Differences and similarities of supported Ge–Pt/C catalysts prepared by conventional impregnation and controlled surface reactions

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ABSTRACT

Two methods of modification of monometallic platinum catalyst supported on functionalized active carbon were used for the preparation of Ge–Pt/C bimetallic catalysts: (i) conventional impregnation (CI) and (ii) controlled surface reactions (CSRs). All results, namely the study of germanium anchoring reaction, two test reactions (cyclohexane dehydrogenation and cyclopentane hydrogenolysis), H_2 and CO chemisorption, indicate that the modification of Pt with Ge using CSRs was highly selective, i.e., almost 100% of Ge introduced was anchored to platinum. On the other hand results showed that in catalysts prepared by CI method Ge was located mainly on the support.
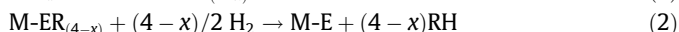
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1. Introduction

It is known that the addition of second inactive metal (such as Sn, Ge or Pb) to noble metals significantly alters the catalytic properties [1–5]. The promoting effect of Ge modifier on supported noble metal catalysts has been evidenced in various transformations of hydrocarbons [6–8], in selective hydrogenation of fine chemicals [2,9], reduction of aromatics [10]. It has to be emphasized that in all these studies Al_2O_3 or SiO_2 was applied as catalyst support.

It has been demonstrated that in the modification of supported metal catalysts by germanium, the intimate contact between the noble metal and the modifier, i.e., the selective modification of catalytically active sites can only be achieved by either (i) "redox-type" surface reactions [2,11] or (ii) using controlled surface reactions (CSRs) [1,3,4,7]. The latter one is often called as surface organometallic chemistry (SOMC) [12].

The basic surface chemistry involved in the two-step modification of monometallic supported catalysts by a group IVa organometallic compounds, such as ER_4 (E = Ge, Sn, Pb; while R = CH_3, C_2H_5, C_4H_9) can be given by the following general equations [13–16]:

$$MH_a + ER_4 \rightarrow M\text{-}ER_{(4-x)} + x RH \qquad (1)$$
$$M\text{-}ER_{(4-x)} + (4-x)/2\, H_2 \rightarrow M\text{-}E + (4-x)RH \qquad (2)$$

The anchoring reaction (1) between ER_4 and hydrogen adsorbed on the supported metals (MH_a) (M = Pt, Rh, Ru and Ni) proceeds via stepwise hydrogenolysis of the E–R bond with the elimination of RH and formation of Primary Surface Complexes (PSCs), described as $M\text{-}ER_{(4-x)}$. The PSCs are decomposed in H_2 atmosphere with the formation of alloy type surface species (reaction (2)) [17,18].

In this study we describe the details of the preparation of Ge–Pt/C catalysts emphasizing the differences between two methods: (i) conventional impregnation (CI), and (ii) CSRs. The goal of this work is to find modes and ways to increase the amount of Ge anchored onto the Pt and maintain the overall control of germanium anchoring, i.e., suppressing the amount of Ge introduced onto the support. CO and H_2 chemisorption measurements and two test reactions (cyclohexane dehydrogenation and cyclopentane hydrogenolysis) were applied to characterize the catalysts prepared.

2. Experimental part

Catalysts preparation. A commercial granular activated carbon derived from a pit of peach (GA-160 from Carbonac) with a final particle size between 100 and 140 mesh was used. This support

was purified, functionalized with HNO_3, and then dried according to the technique described elsewhere [19,20]. The textural properties of the activated carbon were only slightly modified by the functionalization treatment with HNO_3 (S_{BET} = 876 $m^2 g^{-1}$ and $V_{micropore}$ = 0.29 $cm^3 g^{-1}$). The parent 5 wt.% Pt/C catalyst was prepared by conventional impregnation of the functionalized activated carbon with an aqueous solution of H_2PtCl_6 and than was dried at 120 °C overnight. PtGe1-4-CI series of catalysts were prepared by impregnation of the Pt/C catalyst with a solution of $GeCl_4$. The impregnation was carried out at 25 °C for 6 h, using a volume of impregnation solution/mass of support ratio of 30 ml g^{-1}, and stirring rate of 600 rpm.

