

n-Hexane Transformation over Bimetallic Catalysts PtGe/Al₂O₃ obtained by Organometallic Grafting

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Summary

The aim of this work is to study the performances of the bimetallic catalysts Pt-Ge/Al₂O₃ obtained by organometallic grafting for a possible application in reforming. Two types of catalysts have been prepared, with small amount of germanium content; 1/8, 1/2 monolayer (PGe1/8, PGe1/2) and large amount; 1, 2 monolayer (PGe1, PGe2). These catalysts underwent various techniques of characterization: electronic microscopy by transmission (MET), chemisorption of hydrogen, carbon monoxide adsorption (FTIR). The rearrangement of hexane was selected for model reaction to evaluate their performances. The catalysts with lower germanium, are appropriated for isomerisation reaction, conversion, and product no more fragmentation and aromatisation that is opposite to large germanium content. The catalytic structure induced by Ge deposit governed catalysts activities, conversion, coke formation and selectivity products.

Keywords: Pt-Ge, catalysts, coke, bimetallic, n-hexane, organometallic grafting

Résumé

L'objectif de ce travail est l'étude de la performance de catalyseurs bimétalliques PtGe/Al₂O₃ obtenus par voie organométallique pour une éventuelle application en reformage. Deux types de catalyseur ont été préparés, une avec de faibles teneurs en germanium correspondants à 1/8 et 1/2 monocouches (PGe1/8, PGe1/2) et une autre avec des quantités plus importantes correspondant à 1, 2 monocouches (PGe1, PGe2). Ces catalyseurs ont été caractérisés par différentes techniques: microscopie électronique à transmission (MET), chimisorption de l'hydrogène, du monoxyde de carbone (FTIR). Le réarrangement du n-hexane a été choisi pour modèle de réaction. Pour les catalyseurs à faibles teneurs en Ge, on observe une meilleure conversion, une importante isomérisation et moins de fragment et d'aromatique contrairement aux catalyseurs à fortes teneurs en Ge. La structure catalytique induite par le dépôt de Ge a régi l'activité catalytique, la conversion, la formation de coke et la sélectivité des produits.

Mot-clés: Pt-Ge, catalyseurs, coke, bimétallique, n-hexane, greffage organométallique

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1. Introduction

The surface organometallic reaction was introduced to give answer to many questions about interaction between bimetallic catalysts [1-3]. Their development has seen applications in various scientific works [3-8]. The earlier results have shown the isolated behaviour of these catalysts obtained by this method of preparation according to the amount of monolayer added [3,5,6,9,10]. In the continuity of our study, we used these catalysts to test reforming reactions. The addition of a second metal to Pt has a beneficial effect on the catalytic performance [11]. Generally, this reaction used platinum as metal base combined with one or two other active/passive atoms then support acid is often used to promote the isomerisation reactions [12-15]. Commercial catalysts reforming commonly involve Pt-Re, Pt-Ir, Pt-Sn, and possibly Pt-Ge catalyst [16]. The aim of our study is to promote through our catalytic materials reactions desirable in reforming. In this work, we present in the experimental part, the preparation of catalysts and catalytic tests. In the end last part, we present the results and discussion.

2 Experimental

2.1 Catalysts preparation

Monometallic Pt catalyst was prepared by ion exchange of $\text{Pt}(\text{NH}_3)_2(\text{NO}_3)_2$ (Merck) in ammonia solution (PH=12) on δ -Degussa alumina (surface area $100 \text{ m}^2\text{g}^{-1}$, particle size, 0.1-0.25 nm). The Pt catalyst content was 1wt%. After exchange, the sample was dried for 12 h at 393 K and the catalyst powder heated in air to 773 K for 4 h, purged with N_2 and finally reduced in pure flowing H_2 for 8 h at 773 K. Bimetallic Pt-Ge samples were obtained by using the surface organometallic grafting method in an in-situ reactor. The prerduced parent sample (using H_2 flow at 473 K for 2 h, followed by cooling in air flow) was immersed in heptane solution in

air atmosphere. After hydrogen adsorption (293 K for 1 h), the organometallic

compound, $\text{Ge}(\text{n-C}_4\text{H}_9)_4$ (Aldrich) was anchored in air at 343 K for 6 h. The samples were then washed with heptane (Merck) and dried in air flow at 393 K for 1 h and finally reduced in H_2 flow (473 K for 4 h). The amount of $\text{Ge}(\text{n-C}_4\text{H}_9)_4$ introduced was selected in such a way as to obtain 0, (PB60), 1/8 (PGe1/8), 1/2 (PGe1/2), 1 (PGe1), and 2 monolayers (PGe2) of Ge, as calculated for surface Pt atoms.

