ISSN 0023-1584, Kinetics and Catalysis, 2007, Vol. 48, No. 4, pp. 562–566. © MAIK "Nauka/Interperiodica" (Russia), 2007.
Published in Russian in Kinetika i Kataliz, 2007, Vol. 48, No. 4, pp. 600–605.

MECHANISMS OF CATALYTIC REACTIONS

Catalytic and Physicochemical Properties of Pt/α-GeO_2 Systems in Reaction of Selective Hydrogenation of α,β-Unsaturated Aldehydes in a Gas Phase[1]

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Received June 29, 2006

Abstract—Hydrogenation of crotonaldehyde in a gas phase over Pt/α-GeO_2 catalysts was investigated. The systems were characterized by BET, XRD, TPR, TEM, ToF-SIMS, and FTIR methods. The optimum pretreatment parameters were studied. The best catalytic performance shows the catalyst 5 wt % Pt/α-GeO_2 (69% selectivity to crotyl alcohol at 200 μmol s^{-1} g_{Pt}^{-1} activity and 10% conversion of crotonaldehyde). Lower loaded catalysts (2 and 1 wt % Pt) show lower, but also promising activity and selectivity. This good catalytic performance was related to the physicochemical properties of the catalyst. GeO_2 in the presence of Pt undergoes a partial surface reduction at temperatures higher than 100°C probably leading to the creation of the active Pt–Ge centers responsible for high selectivity to crotyl alcohol. Reduction at a temperature ≥200°C deactivates the catalytic systems due to the formation of inactive PtGe alloys.

DOI: 10.1134/S0023158407040131

INTRODUCTION

The catalytic hydrogenation of the organic functional group is probably the most common application of heterogeneous catalysts in the synthesis of organic compounds. A number of catalyst reductions have been discussed with emphasis on the reaction selectivity (chemo-, region-, stereo-, diastereo-, and enantioselectivity) [1]. Catalytic hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols is an important step in preparation of various fine chemical products (reaction products are widely used as flavors and perfumes).

This reaction is not easy to realize because the C=C double bond is much more prone to hydrogenation than the C=O group for both thermodynamic and kinetic reasons. Therefore, it is desirable to find catalysts which may control the intermolecular selectivity by preferential hydrogenation of the C=O and keep the olefinic double bond intact [2].

Partly reducible oxides like TiO_2, CeO_2, and Y_2O_3, which have coordinatively unsaturated cations on the surface, have been found to improve the selectivity of the discussed reactions, probably due to the creation of metal-support interfacial sites that are responsible for such enhancement. Collins et al. [3] and Shpiro et al. [4] reported a promotional effect of noble metals on the reduction of gallium and germanium oxide. Ga_2O_3 and GeO_2 may be considered as a reducible oxide of potential usefulness as a catalyst support. In our previous studies [5–7], we examined the catalytic performance of Ga_2O_3-supported platinum catalysts. We found that some of them, especially 5 wt % Pt/α-Ga_2O_3, obtained from the chlorine free precursor $Pt(acac)_2$, show very promising activity and selectivity to the desired product, i.e., crotyl alcohol.

EXPERIMENTAL PROCEDURES

Catalyst Preparation

α-GeO_2 (Teck Cominco Metals Ltd.—S_{BET} = 3.8 m^2/g) was impregnated with a methanolic solution of platinum acetylacetonate in an amount appropriate to obtain the expected content of the active phase (1, 2, and 5 wt % of platinum). Methanol was slowly evaporated on a hot plate. Then the catalysts were dried at 100°C for 2 h and finally calcined in air at 200°C for 2 h. The real content of platinum in the catalysts was very close to the nominal content, which was checked by ICP analysis.

Methods

Specific BET surface areas were measured, based on low temperature (–195°C) nitrogen adsorption using a Sorptomatic 1900 (Carlo Erba Instruments).

XRD in-situ analysis was carried out in the reaction chamber XRK 900, Anton Paar, in a stream of 5%

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

Table 1. Characterization of catalysts

Systems	Real content of Pt	S_{BET}, m^2/g
α-GeO_2	–	3.8
1 wt % Pt/α-GeO_2	0.95	3.9
2 wt % Pt/α-GeO_2	1.66	4.1
5 wt % Pt/α-GeO_2	4.86	4.5

H_2/Ar, in the temperature range 50–500°C, with a heating rate of 1°C/min, using an X'PERT PRO MPD PAN polycrystal diffractometer.