Prior to the use of CSRs, the parent Pt/C catalyst was re-reduced in flowing hydrogen at 350 °C for 3 h. It should be mentioned, that catalysts supported on functionalized carbon couldn't tolerate higher reduction temperatures, due to the instability of surface groups of the support above 400 °C [21,22]. Tetraethylgermanium ($Ge(C_2H_5)_4$) was applied as a precursor compound. Further details on the two steps CSRs and analysis can be found elsewhere [15,16].

Characterization. Prior to the chemisorption measurements and test reactions, catalysts were re-reduced in situ under flowing H_2 at 350 °C for 3 h. Our earlier results [22] indicated that after reduction at 350 °C the Pt was completely reduced. Hydrogen and CO chemisorption measurements were carried out in conventional equipment (ASDI RXM 100 equipment (Advanced Scientific Designs Inc.)). The double isotherm method has been used in chemisorption studies.

Test reactions of the metallic phase (cyclohexane dehydrogenation (CHD) and cyclopentane hydrogenolysis (CPH)) were carried out in a flow reactor. CHD was carried out at 250 °C by using a H_2/CH molar ratio = 26. CPH was performed at 350 °C by using a H_2/CP molar ratio = 29. Further details can be found elsewhere [19,22].

3. Results and discussion

Study of the germanium anchoring step. In order to achieve high germanium content high initial concentration of $Ge(C_2H_5)_4$ was used (see $[Ge]_o/Pt_s$ ratio in Table 1) and the temperature of anchoring reaction (1) (T_r) was increased up to 155 °C.

It is necessary to mention that the results of blank experiment using Pt free carbon support under standard preparation conditions unambiguously confirmed the lack of any reaction between $Ge(C_2H_5)_4$ and carbon support even at 155 °C. For this reason anchoring of $Ge(C_2H_5)_4$ onto the functionalized carbon support by CSRs can be excluded. Similar results have been reported by Crabb and Ravikumar [23] for the deposition of Ge atoms on Pt/C catalysts using SOMC techniques, indicating that the reaction between Pt and the Ge precursor is highly selective.

The main experimental data of Ge anchoring are summarized in Table 1. Table 1 shows that the stoichiometry of reaction (1), i.e., the value of x ($x = 4n^I/(n^I + n^{II})$) is in the range of 0.62–3.77 and strongly depends on the temperature of Ge anchoring.

It has been found [24] that $Ge(n-C_4H_9)_4$ reacts irreversibly with surface hydroxyl groups of SiO_2, Al_2O_3 or $SiO_2–Al_2O_3$ at about 250 °C, resulting in the release of one butyl ligand per grafted germanium (x = 1.0) and formation of highly thermal stable (up to 400 °C) grafted $–OGe(n-C_4H_9)_3$ complex. Consequently, due to the high thermal stability of Ge–C bond, the high extent of loss of the alkyl groups of the PSCs ($Pt–Ge(C_2H_5)_{(4-x)}$) can entirely be attributed to the involvement of Pt.

The formation of ethane during germanium anchoring at three different temperatures is shown in Fig. 1A–C. As far as germanium anchoring was carried out in the presence of gas-phase hydrogen therefore no ethylene was detected. As seen from the kinetic curves presented in Fig. 1A–C upon increasing the value of T_r both the initial rate of reaction (1) and the amount of ethane formed increased.

The w_0 values (see Table 1) showed good temperature dependence, resulting in an apparent energy of activation for anchoring reaction (1) of 50.8 ± 4 kJ/mol. Slightly lower value of the activation energy (42.6 ± 1.9 kJ/mol) was reported in our earlier studies for surface reaction between $Sn(C_2H_5)_4$ and preadsorbed hydrogen on Pt/SiO_2 catalyst [15].

As far as almost constant $[Ge]_o/Pt_s$ ratio ($[Ge]_o/Pt_s \approx 26$), but different reaction temperatures were used in germanium anchoring experiments the change of the shape of TPD patterns given in Fig. 2 clearly reflects the differences between the PSCs formed at various temperatures (T_r = 55, 105 and 155 °C).

The sample PtGe1-SR obtained at T_r = 55 °C has the most broad TPD profile as shown in Fig. 2. The contribution of the low temperature TPD peaks (LTP) below 75 °C is relatively low, whereas the contribution of the high temperature peaks (HTP) between 140 and 200 °C is high.