2.2 Characterisation tests

The accessible metal fraction of Pt was determined by irreversible H_2 chemisorption. The volumetric adsorption was measured at 298 K. The volumetric adsorption experiments were performed at room temperature in a conventional vacuum apparatus. Hydrogen uptake was determined using double isotherm method [17]: the first isotherm gave the total gas uptake and the second, obtained after 1 h of evacuation at room temperature, the weakly adsorbed gas. By difference, the amount of strongly adsorbed gas was determined. Infrared spectroscopy characterization was performed with an FTIR Nicolet Magma 750 spectrometer study domain 4000 to 500 cm^{-1} employing CO. The sample wafers were formed by pressing approximately 35 mg of the catalyst powder. The disks were transferred to an all-glass infrared cell provided with CaF_2 windows. The pretreatment involved the reduction in flowing H_2 at 573 K and 773 K, following by evacuation at the same temperature 10^{-6} mbar. Amount of CO was introduced into the cell during 3 min time of balance at room temperature then sample spectra were recorded. Transmission electron microscopy (MET) was performed with a Philips CM 120 electron microscope operating at 120 KV with a theoretical resolution of 0.35 nm. Samples were

included in a polymeric resin and cut into small (about 40 nm) sections with a diamond knife. Cuts were put onto a TEM grid. The average particle size (average diameter) was determined on several pictures using the formula: $\sum n_i d_i^3 / \sum n_i d_i^2$.

2.3 Catalytic tests

The n-hexane (Merck) reaction was carried out in a closed-loop reactor (V=70ml) described previously [6,18,19] connected to a gas chromatograph with a 50-m CP-Sil 5CB glass capillary column and a FID detector. The analysis reactions were carried out at a standard n-hexane pressure of 1,33 kPa and hydrogen pressures of 32 kPa (H₂/nH: 24). The reaction temperature ranged from 543 K to 633 K. The sampling took place after 5min. Regeneration between runs was carried out with 4 Kpa air for 2 min followed by evacuation and 3 min of hydrogen treatment at 13,3 Kpa. The turnover frequency (TOF) values were calculated as the number of hexane molecule reacted per surface Pt atom, calculated from hydrogen adsorption, using the length of the run as the contact time. The selectivities were expressed as moles of hexane reacted rather than product moles. The fragments are products with less than six atoms carbon (methane, ethane, propane, isobutane, isopentane, cyclopentane and dimethylbutane). The isomers are 2 methypentane and 3 methypentane.

3 Results and discussion

3.1 Characterisation

The accessibility of surface Pt atoms was measured by H₂ chemisorption and CO adsorption techniques. H₂ chemisorption values gave significantly less surface Pt than that measured by IR spectroscopy of CO adsorption for bimetallic catalysts PGe1 and PGe2 (Table1). The results obtained are in good agreement with one of measured by D.Teschner^[10]. The presence of germanium decreased the amount of adsorbed H₂ in all the cases. This

behaviour has also been observed for other bimetallic platinum-based catalysts, like Pt-In^[20], PtSn^[21], Pt-Ge^[6,22] and Pt-Sb^[23], Pt-Sb^[24]. This decrease was higher for hydrogen chemisorption than for CO adsorption. The chemisorption of hydrogen occurs after dissociation of H₂ molecule; therefore, it requires two neighbouring active surface sites. In turn, CO could chemisorb on a surface. These bimetallic catalysts have single Pt atoms surrounded by Ge that can apparently adsorb CO in the linear mode whereas fewer active doublets are available for H₂ dissociation. Average particle size was calculated based on these measurements considering pure Pt and compared with data measured by TEM (without distinguishing between Pt and Ge). The different techniques gave coherent results for samples with low Ge loading (Table 1). According, the particle size values from H₂ chemisorption (Table1) were significantly higher, but without any physicochemical meaning in this case. Further, the average particle estimated from CO adsorption was in fair agreement with those measured by TEM (Table1)^[10]. The theoretical amount is known but the one on the catalysts remains unclear. The techniques (atomic adsorption spectra, fluorescence spectroscopy) have not been able to quantify them with greater accuracy.