TPR profiles of the catalysts were obtained with an AMI-1 apparatus (Altamira Instruments, United States) using an Ar–H_2 mixture (5 vol % H_2), flow rate 50 cm^3/min, sample weight 100 mg, and temperature increase 10 K/min.

The ToF–SIMS investigations were performed in the static mode using ION–TOF instruments (TOF SIMS IV) equipped with a 25 kV pulsed $^{69}Ga^+$ primary ion gun. Spectra were collected (from different areas) in order to determine the Pt distribution on the support. The Pt/O^- and Pt/total count intensity ratios were calculated. The analyzed area corresponds to a square of 500×500 μm. Samples were measured just after appropriate pretreatment ("fresh" samples), and then their surfaces were "cleaned" by the bombardment of ^{69}Ga primary ions ("clean" samples) (DC mode, current 25 nA, 2 min).

TEM images were recorded on a TOPCOM 002B electron microscope, operating at 200 kV, with a point-to-point resolution of 0.18 nm. Various regions of the grid were observed, and particle sizes were measured from the observation of 250–350 particles. The following formula was used to calculate the mean surface diameter:

$$d_s = \sum n_i d_i^3 / \sum n_i d_i^2,$$

where n_i is the number of particles of diameter d_i.

FTIR experiments were carried out using a Shimadzu 8501 spectrometer. Catalyst samples (80 mg) in the form of 25-mm discs were placed in a quartz cell fitted with NaCl windows and an external furnace. After 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 the spectra were recorded.

Crotonaldehyde Hydrogenation

Catalytic tests were carried out in a glass tube reactor at atmospheric pressure at 80°C. A known quantity (50–250 μl) of crotonaldehyde (CROTAL) (MERCK) was introduced to the installed on-line reservoir at 0°C, which maintained 8 Torr of CROTAL partial pressure at the hydrogen flow 50–60 cm^3/min. Beyond the CROTAL reservoir, the gas line was thermostated at about 60°C to avoid any condensation. The reaction products were drawn off from the flow line at different times during the catalytic run and analyzed by gas chromatography. The reaction activities were calculated using the formula $A = \alpha F/w$, α being the CROTAL conversion; F, the CROTAL flow [mol/s]; and w, the platinum weight [g]. Prior to the catalytic tests, the catalysts were reduced in the reactor in a stream of hydrogen at a chosen temperature in the temperature range between 80 and 225°C. The analyses were carried out until the quasi-stable state of the reaction.

RESULTS AND DISCUSSION

The BET surface and the real content of platinum of the catalysts are presented in Table 1. ICP measurements show that the real content of platinum is close to the nominal one. Supporting of platinum on α-GeO_2 slightly increases the specific area of the catalysts.

Catalytic tests were carried out in the gas phase at a reaction temperature equal to 50 and 80°C, after one hour reduction in the temperature range of 80 to 225°C (80, 100, 120, 150, 170, 200, and 225°C). In our previous paper, we reported in detail the influence of certain parameters such as the catalyst reduction temperature, reaction temperature, and amount of active phase on the catalytic activity and selectivity to crotyl alcohol [8].

The results are summarized in Tables 2 and 3. The optimum temperature of catalyst reduction appeared to be 120°C. Increase of the reduction temperature above 120°C leads to the gradual decrease of both activity and selectivity of the catalysts, which become completely inactive when reduced at the temperatures ≥200°C.

To rationalize the catalytic properties, some characterization of catalysts was carried out.

Table 2. Influence of reduction and reaction temperature on catalytic activity and selectivity for the 5 wt % Pt/α-GeO_2 catalyst (reduction at 120°C, $C_v = 10\%$) [8]

	Temp, reaction, °C									
	50					80				
Temp, reduction, °C	80	120	170	200	225	80	**120**	170	200	225
Selectivity to crotyl alcohol, %	55	67	54	28	0	58	**69**	59	30	0
Activity, μmol s^{-1} g_{Pt}^{-1}	109	150	80	30	0	145	**200**	90	20	0