Unusually low activity at T_r = 55 °C (see values w_0 and Ge/Pt_s in Table 1) and the low value of x (x = 0.62) indicates that $Ge(C_2H_5)_4$ is highly stable at this temperature and the extent of anchoring reaction is relatively low. Consequently, in this case mainly chemisorption of $Ge(C_2H_5)_4$ on platinum surface takes place.

In our earlier studies it has been demonstrated [25] that one of the reasons of the appearance of HTP can be attributed to the formation of coordinatively saturated $–Sn(C_2H_5)_4$ surface species strongly adsorbed onto the platinum. Due to coordinative saturation these species are much less reactive towards hydrogen than those having less alkyl groups.

At T_r = 105 °C and 155 °C the presence of hydrogen resulted in high extent of dealkylation of $–Ge(C_2H_5)_{(4-x)}$, what is reflected by low n^{II} and high x values (see data given in Table 1).

The high value of x (x = 3.0 or 4.0) indicated that in reaction (1) coordinatively unsaturated moieties $–Ge(C_2H_5)$ (x = 3.0) and "naked" Ge (x = 4.0) were exclusively anchored to the platinum. Moreover, this finding indicated also that upon performing surface reaction (1) at T_r = 155 °C the hydrogenolysis of the Ge–C bonds in anchored PSCs was almost complete and mostly "naked" Ge atoms were formed. "Naked" Ge atoms can present on the platinum surface as adatoms and can migrate into the bulk of platinum leading

Table 1
Summary of data of germanium anchoring.

No.	T_r °C	Solvent	$[Ge]_0/Pt_s$	$w_0 \times 10^{-6a}$	$n^I \times 10^{-6b}$	$n^{II} \times 10^{-6c}$	x	Ge wt.%[d]	Ge/Pt_s[e]
PtGe1-SR	55	Hexane	25.0	0.3	7.1	38.8	0.62	0.08	0.11
PtGe2-SR	105	Decane	24.7	2.7	98.4	25.4	3.18	0.22	0.29
PtGe3-SR	155	Decane	28.6	20.0	350.8	21.7	3.77	0.68	0.87

[a] Initial rate of germanium anchoring in reaction (1), (mol $g_{cat}^{-1} \times min^{-1}$).
[b,c] Amount of ethane formed in reaction (1) and (2), respectively (mol g_{cat}^{-1}).
[d] Ge content calculated from the material balance of germanium anchoring.
[e] Amount of Ge anchored per surface Pt atom, calculated using CO/Pt = 0.42. $[Ge(C_2H_5)_4]_0$ = 15.5 × 10^{-2} M; atmosphere of reaction (1): H_2; duration: 4 h.
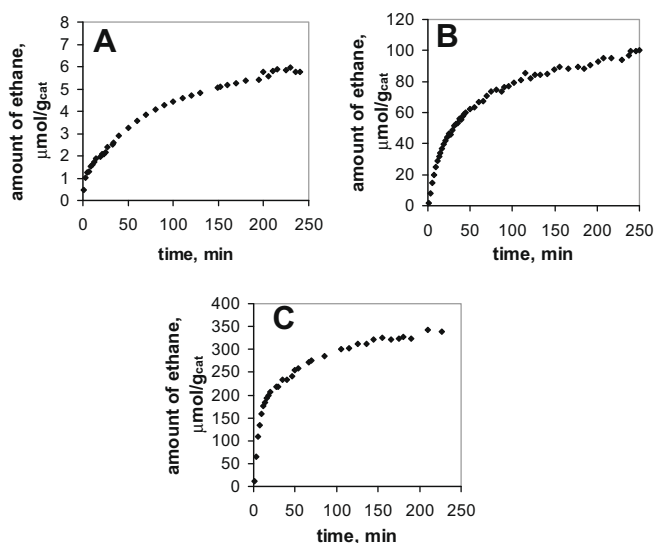
Fig. 1. Kinetic curves of ethane formation during germanium anchoring in excess hydrogen. (A) T_r = 55 °C; (B) T_r = 105 °C and (C) T_r = 155 °C.

Fig. 2. Influence of the reaction temperature on the TPD patterns of PSCs formed during germanium anchoring. (●), Catalyst PtGe1-SR (T_r = 55 °C); (□), catalyst PtGe2-SR (T_r = 105 °C); (△), catalyst PtGe3-SR (T_r = 155 °C).

to site isolation effects and forming surface or bulk alloy type species even during the anchoring step (1).

