Journal of Catalysis **208,** 490–493 (2002)
doi:10.1006/jcat.2002.3554

RESEARCH NOTE

Specific Behavior of Tailor-Made Pt–Ge/Al_2O_3 Catalysts in Transformation of Hydrocarbons

A. Wootsch,[*,†,1] L. Pirault-Roy,[†] J. Leverd,[*,†] M. Guérin,[†] and Z. Paál[*]

[*]*Institute of Isotope and Surface Chemistry, Chemistry Research Center, Hungarian Academy of Sciences, P.O. Box 77, Budapest, H-1525 Hungary; and* [†]*LACCO-UMR 6503 CNRS-Université de Poitiers, Faculté des Sciences, 40, Avenue du Recteur Pineau, F-86022 Poitiers Cedex, France*

Received December 12, 2001; revised January 29, 2002; accepted February 2, 2002

Germanium in amounts corresponding nominally to 2 or 1/8 monolayers was added to a 1% Pt/Al_2O_3 catalyst by controlled surface reaction. These catalysts, noted as *Ge2* and *Ge1/8*, were tested in transformation of hexane, benzene, and cyclohexene in hydrogen excess and compared with the Ge-free parent sample. All catalysts produced isomers, methylcyclopentane, fragments, benzene, and hexenes from hexane at $T = 603$ K. *Ge2* gave the highest TOF values, likely by preventing carbon accumulation. The selectivity of a saturated C_6 product was highest on *Ge1/8*, which also gave cyclohexane in amounts that increased as more H_2 was present. Particular Pt(111) arrangements required for the formation of benzene may have been selectively blocked by Ge on the *Ge1/8* sample. This was supported by comparing benzene and cyclohexene transformation. The *Ge1/8* sample was almost inactive in benzene hydrogenation, and active in cyclohexene transformation, whereas the parent and the *Ge2* sample were active in both reactions. The catalyst *Ge1/8* may serve as a basis for development of novel reforming catalysts producing isomers and less aromatic compounds. © 2002 Elsevier Science (USA)

Key Words: **tailored catalyst; controlled surface reaction; hexane; benzene; cyclohexane; Pt–Ge/Al_2O_3.**

INTRODUCTION

Multimetallic formulations are widely used to enhance the performances of catalysts (1, 2). Various routes exist for the preparation of such tailored catalysts using "controlled surface reactions": the redox method (3, 4) or organometallic grafting (2, 5–8). These catalysts are rather active and selective in various reactions as selective hydrogenation (2, 6, 7) or in transformation of hydrocarbons (1, 6, 9). Platinum-based mono- as well as bimetallic catalysts are also of great interest in oil refining. The commercial refining catalysts usually consist of Pt–Re, Pt–Sn, Pt–Ir, and possibly Pt–Ge combinations (1). Adding metals with low dehydrogenation activity, such as Re, Sn, and Ge, hinders the formation of unsaturated surface species, precursors of carbonaceous deposits (1, 10, 11). Others, such as Ir and Rh, fragment the coke precursors and hinder the deactivation in this way (1, 10). The addition of a second metal prevents the sintering of Pt particles and also hinders deactivation by the ensemble effect, since the carbonaceous deposit cannot envelop the noncontiguous Pt surface (1, 12). Until now there have been only a few reports of the catalytic properties of the tailor-made platinum–germanium catalytic system in skeletal reactions of hydrocarbons (9). In the current investigation we attempt to focus on the unusual properties of Pt–Ge catalysts—prepared by a special method—in the skeletal reactions of C_6 hydrocarbons.

METHODS

Catalysts Preparation

Highly dispersed 1 wt% Pt catalyst (D, ~80%) supported on δ-alumina from Degussa Aluminum Oxid C was prepared by ion-exchange from $Pt(NH_3)_2(NO_2)_2$ precursor in ammonia solution (pH, 12). After drying (393 K), it was calcined in dry air (4 h, 773 K) and reduced in a H_2 flow (2 h, 673 K) to obtain the "parent" Pt catalyst (noted as P, 1% Pt, dispersion $D = 76\%$, as measured by H_2 chemisorption). To prepare Pt–Ge bimetallic catalysts, $Ge(n\text{-}C_4H_9)_4$ in heptane solution was anchored under inert atmosphere on the surface of platinum particles where hydrogen was first preadsorbed (13). The preparation steps were as follows: reactivation of the parent catalyst under H_2 (473 K, 2 h), hydrogen adsorption (293 K, 1 h), anchoring of the organometallic compound (Ar, 343 K, 6 h), washing with heptane, drying (Ar, 393 K, 1.5 h), and reduction (H_2, 473 K, 2 h); they were achieved in an *in situ* reactor (13). The introduced amount of $Ge(n\text{-}C_4H_9)_4$ was chosen in order to obtain two different catalysts: one with a very low Ge content (*Ge1/8*; 350 ppm Ge corresponding

---

[1] To whom correspondence should be addressed. Fax: (+33) 5 49 45 34 99. E-mail: wootsch@hotmail.com.