Table 3. Catalytic test results (temp. red. = 120°C, temp, reaction = 80°C, C_v = 10%) for 1, 2, and 5 wt % Pt/α-GeO_2 systems at the quasi–stable state regime after 120 min of reaction [8]

	1 wt % Pt/α-GeO_2	2 wt % Pt/α-GeO_2	5 wt % Pt/α-GeO_2
Selectivity to crotyl alcohol, %	49	56	69
Activity μmol s^{-1} g_{Pt}^{-1}	125	150	225

XRD analysis of the 5 wt % Pt/α-GeO_2 catalyst is presented in Fig. 1. In situ measurements in the reductive atmosphere were carried out in the temperature range 50–400°C. The line characteristic for Pt (200) is clearly observed for the catalyst reduced at 100°C at 2θ = 47.2° (Fig. 1a). An increase of the reduction temperature leads to the decay of platinum peaks, and at 300°C, lines characteristic for the PtGe alloy appear. Further increase of the reduction temperature causes the conversion of PtGe to the $PtGe_2$ alloy (Fig. 1b). We suggest that, in the low temperatures (100–150°C) in which the catalyst shows its best catalytic performance, active Pt^0–$Ge^{\delta+}$ centers with increasing selectivity towards CROTOL are formed due to the slight, surface germania reduction.

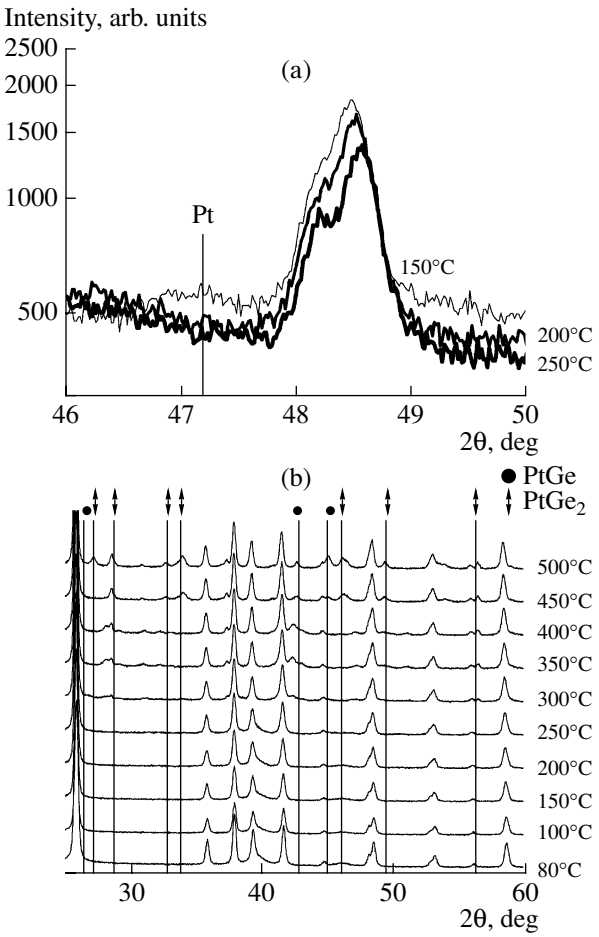

Fig. 1. XRD patterns for 5 wt % Pt/α-GeO_2 catalyst.

Figure 2 presents TPR profiles of the support and catalysts calcined at 200°C. The pure support GeO_2 starts to reduce rapidly at a temperature about 580°C. As seen from XRD, TPR peaks of the catalysts can be ascribed to the reduction of α-GeO_2 as platinum occurs in a metallic state just after calcinations. Hydrogen starts to be consumed at temperatures above 100°C. The amount of hydrogen consumed in the temperature range 200–400°C increases with the increase of platinum in the catalyst. Such a course of TPR confirms conclusions drawn from XRD results. As we already mentioned, we believe that, at temperatures below 200°C, the process of support reduction occurs in a very limited extent leading to the creation of Pt^0–$Ge^{\delta+}$ centers on the surface. The significant increase in the hydrogen consumption observed above 200°C coincidences with the drop of catalytic activity. It is likely that at such high temperatures all the platinum is converted to the inactive PtGe alloys. Starting from 400°C, bulk reduction of GeO_2 promoted by platinum takes place.

ToF-SIMS and TEM analyses were made for 5 and 2 wt % Pt/α-GeO_2, and the results are presented in Table 4 and Fig. 3.