Nevertheless, it was observed for the same catalysts the presence of germanium in the first coordination sphere of platinum in all samples by EXAFS (Extended X-ray Absorption Fine Structure)^[6]. We are then sure of the presence of germanium on catalysts and even connection between germanium and platinum atoms.

3.2 Catalytic tests

We have tested the n-hexane transformation in a temperature ranged from 543K to 633K for the monometallic and bimetallic catalysts grafted with various amounts of germanium. The activities were expressed as TOF values.

Table 1: Nominal Ge content, metallic accessibility values of Pt-Ge/Al₂O₃ catalysts as measured by different techniques.

Catalysts	Introduced Ge		Accessible Pt(%)		Particle size (nm)		
	monolayer	ppm	H ₂ ads	CO-IR	TEM	H ₂ ads ^a	CO-IR ^a
P	-	-	60	66	1.6	1.7	1.5
PB60	0	0	51	-	1.8	2	-
PGe1/8	1/8	280	52	62	1.7	2	1.6
PGe1/2	1/2	466	48	50	1.6	2.1	2
PGe1	1	1137	44	48	1.7	2.3	2.1
PGe2	2	4468	40	46	1.9	2.5	2.2

^a calculated upon the number of accessible Pt using spherical particle model

The figure 1 shows catalysts conversion and TOF respectively.

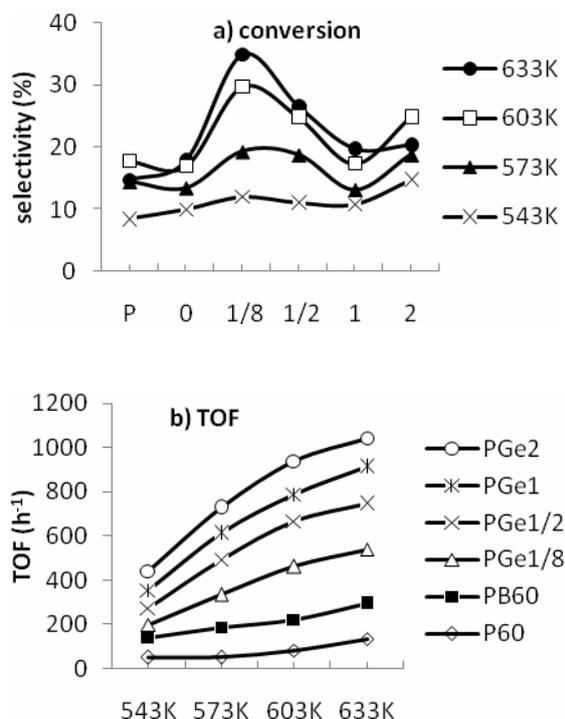


Figure 1: a) hexane conversion and b) TOF values at different temperatures

The small amounts of germanium content (1/8 and 1/2 monolayer) heighten the conversion and bimetallic catalysts were most active in hexane transformation than the parent and blank catalysts. The catalytic activities observed are linked to their contents. TOF value increases from the low to the large germanium content because more we put germanium on the surface we reduce surface accessibility.

