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NOTES

A Study of the Platinum–Gallium Catalytic System

A system involved in meaningful industrial studies (*1–3*), unfortunately not well understood, is the platinum–gallium supported on alumina catalyst. Ryndin *et al.* (*4*) studied the conversion of *n*-hexane as well as the chemisorption of oxygen and H_2 over platinum–gallium-supported catalysts prepared by decomposition of metallo–organic complexes over Al_2O_3. The authors concluded that for all the catalysts studied the dispersion of platinum was enhanced by the addition of 0.48–0.67% of gallium. A platinum–gallium interaction similar to that present in bimetallic platinum–tin systems was invoked to explain the results. Bursian (*5*) reported a drop in catalytic activity for cyclohexane dehydrogenation for a platinum–gallium catalyst compared to the monometallic platinum system. The formation of Pt–Ga alloys was suggested.

The main purpose of this work is to shed some light on the catalytic behavior of the platinum–gallium γ-Al_2O_3 system. In order to do so adsorption of pyridine, dispersion studies, and the transformation of *n*-hexane and methylcyclopentane were used as tools for the characterization of catalysts.

γ-Alumina (Ketjen CK-300), surface area 180 m^2/g, was used as the support. The catalysts were prepared by use of the incipient wetness technique as follows: a known amount of preconditioned alumina (*6*) was impregnated with a known volume of Ga(III) solution ($Ga(NO_3)_3 \cdot 9H_2O$, Koch-Light laboratories) in order to obtain the desired concentration of gallium; this loading varied from 0 to 0.7% in weight of Ga (Table 1). After drying the solid for 12 h at 393 K and a calcination period of 12 h at 873 K a certain amount of platinum was introduced (as H_2PtCl_6, Merck) in order to obtain a series of catalysts with 0.6% in weight of platinum. The solid was then dried at 393 K for 12 h and calcined in air for 24 h at 773 K.

The dispersion measurements were carried out in a conventional calibrated recirculation system similar to that used in Ref. (*6*). The catalyst was prereduced at 773 K for 2 h. After the reduction H_2–O_2 cycles were performed in the following way: 120 Torr of either H_2 or O_2 was introduced at room temperature and recirculated over the sample until a constant pressure was obtained; this was followed by vacuum ($<10^{-5}$ Torr) for 60 min and the sequence was repeated with the other gas. The percentage dispersion was calculated according to Benson and Boudart (*7*) assuming a 1 : 1 surface stoichiometry (H : Pt).

A Perkin–Elmer 621 IR spectrophotometer (resolution 2 cm^{-1}) was used to study the pyridine adsorption. The sample wafers had a thickness of about 20 mg/cm^2. A vacuum-tight spectroscopic cell similar to that described in Ref. (*8*) was used. The cell could be attached to a conventional BET vacuum system. After reduction with pure H_2 (773 K) the catalysts were evacuated ($<10^{-5}$ Torr) at 773 K for 1 h and cooled to room temperature. The sample was then exposed to 20 Torr of pyridine vapor for a period of 0.5 h at 298 K. The wafer was then evacuated for 1 h at 423 K before the spectra were recorded.

Methylcyclopentane (Merck, reagent grade) and *n*-hexane (Merck, reagent grade) were distilled prior to the reactions and showed no impurities by GC analysis. Other purification procedures have been described previously (*14*).

The catalytic reactions studied were the transformations of methylcyclopentane and *n*-hexane. The reactions were carried out in

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TABLE 1

Catalyst	% Pt[a]	% Ga[b]	Percentage dispersion[c] (% D)	Integrated intensity[d] (arbitrary units)	Activity[e] (moles/ h · g surface Pt)	Activity[f] (moles/ h · g surface Pt)
0.0 Ga	0.57	0.00	77	2.9	4.8	7.1
0.1 Ga	0.64	0.10	75	4.6	7.0	5.3
0.2 Ga	0.62	0.20	75	5.4	7.5	4.6
0.4 Ga	0.63	0.38	75	6.3	6.2	4.6
0.7 Ga	0.61	0.70	81	6.4	6.6	3.8

[a] Measured by atomic absorption.

[b] Measured by atomic emission.

[c] The percentage dispersion (% D) is defined as (surface Pt atoms)/(total Pt atoms) × 100.

[d] Infrared integrated intensity for pyridine adsorption (1451 cm^{-1} band) desorbed at 423 K.

[e] Total catalytic activity for the transformation of methylcyclopentane.