ToF-SIMS results are difficult to interpret because of the weak signal of platinum. However, one can observe that the intensity ratio of Pt/O^- is lower for samples reduced at 120 and 200°C, both for fresh and clean

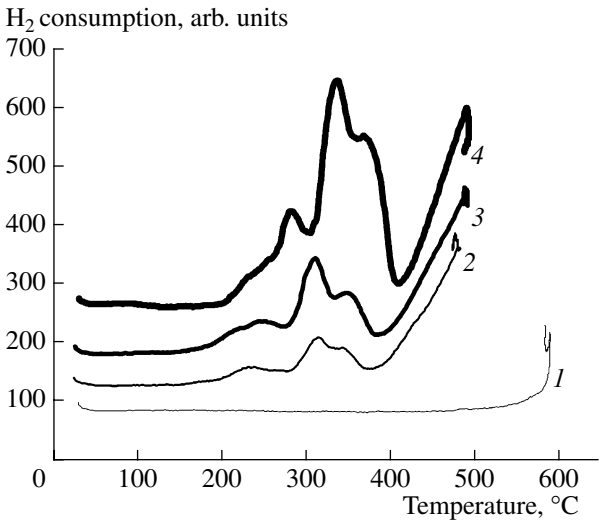

Fig. 2. TPR profiles for Pt/α-GeO_2 systems: (*1*) GeO_2, (*2*) 1% Pt/GeO_2, (*3*) 2% Pt/GeO_2, and (*4*) 5% Pt/GeO_2.

Table 4. ToF–SIMS characterization of Pt/α-GeO_2 catalysts

Intensity ratio × 10^{-3}	red 80°C		red 120°C		red 200°C	
	"fresh"	"clean"	"fresh"	"clean"	"fresh"	"clean"
2 wt % Pt/α-GeO_2						
Pt/O^-	2.92	0.75	2.63	0.51	2.46	0.52
Pt/total counts	0.7	1.2	0.6	1.0	0.6	1.1
5 wt % Pt/α-GeO_2						
Pt/O^-	4.52	0.65	3.5	0.78	3.41	0.63
Pt/total counts	0.9	2.1	0.6	1.2	0.7	1.2

samples, than for the sample reduced at 80°C. This circumstance means that surface reduction of GeO_2 occurs up to 200°C, which is connected with the presence of platinum.

TEM images were made for samples after their reduction at 120°C, that is, when the systems were the most active and selective. A great number of particles are in the range from 2 to 5 nm for the 2 wt % catalyst and between 5 and 10 nm for 5 wt % systems. TEM images point to significant active phase dispersion on the catalyst surface, which is worth mentioning taking into account the value of the specific surface area of α-GeO_2 (3.8 m^2/g). The main particle size determined from XRD patterns was equal to 11 nm. Thus, the results from TEM and XRD analysis are in good accordance.

FTIR measurements were made for the 5 wt % catalyst after its reduction at 120°C. CO and crotonaldehyde were adsorbed. All bands obtained for these spectra are given in Table 5.

In the FTIR spectra of the investigated catalyst after CO sorption, one can observe a band only at 2082 cm^{-1}, which is responsible for the linear bond between CO molecules and the Pt atom (Table 5). For crotonaldehyde sorption there are two characteristic bands at 1683 and 1459 cm^{-1}. The first one can be attribute to the "on-top" η_1 model of adsorption by the carbonyl group O atom on the Pt atom, and the second one has the di–σ_{CC}