We have not forgotten that TOF is the ratio between the amounts of molecules reacted with the surface accessibility. All TOF were obtained using the surface estimated by the chemisorption of hydrogen which requires a dissociative adsorption of H₂. It is also coke formation which diminishes the accessible surface of catalysts. The electronic interaction between Pt and Ge atoms can influence hexane conversion. The coexistence of electronic and geometric effects was demonstrated on supported Pt-Sn catalyst [25]. The electron acceptor effect of Ge also may be important [26]. The defined compound such as Pt_xGe_y should be formed on catalyst with high germanium content PGe2 [27,28]. These effects enhance interaction and the sites at interface between metal and support are more reactive. These reasons should increase highly conversion to these catalysts than catalysts with low germanium content but the opposite was observed. Furthermore, there is a possible exaltation of the acidity caused by the formation of GeO_x species near platinum [26,29]. The deposition of coke has then more inhibited catalysts with higher Ge content surface. Thus, the addition of low-monolayer (low Ge content) protected filing excessive carbon on the surface compared to the high monolayer of germanium (strong Ge content) and allowed their high conversion. The Figure 2 shows the selectivity from the different reactions

products: fragmentation, isomerisation, aromatisation and methylcyclopentane. Catalysts grafted with low germanium content PGe1/8 and PGe1/2 product no more fragmentation and aromatisation but an exalted isomerisation products than catalysts with high germanium content PGe1, PGe2 and parent and blank catalysts. Isomerisation and aromatisation evolution are in agreement with those obtained by Margitfalvi [31,32].

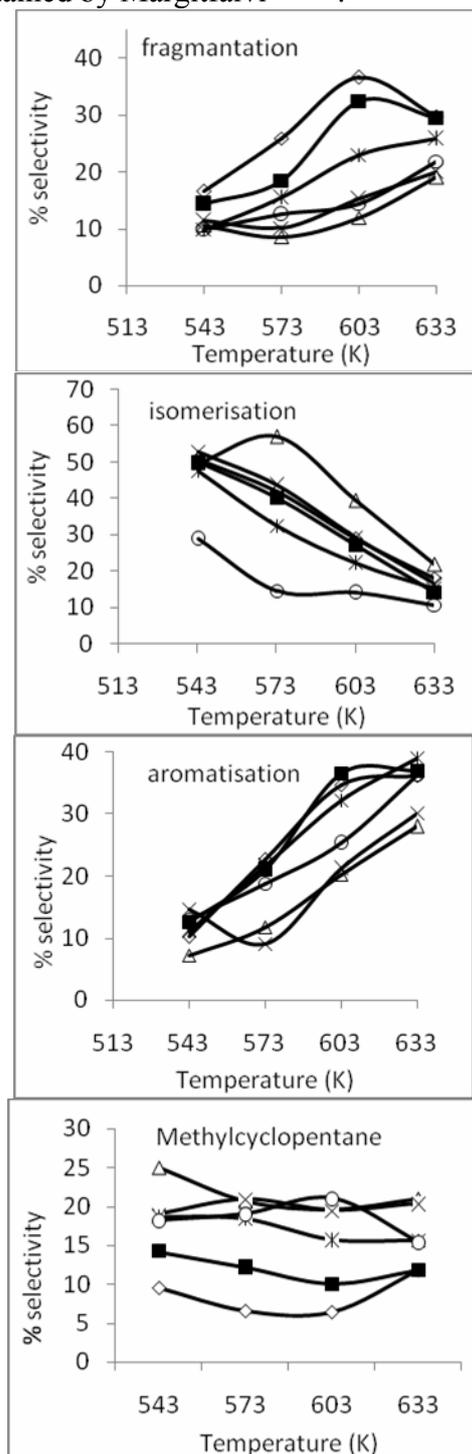


Figure 2: The selectivity (%) from fragmentation, isomerisation, methylcyclopentane and aromatisation reactions at different temperatures \diamond Pt ; \blacksquare PtGe0 ; Δ PtGe1/8 ; \times PtGe1/2 ; \circ PtGe2 ; $*$ PtGe1