[f] Total catalytic activity for the transformation of *n*-hexane.

a glass microreactor attached to a conventional flow system operating at atmospheric pressure as described previously (*14*). A fresh sample of catalyst (60–80 mesh) was used. The effluent gases were analyzed by on-line gas chromatography (8 m × $\frac{1}{8}$ in column packed with squalane on chromosorb W (13%)). The operating conditions for all the catalysts studied were as follows: the total flow was 40 cm^3 (STP)/min; the mass of catalyst was 60 mg; the H_2/C_6H_{12} molar ratio was 18; and the temperature of reaction was 723 K. A 1-h reduction with pure H_2 at 773 K and 1 atm preceded the reactions. The total catalytic activity was defined as the sum of the activities for the different reactions observed: (1) cracking (production of C_1–C_5 hydrocarbons from *n*-hexane); (2) ring opening hydrogenolysis (production of C_6 paraffins from methylcyclopentane); (3) aromatization (production of benzene from methylcyclopentane); (4) dehydrocyclization (production of methylcyclopentane and benzene from *n*-hexane); (5) dehydrogenation (formation of methylcyclopentenes from methylcyclopentane); (6) isomerization (production of branched C_6 paraffins from *n*-hexane). For every possible reaction the amount of each product was expressed in terms of the amount of converted reactant. The measured conversions were always less than 8%.

The percentage dispersion was essentially constant throughout the series (Table 1). Infrared spectra of pyridine absorbed on the series of catalysts all showed the following bands: 1451, 1485, 1578 (shoulder), 1616 cm^{-1}. These bands can be assigned according to the literature (*8, 9*) to the 19b, 19a, 8b, and 8a breathing vibrations of the pyridine lewis-bound to the alumina support. The absence of a band in the 1545-cm^{-1} region which would correspond to pyridinium ions suggests the lack of Brønsted acidity in these systems. Table 1 shows the integrated intensities of the 1451-cm^{-1} band after desorption of pyridine at 423 K. An increase in intensity with the gallium content is notable.

Table 1 summarizes the total catalytic activity for the transformations of methylcyclopentane and *n*-hexane. The results show in the case of the former a slight increase in the catalytic activity with a subsequent drop with respect to the amount of gallium

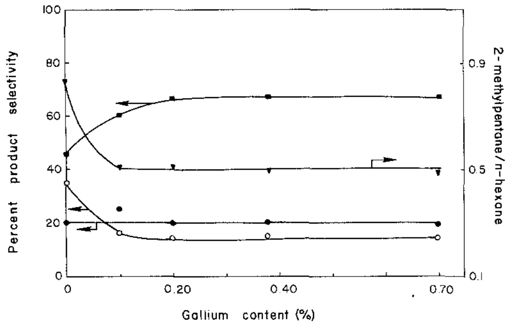

FIG. 1. Percentage product selectivity (left scale) and 2-methylpentane/n-hexane ratio (right scale) vs gallium content for the methylcyclopentane reactions. (■) Dehydrogenation, (●) aromatization, (O) ring opening hydrogenolysis.

present. For the n-hexane transformation a decrease is observed when the loading of gallium is increased. The selectivity pattern for the methylcyclopentane reaction is shown in Fig. 1. A decrease in the 2-methylpentane(2MP)/n-hexane(n-C_6) molar ratio with the addition of small quantities of gallium is observed.

The activity for the dehydrogenation reaction (formation of methylcyclopentenes) shows an increase with the loading of gallium. The activity for the ring opening hydrogenolysis (production of 2MP, n-C_6, and 3MP) shows a decrease while the activity for the aromatization reaction (formation of benzene) shows no significant changes throughout the series of catalysts.

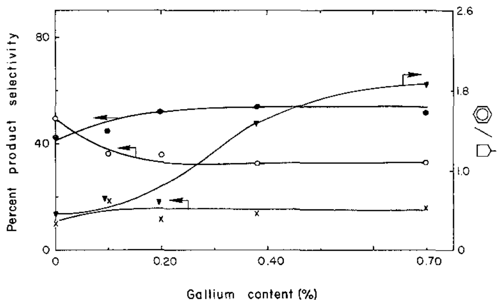

FIG. 2. Percentage product selectivity (left scale) and benzene/methylcyclopentane ratio (right scale) vs gallium content for the n-hexane transformations. (●) Isomerization, (O) dehydrocyclization, (X) cracking.

Figure 2 summarizes the results for the different reactions involved in the transformations of n-hexane. The isomerization reaction (formation of branched C_6 paraffins) and the cracking reaction (formation of lower hydrocarbons C_6) show a very mild change with the addition of gallium. A very different behavior is observed for the benzene/methylcyclopentane ratio. In this case a strong increase in the ratio is observed with the addition of gallium.