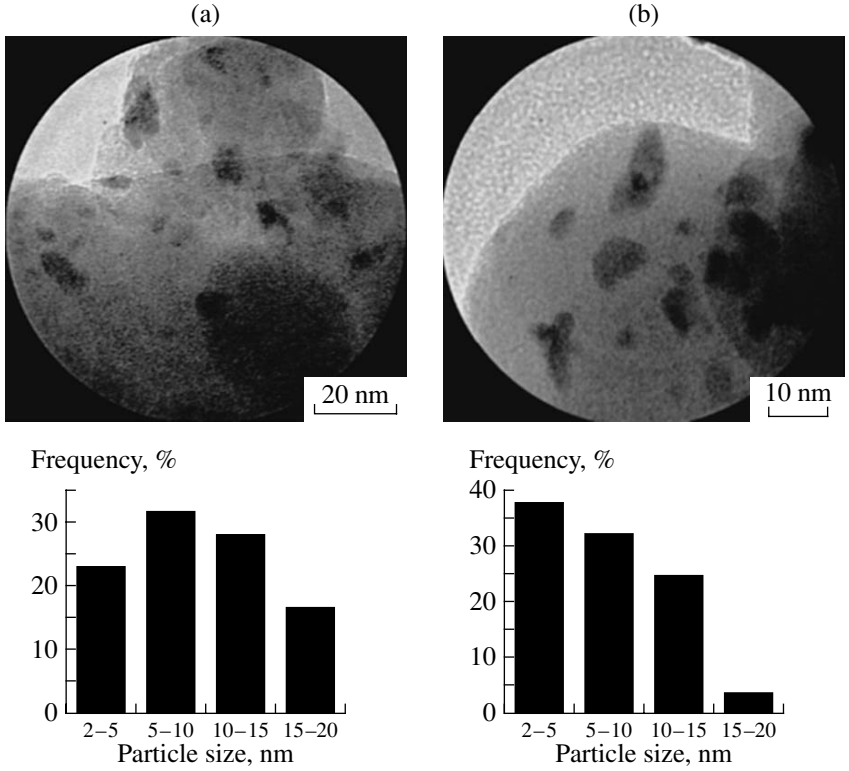

Fig. 3. TEM images for 5 (a) and 2 wt % (b) Pt/α-GeO_2 catalysts after reduction at 120°C.

Table 5. Results from FTIR analysis

CO adsorption		Crotonaldehyde adsorption	
Bands, cm^{-1}	5 wt % Pt/α-GeO_2	bands, cm^{-1}	5 wt % Pt/α-GeO_2
2169	–	1718	Tension oscillation of C=O bond in a gaseous molecule of aldehyde
2117	–	1683	"On-top" adsorption
2082	Bond between the CO molecule and the Pt atom	1459	Di–σ_{cc} η_2 adsorption
2013	–	1162	Tension oscillation of C=C bond or skeleton of CH_3 group
1874	CO adsorption on surface	–	–

η_2 form [9] (Table 5). Sorption by the carbonyl group is stronger than by σ_{CC} bond sorption, so it can be concluded that C_4H_6O is chemical sorption at the catalyst surface. Sorption by the C=O group can explain the high selectivity and activity towards hydrogenation of α,β-unsaturated aldehydes to the desired product—α,β-unsaturated alcohols.

Adsorption of C_4H_6O was carried out also after catalyst reduction at 200°C (catalysts were inactive). There was no crotonaldehyde sorption on the catalyst's surface, and consequently, only the band from gaseous crotonaldehyde was observed. This fact also explains the lack of selectivity and activity for the catalyst after reduction at temperatures equal to or higher than 200°C.

CONCLUSIONS

To summarize the results presented in this paper, we can affirm the following:

(1) Pt/α-GeO_2 catalysts show promising activity and selectivity to crotyl alcohol in the reaction of crotonaldehyde gas phase hydrogenation.

(2) The best results obtained for these catalytic systems were

• 5 wt %—69% of selectivity to crotyl alcohol at 200 μmol s^{-1} g_{Pt}^{-1}

• 2 wt %—56% of selectivity to crotyl alcohol at 150 μmol s^{-1} g_{Pt}^{-1}

• 1 wt %—49% of selectivity to crotyl alcohol at 125 μmol s^{-1} g_{Pt}^{-1}.

(3) The optimum parameters were elaborated:

• reaction temperature = 80°C

• reduction temperature = 120°C

• platinum loading = 5 wt %.

(4) Platinum acetylacetonate $Pt(acac)_2$ gives quite high and regular platinum dispersion despite the low specific surface area of the support.

(5) Germanium oxide is reducible from 550°C, whereas in the presence of Pt, its surface reduction occurs up to 200°C.

ACKNOWLEDGMENTS

We gratefully acknowledge the delivery of the α-GeO_2 sample by Teck Cominco Metals Ltd.

We gratefully acknowledge Dr. Jacek Grams for ToF-SIMS analysis and helpful discussions.

This work was supported by grant number 3 T09B 11326 (0112/T09/2004/26).

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