
	5 wt % Ir/α-Ga_2O_3					5 wt % Ir/β-Ga_2O_3				
	1718	1683	1440	1371	1162	1718	1683	1450	1371	1162
“Fresh sample”	–	–	–	–	–	–	–	–	–	–
Reduction at 200°C	–	–	–	–	–	–	–	–	–	–
C_4H_6O ads. at Rt	–	+	+	+	+	–	+	+	+	+
evacuation at Rt	+	+	+	+	+	+	+	+	+	+
evacuation at 80°C	+	+	+	+	–	+	+	+	+	–
evacuation at 200°C	+	+	+	+	–	+	+	+	+	–

The FTIR spectra were made for both catalysts. For polyfunctional molecules, such as crotonaldehyde, several possible adsorption structures on the platinum catalysts surface can exist [19, 20].

For adsorption through the C=C double bond, two structures are possible, ascribed as $\pi_{CC}\eta_2$ and di-$\sigma_{CC}\eta_2$, which correspond to the adsorption band at 1641 and 1543, 1452 cm^{-1}, respectively.

For adsorption through the C=O double bond, three structures are possible, ascribed as $\pi_{CO}\pi_2$, di-$\sigma_{CO}\eta_2$, and the η_1 “on top” adsorption by an oxygen atom, which corresponds to the absorption bands at 1693, 1660, and 1680 cm^{-1}, respectively.

Finally, there is the structure where the adsorption involves both double bonds, the C=C and C=O, ascribed as η_4, with 1693 and 1641 cm^{-1} bonds.

The bands observed at those catalysts after different pretreatment parameters are presented in Table 2. The most important bands of all are those at 1683 cm^{-1}, which correspond to “on-top” η_1 adsorption of crotonaldehyde on the catalyst surface, which is connected with high catalyst selectivity to the desired product in the hydrogenation of α,β-unsaturated aldehydes [19, 20]. Bands at 1371 and 1162 cm^{-1} can be ascribed to coordination oscillation $\nu_{C=O}$, $\delta_{C\text{–}H}$, and γ_{CH_3} of adsorbed crotonaldehyde.

The detailed tests of the reaction of crotonaldehyde hydrogenation in the gas phase were carried out in order to determine the influence of the following on the catalytic performance of the iridium catalysts under study:

the polymorphic form of the support–gallium oxide (α, β),

the catalyst calcinations temperature,

and the catalyst reduction temperature.

The reaction was carried out at the temperature 80°C. Such a temperature was found as an optimum one in our earlier catalytic tests for platinum and ruthenium catalysts [12, 21, 22].

The parameters that strongly influence catalytic performance of the selective hydrogenation catalysts are the temperatures of their calcination and prereduction. The influence of the calcination temperature on the

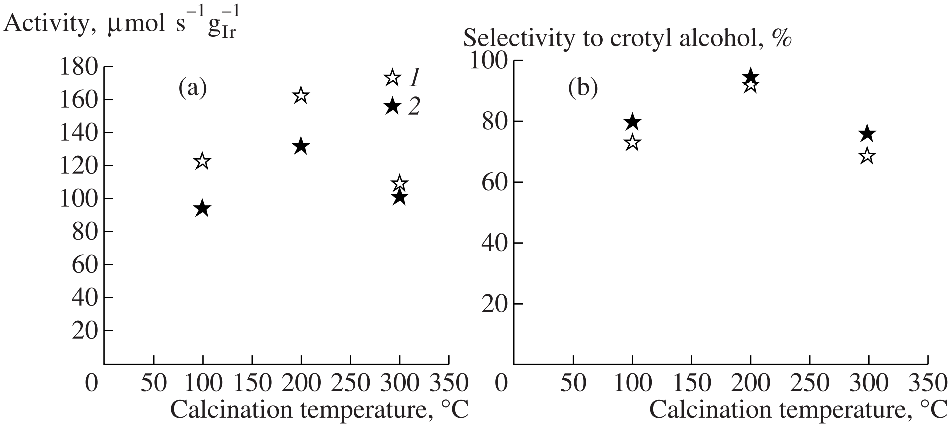

Fig. 5. Influence of the catalyst calcination temperature on the (a) activity and (b) selectivity to crotyl alcohol (temp. reaction = 80°C, conv. < 20%).

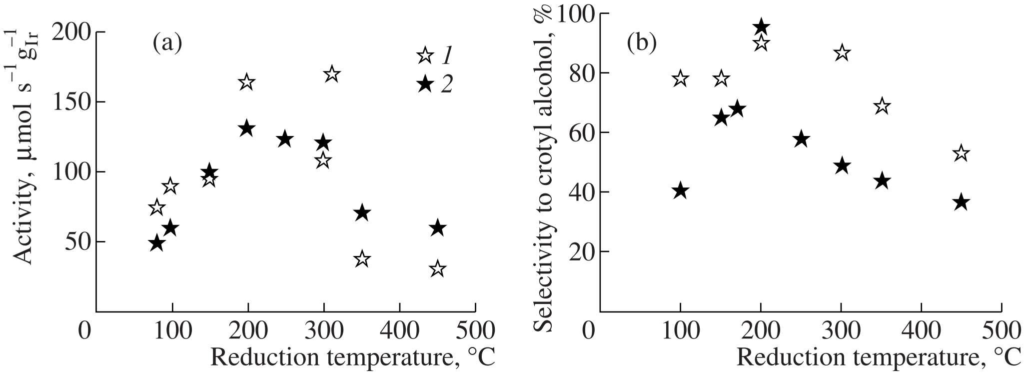

Fig. 6. Influence of the catalyst reduction temperature on the (a) activity and (b) selectivity to crotyl alcohol (temp. reaction = 80°C, conv. < 20%).