To account for the results obtained in this work the support must be considered. Early work (*10, 11*) has shown that gallium ions have a strong preference for tetrahedral sites when added to γ-Al_2O_3. They will occupy vacant tetrahedral sites at low concentrations. At higher concentrations they could interchange with Al^{+3} ions present originally in tetrahedral sites or even form Ga_2O_3. Recent work by Dumesic and coworkers (*9, 12*) on pyridine adsorption on silica doped with Ga^{+3} and other cations has shown a correlation between the frequency of the 19b band and the strength of pyridine bonding with the Sanderson electronegativity (*13*). The authors (*9, 12*) suggested that the strength of Lewis acid sites generated by doping various cations on silica could be related to the electronegativity of the dopant cation. Since Ga^{+3} has a higher Sanderson electronegativity than Al^{+3}, stronger Lewis acid sites and a higher frequency of the 19b band for pyridine adsorption should be expected for the Ga^{+3}-modified catalysts compared to those of the catalyst where gallium is not present.

The pyridine adsorption experiments in our work showed no detectable modification in the frequency of the 19b, 8b, 19a, or 8a bands for the catalysts that contained gallium compared to that of the 0.0 Ga catalyst and the γ-Al_2O_3 support (*14*). There is, however, a significant change in the intensity of the 19b band upon addition of gallium (Table 1).

From the frequency values obtained there is no evidence to confirm the appearance of new acid sites on the catalyst surface upon addition of gallium (III) ions. However, one may expect the gallium peaks to be obscured by the alumina peaks if the frequencies for the former and the latter are close (*9–15*). Data in Ref. 9 shows that for silica doped with Ga^{+3} ions the frequencies for the Lewis bound pyridine 19b, 19a, 8b, and 8a bands are 1459, 1493, 1579, and 1623 cm^{-1} (these values are basically independent of the desorption temperature). Considering the gallium loading and the proximity of the frequency values (*8, 9, 12*) it is understandable to find no changes in frequency with the addition of gallium. A similar behavior has been observed with alumina-supported iron (*12*).

The increase in intensity of the 19b band upon addition of gallium correlates well with an increase in acidity. This fact is supported by the following catalytic results: (a) the 2-methylpentane/*n*-hexane ratio obtained in the methylcyclopentane transformation decreases from 0.85 to 0.50 with the addition of 0.10% of gallium. Anderson *et al.* (*16*) have interpreted their data on Pt/TiO_2 catalysts using the adlineation model (*17*) but replacing the acid site by a cationic (Ti^{+3}) site on the support. The tendency to produce *n*-hexane was suggested to depend on the relative proportions of M–Ti^{+3} and M–M sites available to the methylcyclopentane. Our results agree with the above model since the *n*-hexane obtained increases with the acidity of the support. (b) The selectivity toward the production of benzene from *n*-hexane increases strongly at the expense of the methylcyclopentane formed upon the addition of gallium. This is an expectable result assuming a classical bifunctional mechanism (*18*) or a scheme similar to the one presented by Burch and Garla (*19*).

In addition, a comment on the drop of the total activity for the *n*-hexane transformation with the loading of gallium must be made. Figure 2 shows that the reaction responsible for the drop is the production of methylcyclopentane, since the formation of benzene increases with the loading of gallium. A possible explanation could be that the routes for the formation of benzene and methylcyclopentane are different. For the formation of the latter the five-ring closure of *n*-hexane (on the metal phase) to methylcyclopentane could be the rate-determining step as suggested by Chow and McVicker (*20*), while benzene would require acid sites for its formation. Further studies are needed to shed more light on this matter.

Finally, the following facts suggest that the platinum particles are not modified electronically or geometrically by the presence of gallium (*21*): (a) lack of changes in the turnover and activation energy for the hydrogenation of benzene; (b) lack of change in the metallic dispersions; (c) gallium is not reduced at all under our experimental conditions; (d) the vibrational frequency as well as the intensity of the band remain constant for the CO adsorption in the series of catalysts.

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T. ROMERO
B. ARENAS
E. PEROZO
C. BOLÍVAR
G. BRAVO
P. MARCANO
C. SCOTT
M. J. PÉREZ ZURITA
J. GOLDWASSER[1]

Escuela de Química
Facultad de Ciencias
Universidad Central de Venezuela
Apartado 47102
Los Chaguaramos
Caracas 1050, Venezuela

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[1] To whom all correspondence should be addressed.