0021-9517/02 $35.00

to 1/8 monolayer, $D = 65\%$) and another with more Ge (*Ge2*; 5600 ppm Ge corresponding to 2 monolayers, $D = 15\%$). The dispersion values were measured by H_2 chemisorption.

Catalytic Tests

Catalytic runs were carried out in a closed-loop reactor (volume, ∼70 ml) described earlier (14) using mixtures of 10 Torr of hexane (*n*H), benzene (B), or cyclohexene (cH) with hydrogen (60–480 Torr). Hexane was reacted at 603 K, and benzene and cyclohexene at $T = 423$ and 453 K. Approximately 20 mg of catalyst was prereduced *in situ* with 400 Torr of H_2 for 1 h at $T = 653$ K before hexane reaction; another lot was prereduced at $T = 483$ K for benzene and cyclohexene transformation. The turnover frequencies (TOF) (15) were calculated as the number of hexane molecules reacted per one surface Pt atom, using the length of the run (5 min) as the "contact time" (14). Regeneration involved air and hydrogen treatment at the reaction temperature, as described earlier (14).

RESULTS AND DISCUSSION

The addition of Ge increased the catalytic activity in hexane transformation (Fig. 1). The highest TOF value was found with *Ge2* followed by *Ge1/8*, with the parent catalyst showing the lowest activity at about the same conversion (10–20%). In the case of *Ge1/8* only one-eighth of the surface would be covered by germanium. The dispersion value observed (65% vs $76 \times 7/8 = 66.5$) agrees well with this assumption. Small Ge ensembles and/or individual Ge atoms—located probably on certain sites of the catalysts—can activate the neighboring Pt atoms, thus hindering carbon accumulation (1). Alternatively, electron-deficient Pt atoms in the vicinity of Ge may also exhibit higher activity (16). These effects may be more pronounced on the *Ge2* sample. In this case hydrogen chemisorption showed 15% platinum accessibility, although the amount of Ge introduced corresponded to two monolayers. Thus, Ge must have aggregated randomly on the surface to form 3D islands and/or diffuse to subsurface position. The residual Pt atoms in the vicinity of these Ge may, indeed, be more active in hexane transformation. Possibly the much-increased activity is only apparent. The catalysts were pretreated at higher temperature before hexane transformation ($T = 653$ K) than before the chemisorption measurements ($T = 473$ K). The possible restructuring of catalysts during this period might also be more pronounced in the case of *Ge2*.

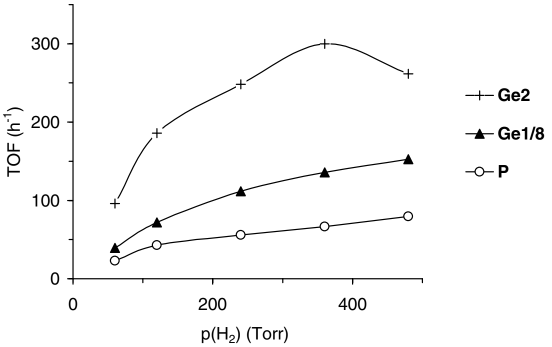

FIG. 1. Turnover frequency of hexane (nH) transformation as a function of hydrogen pressure on the three examined catalysts. $T = 603$ K, sampling time $t = 5$ min, $p(nH) = 10$ Torr.

The selectivity pattern was rather similar on the different catalysts (Fig. 2) and agreed well with those reported for "monofunctional" Pt catalysts (12, 14, 17). Hexenes were produced on *Ge2* only (Fig. 2c); their formation required single Pt atoms (18). The fraction of such sites must be relatively high when the surface is covered by much germanium. The selectivity pattern of the *Ge1/8* sample was very unique, inasmuch as cyclohexane appeared among the products in high hydrogen excess (Fig. 2b), showing a mirror image of benzene selectivity.