Fragmentation is requiring ensembles of several Pt atoms [32,33]. Earlier observations on monofunctional Pt catalysts [19,34] showed that this reaction lies on a different compensation line than others. Several authors have attributed deeply dissociated (e.g., α, α, γ) intermediates to hydrogenolysis [32,33], the formation and decomposition of which must involve several elementary steps. Internal rupture has also been reported and considered closely related to isomerisation and may involve a not too deeply dehydrogenated intermediate [35,36]. Here the geometric requirements are not as strict as in aromatisation. Benzene formation (aromatisation) requires ensembles of three Pt atoms in triangular symmetry [38]. This route has confirmed by the appearance of cyclohexadiene from both trans- and cis hexa-1,3,5-triene reactant on Pt [37]. According to the results observed, the number of triangular three-atom ensembles for aromatisation and multiple Pt atom sites arrangement for fragmentation in “random” [33] are small on Ge1/8 [38,39] but the two-atom ensembles needed for C5-cyclization and ring opening [40] are present. That would be one the origin of an increase of methylcyclopentane, isomerisation and decrease in aromatisation and fragmentation reaction. For the high Ge atoms contents, depositing become randomly and their surface remain in spite more favourable to fragmentation and aromatisation reaction. The surface of catalysts structure could govern orientation of the reaction. Aromatic selectivity has decreased cause to the dilution of high coordination plans by germanium [6]. The platinum plans (111), which are necessary for the transformation of the hexane intermediate to benzene, are

fewer sites of three atoms than catalysts with higher germanium content. This effect has been observed in the transformation of benzene to cyclohexane with this type of catalyst^[6]. Cyclohexane cannot be observed among the products of hexane transformation on most monofunctional Pt catalysts. The usual assumption for cyclohexane formation is acid-catalyzed ring enlargement of the primary C5-cyclic intermediate from hexane^[11]. This route is not likely on monofunctional Pt but it is possible that cyclohexane can be formed supported by the fact that there are almost no sites with three platinum atoms to produce benzene with an excess of hydrogen^[6]. In our case, the number of sites is sufficient to avoid production of cyclohexane. The accessible metal of catalyst is one of the differences between our results and those of previously obtained catalysts. According to the mechanism of formation of benzene, there may be formed coke deposit on the surface of the catalyst^[34,37,39]. That confirms the high deposit of coke on catalysts with high germanium content, which reduces catalysts surface and enhances TOF as observed. In the case of catalysts with low Ge content, the deposit of coke is limited in order to inhibit fragmentation reaction as observed. The reduction of the selectivity of aromatisation is due to the selective Ge deposit on the three atoms ensemble needed to benzene formation as it was already observed.

4. Conclusion

Several catalytic structures can be obtained depending on the amount of germanium introduced. For the catalysts with low Ge content, the selective deposition of Ge to the high coordination leads to the diminution of aromatisation. These catalysts are less inhibited by coke which increases hexane conversion. The catalysts with high Ge content, lead to a random deposition of Ge, the

exaggerated poisoning on the surface by coke and give low conversion. The evaluation of performance of catalysts with n-hexane tested has shown that small germanium content offers interesting perspectives.

Bibliographie

- [1] Margitfalvi J., Szabó S., Nagy F., *Catalytic Dehydrogenation / Elsevier, 1986 Amsterdam*
- [2] Ryndin Y.A., Yermakov Y.I., Basset J.M.; *Surface organometallic chemistry molecular approaches to surface catalysis / Kluwer, Edition, 1988, Dordrecht*
- [3] Candy J.P., Didillon B., Smith E. L., Shay T. B., and Basset J.M.; *Jour. Mol. Catal. (1994) 86, 179-204*
- [4] Didillon B., Mansour A. Candy J.P., Bournonville J.P. and Basset J.M.; *Studies Surface Sciences. Heterogeneous Catalysis and fine Chemicals II, /M.Guisnet et al. edition, 1991, Amsterdam*
- [5] Chamam M., Károly L., Pirault-Roy L., Boghian I., Paál Z. and Wootsch A.; *Appl. Catal. A: General, (2007), 332, 27-36*
- [6] Wootsch A., Paál Z., Györffy N., Ello A. S., Boghian I., Leverd J. and Pirault-Roy L.; *Jour. Catal. (2006) 238, 67-78*
- [7] Pirault-Roy L., Teschner D., Paál Z. and Guérin M.; *Appl. Catal. A: General, (2003) 245, 15-31*
- [8] Nédez C., Choplin A., Corker J., Basset J.M., Joly J.F. and Benazzi E.; *Jour. Mol. Catal. (1994) 92, 239-244*
- [9] Chamam M., Wootsch A., Pirault-Roy L., Boghian I. and Paál Z.; *Catalysis Communications, (2007) 8, 686-692*
- [10] Teschner D., Pirault-Roy L., Naud D; *Appl. Catal. A: General. (2003) 252, 421-426*
- [11] Paál Z., *Catalytic Naphtha Reforming /G.J.Antos, A.M.Aitani, Dekker; 2004 New York,*
- [12] Chandler B.D., Schabel A. B., and Pignolet H. L; *Jour. Catal. (2000) 193, 186-198*