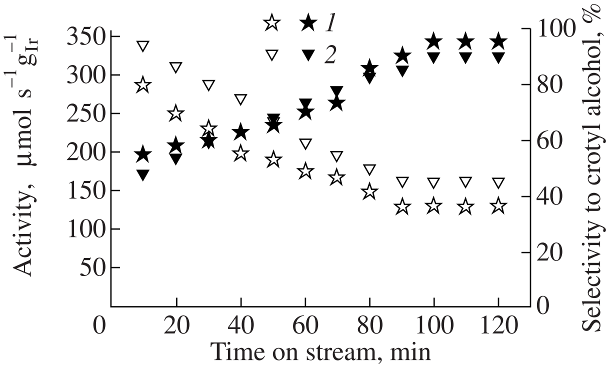

Fig. 7. Activity (empty symbols) and selectivity to crotyl alcohol (full symbols) for 5 wt % Ir/α-Ga_2O_3 and 5 wt % Ir/β-Ga_2O_3 catalysts after reduction at 200°C (conv.< 20%).

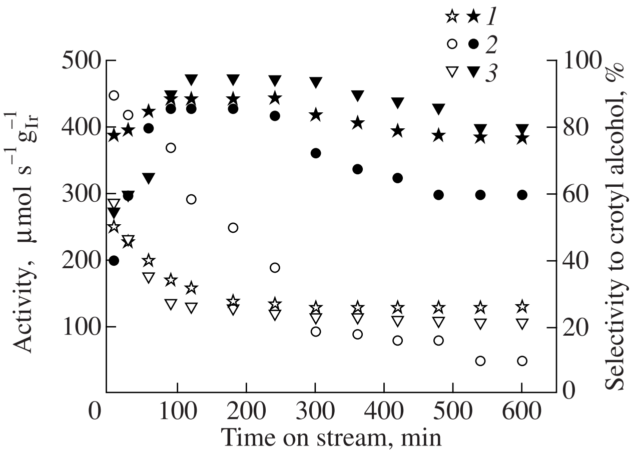

Fig. 8. Stability of Pt, Ru, and Ir catalysts supported on α-Ga_2O_3 in terms of activity (empty symbols) and selectivity (full symbols) (temp. reaction = 80°C, conv. < 20%).

activity and selectivity to crotyl alcohol is shown in Fig. 5. Prior to the reduction, catalysts were calcined at the temperatures 100, 200, and 300°C, respectively, which is shown in Fig. 8. The optimum calcination temperature appeared to be 200°C.

Figure 6 presents the influence of the catalyst reduction temperature on their activity and selectivity to crotyl alcohol. Optimum results in terms both of activity and selectivity were obtained after reduction at 200°C. Reduction at temperatures higher than 200°C leads to a remarkable drop of both activity and selectivity.

In Fig. 7 the changes of activity and selectivity during the first 120 min of the reaction are presented. The decrease of activity is accompanied by an increase of selectivity towards the desired product—crotyl alcohol. With a relatively high activity (about 150 μmol s^{-1} g_{Ir}^{-1}), both catalysts show optimum selectivity >90% after 100 min time on stream. An elongation of time on stream to 10 h leads to a moderate decrease in both activity and selectivity.

In Fig. 8 we compare the catalytic performance of 5 wt % Ir/α-Ga_2O_3 elaborated in this work with results obtained for 5 wt % Pt/α-Ga_2O_3 and 5 wt % Ru/α-Ga_2O_3 published in our previous papers [12, 13]. The catalytic properties of 5 wt % Pt/α-Ga_2O_3 and 5 wt % Ir/α-Ga_2O_3 are similar. They show a relatively high activity and selectivity to crotyl alcohol (about 80%) even after 10 h of time on stream.

All catalytical results shown up to now were obtained at relatively low conversions, most often about 10% and always lower than 20%. Figure 9 illustrates the selectivity to crotyl alcohol of the catalysts under study in the high range of crotonaldehyde conversion. A striking feature is the very high selectivity of the 5 wt % Pt/α-Ga_2O_3 catalyst at a high conversion.