Cyclohexane, as a rule, could not be observed among the products of hexane transformation on monofunctional Pt catalysts (14, 17, 19, 20). Radiotracer experiments indicated, however, its formation on Pt–KL from hexane–[^{14}C]cyclohexane mixtures under high hydrogen excess (21). Having postulated the "triene" mechanism of aromatization on Pt (22), involving open-chain hexadiene and triene intermediates, we attributed its formation to the hydrogenation of the primary, unsaturated ring closure product. This was confirmed by the appearance of C_6-cyclic hydrocarbons from *cis*-hexa-1,3,5-triene on Pt (22). With decreasing H_2 availability, the abundance of cyclohexene and cyclo-1,3-diene increased. The latter might be an important surface intermediate of the ring closure step. The appearance of benzene in the gas phase may have occurred by "hydrogenative desorption" from surface C_6H_{6-x} precursors (23). The "triene" pathway was also confirmed on a bimetallic system: a Pt–Cu mixed single crystal (24). Thus, second components like Ge and Cu may decrease the abundance of "three-atom ensembles" of triangular symmetry that are necessary for aromatization of this short-living surface intermediate (25).

The unique catalytic behavior of the *Ge1/8* sample may be explained by its specific surface structure being caused by the controlled preparation method. Two other reactions, hydrogenation of benzene and cyclohexene, were carried out to check the possible active sites. *Benzene hydrogenation* is traditionally explained by the sextet model of Balandin (26, 27), which assumes the adsorption of the aromatic ring parallel to the catalyst surface on three Pt atoms with (111) symmetry. Radiotracer studies (28) have shown that a triangular reaction takes place on different metals: direct hydrogenation to cyclohexane (the main reaction

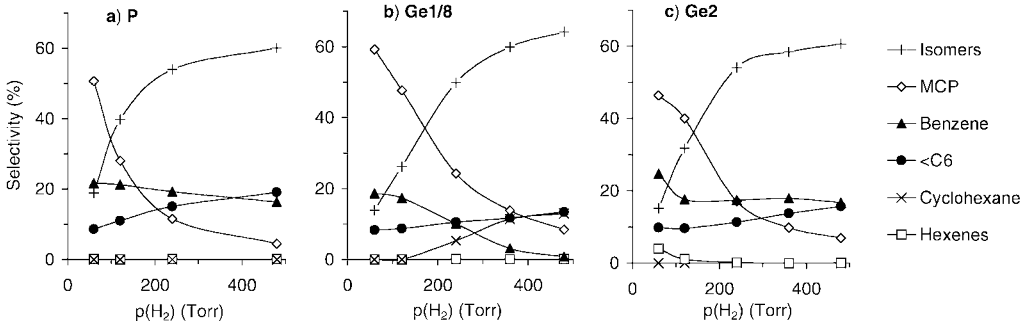

FIG. 2. Selectivity of hexane (nH) transformation as function of hydrogen pressure on a) P b) *Ge1/8* and c) *Ge2* catalyst. T = 603 K, sampling time t = 5 min, p(nH) = 10 Torr.

at low conversions) was accompanied by a stepwise reaction involving cyclohexene as an intermediate. This latter route may involve the parallel π-adsorption as an initial step followed by the formation of intermediate(s) adsorbed "edgewise" (29). The *transformation of cyclohexene* was explained by both sextet and doublet mechanisms (27, 30), which involve "flat-lying" and "edgewise" chemisorption, respectively. Recent single-crystal studies (31) on Pt(111) showed, however, that the situation is more complex: depending on the temperature, cyclohexene is adsorbed in a "half-chair configuration" on two metal atoms (130 K), edgewise, by di-σ bonds (220 K) but at temperatures practicable for hydrogenation (260–283 K); a "tilted" cyclo-C_6H_9 species is attached to three Pt atoms. The sites for these intermediates are different from those required for dehydrogenation to benzene (300–383 K), which takes place via a flat-lying intermediate.

The catalytic activities are compared in Fig. 3. The only product of benzene transformation was cyclohexane. Cyclohexene formed both benzene and cyclohexane. Their ratio depended on the temperature and hydrogen pressure. *Ge2* was the most active catalyst also in these reactions. *Ge1/8* was almost inactive in benzene transformation but was very active in cyclohexene transformation (Fig. 3). Thus, on the *Ge1/8* catalyst the high coordination sites, for example (111) planes, needed for flat-lying benzene chemisorption must be selectively blocked by Ge: it showed low activity in benzene hydrogenation. At the same time, the edgewise or tilted adsorption of cyclohexene was not hindered. Results of hexane transformation indicate that the flat-lying adsorption of the unsaturated C_6-cyclic surface intermediate is less probable on the *Ge1/8* sample. Cyclohexane is produced by hydrogenating this intermediate in high hydrogen excess rather than by hydrogenation of the "ready" surface intermediate of the aromatic structure (22). With less hydrogen present, some benzene can still be formed (see the mirror image in Fig. 2b). On our two other samples and on most of the Pt catalysts described in the literature this intermediate mainly produces benzene. In these cases the proportion of high coordination sites must be higher than on the *Ge1/8*. For *Ge2*, high coordination sites are still active for benzene transformation on the catalyst surface, as are low coordination sites for cyclohexene transformation. Its behavior was rather similar to the parent catalyst so we can assume that Ge was deposited randomly.