- [13] Macleod N., Stirling D, Freyr J.R., Webb G.; *Catal. Today* (1998) 46, 37-54
- [14] Pieck C.L., Marecot P., Querini C., Parera J.M. and Barbier J.; *Appl. Catal. A: General* (1995) 133, 281-292
- [15] Borgna A., Garetto T.F., Apesteguía C.R.; *Appl. Catal. A: General* (2000) 197; 11-21
- [16] Sinfelt J.H., *Handbook of Heterogenous Catalysis*, G.Ertl, H.Knözinger, /J. Weitkam Edition, , 1997 Verlag Chemie, Weinheim,
- [17] Sinfelt J.H., Carter J.L., Yates D.J.C.; *Jour. Catal.* (1972) 24, 283-296
- [18] Paál Z., Groeneweg H., Paál-Lukács J.; *Jour. Chem. Soc. Far. Trans.* (1990) 86, 3159 - 3167
- [19] Wootsch A., Paál Z. ; *Jour. Catal.* (1999) 185,192-198
- [20] Vaarkamp M., Dijkstra P., Grondelle J.V., Miller J.T, Modica F.S.,Koningsberg D.C., and Santen R.; *Jour. Catal.* (1995) 151, 330-337
- [21] Lieske H., and Völter J.; *Jour. Catal.* (1984) 90, 96 -105
- [22] De Miguel S.R., Baronetti C., Castro A. A., Scelza O.A.; *Appl. Catal.* (1988) 45, 61- 69
- [23] Passos F. B., Donato A.G., and Schmal M; *Jour. Catal.* (1998) 178, 478-488
- [24] Cheng C. H., Dooley K. M. and Price G. L.; *Jour. Catal.* (1989) 116, 325-337
- [25] Palazov A., Bonev C., Shopov D., Lietz G., Sárkány A., Völter J.; *Jour. Catal.* (1987) 103, 249-260.
- [26] Garetto T.F., Borgna A., Apesteguía C.R.; *Stud. Surf. Sc. Catal.* (1994) 88; 369-376
- [27] Huang Z., Fryer J.R., Park C., Stirling D., and Webb G.; *Jour. Catal.* (1998) 175, 226-235
- [28] Oya Y. and Suzuki T.; *Metallkde Bd* (1987) 78, H.4; 295-300
- [29] Borgna A., Garetto T.F, Apesteguía C.R and Moraweck B; *Appl. Catal. A : General* (1999) 182, 189-197
- [30] Malgítfalvi J.L., Borbáth I., Hegedüs M., Göbölös S. and Lónyi F.; *React. Kine. Catal. Let.* (1999) 68 ;133-135
- [31] Malgítfalvi J.L., Borbáth I., Hegedüs M., Göbölös S., Tampos A, Lónyi F.; *Stud. Surf. Sc. and Catal.* (2000) 3, 45 - 49
- [32] Anderson J.R.; *Adv. Catal.* (1973) 23, 1- 90
- [33] Sinfelt J.H; *Adv. Catal.* (1973) 23, 91 -119
- [34] Wootsch A., Paál Z.; *Jour. Catal.* (2002) 205, 86 - 96
- [35] Ponec V.; *Adv. Catal.* (1983) 32, 149 -214
- [36] Gault F.G.; *Adv. Catal.* (1981) 30,1-95
- [37] Paál, Z. Tétényi, P.; *Jour. Catal.* (1973) 30, 350 - 361
- [38] Biloen P., Helle J., Verbeek, H. Dautzenberg F., Sachtler W.M.; *Jour. Catal.* (1980) 63, 112 - 118
- [39] Paál Z.; *Adv. Catal.* (1980) 29, 273 - 334
- [40] Paál, Z. Tétényi P., *Nature* (1977) 276, 234 -239