This catalyst shows a selectivity of 75% at a conversion of about 60%, much higher than those of the

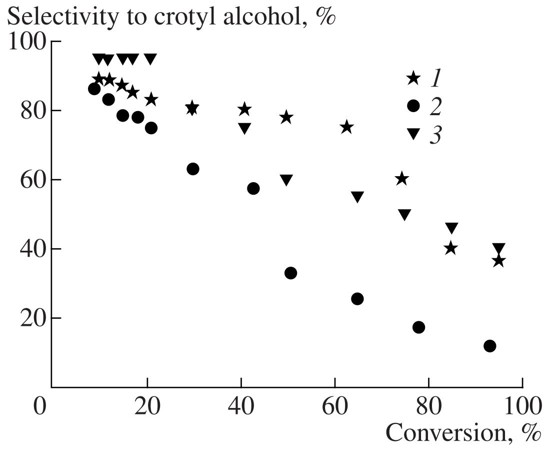

Fig. 9. Selectivity as a function of conversion for Pt, Ru, and Ir catalysts supported on α-Ga_2O_3 (temp. reaction = 80°C).

5 wt % Ru/α-Ga_2O_3 and 5 wt % Ir/α-Ga_2O_3 catalysts (17 and 48%, respectively).

4. CONCLUSIONS

Gallia supported platinum and iridium catalysts appear to be very promising in the reaction of selective hydrogenation of crotonaldehyde to crotyl alcohol. The use of gallium oxide as a support of those metals enhances significantly the C=O bond hydrogenation. The best catalytic performances (high activity and selectivity) is from 5 wt % Ir/α-Ga_2O_3 and 5 wt % Pt/α-Ga_2O_3 prepared from the chlorine free precursor. It was proved that the use of gallium oxide as a support of iridium and platinum leads to a significant increase of the C=O bond hydrogenation selectivity with maintenance of high activity.

These properties of gallia-supported Ir and Pt catalysts are due to (a) surface reducibility of gallium oxide leading to covering (decoration) of platinum and iridium by gallium suboxides and (b) the promoting effect of gallium.

REFERENCES

1. Ponec, V., *Appl. Catal., A*, 1997, vol. 149, p. 27.
2. Gallezot, P. and Richard, D., *Catal. Rev. Sci. Eng.*, 1998, vol. 40, p. 81.
3. Schimpf, S., Gaube, J., and Claus, P., in *Basic Principles in Applied Catalysis*, Baerns, M., Ed., Springer Series in Chemical Physics, 2004, vol. 75, p. 87.
4. Toebes, M.L., Nijhuis, T.A., Hajek, J., Bitter, J.H., van Dillen, A.J., Murzin, D.Yu., and de Jong, K.P., *Chem. Eng. Sci.*, 2005, vol. 60, p. 5682.
5. Makouangou, R.M., Murzin, D.Yu., Dauscher, A.E., and Touroude, R., *Ind. Eng. Chem. Res.*, 1994, vol. 33, p. 1881.
6. Abid, M. and Touroude, R., *Catal. Lett.*, 2000, vol. 69, p. 139.
7. Richard, D. and Gallezot, P., in *Heterogeneous Catalysis and Fine Chemicals*, Guisnet, M., Barrault, J., Bouchoule, C., Duprez, D., Montassier, C., and Perot, G., Eds., Amsterdam: Elsevier, 1988, p. 171.
8. Anisimova, N.V., Zharmagambetova, A.K., Mukhamedzhanova, S.C., and Edygenova, L.N., *React. Kinet. Catal. Lett.*, 1987, vol. 33, p. 399.
9. Cordier, G., Collueille, Y., and Fouilloux, P., in *Catalyse par les metaux*, Imellik, B. et al., Eds., Paris: CNRS, 1984, p. 349.
10. Nishimura, S., *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, New York: Wiley, 2001.
11. Englisch, M., Ranade, V.S., and Lercher, J.A., *J. Mol. Catal. A: Chem.*, 1997, vol. 121, p. 69.
12. Gebauer-Henke, E., Grams, J., Szubiakiewicz, E., Farbotko, J., Touroude, R., and Rynkowski, J., *J. Catal.*, 2007, vol. 250, p. 195.
13. Gebauer-Henke, E. and Rynkowski, J., *Pol. J. Chem.* (in press).
14. Zheng, B., Hua, W., Yue, Y., and Gao, Z., *J. Catal.*, 2005, vol. 232, p. 143.
15. Roy, R., Hill, V.G., and Osborn, E.F., *J. Am. Chem. Soc.*, 1952, vol. 74, p. 719.
16. Paryjczak, T., Zielinski, T., and Jozwiak, W.K., *React. Kinet. Catal. Lett.*, 1985, vol. 29, p. 167.
17. Reyes, P., Rojas, H., and Fierro, J.L.G., *J. Mol. Catal. A: Chem.*, 2003, vol. 203, p. 203.
18. Marzialetti, T., Fierro, J.L.G., and Reyes, P., *Catal. Today*, 2005, vol. 107, p. 235.
19. Delbecq, F. and Sautet, P., *J. Catal.*, 1995, vol. 152, p. 217.
20. Dandekar, A. and Vannice, M.A., *J. Catal.*, 1999, vol. 183, p. 344.
21. Gebauer-Henke, E. and Rynkowski, J., *Przem. Chem.*, 2006, vols. 8–9, p. 609.
22. Gebauer-Henke, E., Gebauer, D., Szubiakiewicz, E., Touroude, R., and Rynkowski, J., *Pol. J. Environ. Stud.*, 2005, vol. 14, suppl. IV, p. 235.