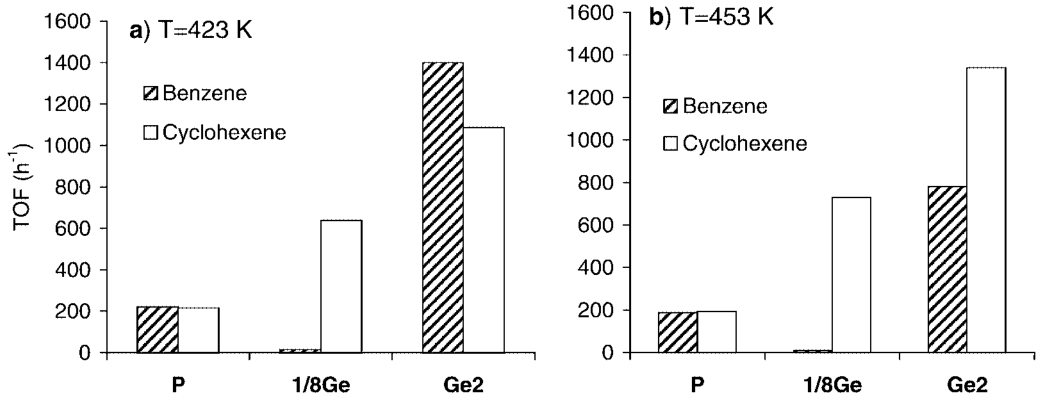

FIG. 3. Comparison of the activity in benzene (B) and in cyclohexene (cH) transformation at T = 423 K (a) and at T = 453 K (b), p(B or cH) = 10 Torr, p(H$_2$) = 120 Torr, t = 5 min.

TABLE 1

Selectivity (in %) of C_6-Saturated Products (Isomers + MCP + Cyclohexane) Produced from Hexane on Different Catalysts at $T = 603$ K, p(nH) = 10 Torr, $t = 5$ min

p(H_2) (Torr)	60	120	240	480
P	69	68	66	65
Ge1/8	73	74	79	86
Ge2	61	72	71	68

In addition to the geometric interpretation other effects may play important roles. The electron acceptor effect of Ge may also be important (16). The "virtual" hydrogen concentration on the clean, carbon-free, Pt sites of *Ge1/8* can be higher than that corresponding to the gas phase (32, 33). This abundant hydrogen may cause favored formation of C_6-saturated products (isomers, MCP, and cyclohexane) as opposed to aromatization (20, 33), as seen in Fig. 2b.

To sum up, Pt–Ge (with a 1/8 monolayer of germanium) on alumina support proved to be very active in producing methylcyclopentane and skeletal isomers from hexane by the monofunctional route, involving C_5-cyclic surface intermediates (34). At the same time the (likely unsaturated C_6-cyclic) precursors of benzene were hydrogenated. This catalyst produced C_6-saturated products with unusually high selectivities (Table 1). The same catalyst was inactive in benzene hydrogenation but hydrogenated cyclohexene. The addition of Ge (by controlled surface reaction) may, therefore, change the structure of Pt ensembles in a way that these become unfavorable for the chemisorption of the aromatic ring parallel to the surface, both in hexane aromatization and in benzene hydrogenation. The present results indicate that the modification of the metallic function by adding a *low amount* of a second metal, in particular Ge, in a controlled way may serve as a basis for developing unique catalysts of practical importance for naphtha reforming (35), producing desirable high-octane-number isomers and/or cycloalkanes with far less aromatic compounds.

ACKNOWLEDGMENTS

The work of J. Leverd in Budapest was supported by the student exchange program between the Ministry of Education in Hungary and the Ministry of Foreign Affairs in France (Formation des Français à l'Etranger—Bureau des Boursiers Français à l'Etranger). A. Wootsch thanks the Embassy of France in Budapest for supporting his present stay in Poitiers. The work was partly supported by the cooperation between the Hungarian Academy of Sciences and the CNRS and, for catalytic studies, by the Hungarian Scientific Research Fund (Grant OTKA T 025599).

REFERENCES

1. Ponec, V., and Bond, G. C., "Catalysis by Metals and Alloys," *Stud. Surf. Sci. Catal.*, Vol. 95, Elsevier, Amsterdam, 1995.
2. Candy, J. P., Didillon, B., Smith, E. L., Shay, T. B., and Basset, J. M., *J. Mol. Catal.* **86**, 179 (1994).
3. Barbier, J., *in* "Handbook of Heterogeneous Catalysis" (G. Ertl, H. Knözinger, and J. Weitkamp, Eds.), Vol. 1, p. 257. Wiley–VCH, Weinheim, 1997.
4. Micheaud-Especel, C., Bazin, D., Guérin, M., Marécot, P., and Barbier, J., *React. Kinet. Catal. Lett.* **69**, 209 (2000).
5. Margitfalvi, J. L., Szabó, S., and Nagy, F., *Stud. Surf. Sci. Catal.* **27**, 373 (1986).
6. Coq, B., and Figuéras, F., *Coord. Chem. Rev.* **178–180**, 1753 (1998).
7. Margitfalvi, J. L., Borbáth, I., Hegedüs, M., and Göbölös, S., *Appl. Catal. A* **219**, 171 (2001).
8. Margitfalvi, J. L., Borbáth, I., Tfirst, E., and Tompos, A., *Catal. Today* **43**, 29 (1998).
9. Coq, B., Chaqroune, A., Figueras, F., and Nciri, B., *Appl. Catal. A* **82**, 231 (1992).
10. Barbier, J., *Appl. Catal.* **23**, 225 (1986).
11. Bond, G. C., *Appl. Catal.* **149**, 3 (1997).
12. Paál, Z., *in* "Catalytic Naphtha Reforming" (G. J. Antos, A. M. Aitani, and J. M. Parera, Eds.), p. 19. Decker, New York, 1995.
13. Teschner, D., Pirault-Roy, L., Paál, Z., and Guérin, M., poster 10-P-40, 5th Europacat V, Limerick, September 2001.
14. Wootsch, A., and Paál, Z., *J. Catal.* **185**, 192 (1999).
15. Boudart, M., *in* "Handbook of Heterogeneous Catalysis" (G. Ertl, H. Knözinger, and J. Weitkamp, Eds.), Vol. 3, p. 958. Wiley–VCH, Weinheim, 1997.
16. Garetto, T. F., Borgna, A., and Apesteguia, C. R., *Stud. Surf. Sci. Catal.* **88**, 369 (1994).
17. Bond, G. C., and Paál, Z., *Appl. Catal.* **86**, 1 (1992).
18. Ponec, V., *Adv. Catal.* **32**, 149 (1983).
19. Sárkány, A., *Catal. Today* **5**, 173 (1989).
20. Paál, Z., *Adv. Catal.* **29**, 273 (1980).
21. Manninger, I., Zhan, Z., Xu, X. L., and Paál, Z., *Appl. Catal.* **51**, L7 (1989).
22. Paál, Z., and Tétényi, P., *J. Catal.* **30**, 350 (1973).
23. Zimmer, H., Rozanov, V. V., Sklyarov, A. V., and Paál, Z., *Appl. Catal.* **2**, 51 (1982).
24. Teplyakov, A. V., and Bent, B. E., *J. Phys. Chem. B* **101**, 9052 (1997).
25. Biloen, P., Helle, J. N., Verbeek, H., Dautzenberg, F. M., and Sachtler, W. M. H., *J. Catal.* **63**, 112 (1980).
26. Balandin, A. A., *Z. Phys. Chem.* **B2**, 289 (1929).
27. Balandin, A. A., *Adv. Catal.* **19**, 1 (1969).
28. Derbentsev, Yu. I., Paál, Z., and Tétényi, P., *Z. Phys. Chem. (Frankfurt)* **80**, 51 (1972); Tétényi, P., and Paál, Z., *Z. Phys. Chem. (Frankfurt)* **80**, 63 (1972).
29. Garnett, J. L., and Sollich, W. A., *J. Catal.* **2**, 350 (1963).
30. Balandin, A. A., and Brusov, I. I., *Z. Phys. Chem.* **B34**, 96 (1936).
31. Somorjai, G. A., and Rupprechter, G., *J. Phys. Chem. B* **103**, 1623 (1999).
32. Biscardi, J. A., and Iglesia, E., *J. Catal.* **182**, 117 (1999).
33. Paál, Z., Székely, G., and Tétényi, P., *J. Catal.* **58**, 108 (1979).
34. Gault, F. G., *Adv. Catal.* **30**, 1 (1981).
35. Martino, G., Courty, P., and Marcilly, C., *in* "Handbook of Heterogeneous Catalysis" (G. Ertl, H. Knözinger, and J. Weitkamp, Eds.), Vol. 4, p. 1801. Wiley–VCH, Weinheim, 1997.