In our earlier studies [15,16] it has been demonstrated that differences in the TPD profiles are attributed to the decomposition of different types of PSCs (with different extent of dealkylation) anchored either onto different sites of the active metal or the support. There is a general observation: the higher the temperature of these TPD peaks the lower the reactivity of the given PSCs. This is revealed by the position of TPD peaks as shown in Fig. 2. The increase of the temperature of germanium anchoring up to 155 °C resulted in pronounced increase of the Ge/Pt$_s$ ratio (Ge/Pt$_s$ = 0.87) and the temperature maximum of TPR curve was shifted to 170 °C (see Fig. 2). The appearance of high temperature TPD peak at 170 °C and shoulder at 250 °C (see Fig. 2) can be attributed to the high thermal stability of Ge–C bond in PSCs with general formula of –Ge(C$_2$H$_5$).

Chemisorption properties. As emerges from data presented in Table 2 the H/Pt ratio in parent Pt/C catalyst is lower that CO/Pt ratio. Similar results were reported by Rodriguez-Reinoso [26], whereas in Ref. [27] the opposite tendency was demonstrated. Several studies have been carried out [27] which relate Pt dispersion to active carbon support characteristics such as surface heterogeneity, surface electronic properties, porous structure, and content of oxygen surface groups on the support.
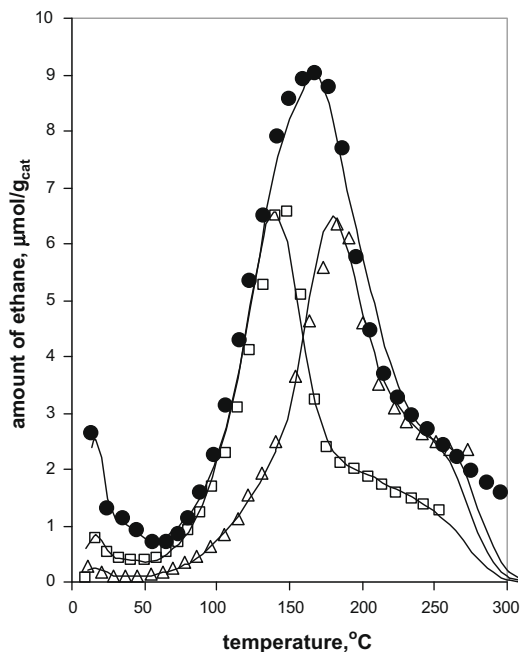
Results given in Table 2 shows that the introduction of germanium to parent Pt/C resulted in significant decrease in both H$_2$ and CO chemisorption values. The trend in the decrease of the H/Pt and CO/Pt ratios as a function of Ge/Pt ratio is different for catalysts prepared by CI and CSRs. As far as H$_2$ chemisorption is an activated process, the presence of Pt–Pt sites is needed to break the H–H bond prior to the chemisorption, whereas on single Pt atoms CO adsorption can take place in the linear mode. Consequently, the H/Pt ratios decrease faster than the CO/Pt one. In the PtGe1-3-SR series of catalysts even at lowest Ge content (Ge/Pt = 0.04) the amount of chemisorbed hydrogen is strongly diminished and remains very low and almost constant (see Table 2). It is necessary to mention that our results are in a good agreement with chemisorption data presented for Ge–Rh/Al$_2$O$_3$ catalysts prepared by SOMC in Ref. [3]. It is necessary to mention that in catalysts prepared by CSRs CO/Pt ratios are also low, but that they are still twice as high as that of the amount of hydrogen chemisorbed.

The decrease of H/Pt and CO/Pt ratios in Ge–Pt catalyst can be attributed to two effects: (i) site blocking and (ii) electronic effect induced by Ge [7,8]. Due to the electron acceptor effect of Ge, CO

Table 2
The influence of the preparation method and the Ge content of different Ge–Pt/C catalysts on the chemisorption properties and catalytic activity in test reactions applied.

Catalyst	Ge, wt. %	Ge/Pt[a](at./at.)	H/Pt	CO/Pt	r_{CH}[b] (mol h^{-1} g$_{Pt}^{-1}$)	X_{CP}^0 (%)[c]	Δ_{CP}[d] (%)
Pt/C	–	–	0.29	0.42	4.50	24.5	57
PtGe1-CI	0.08	0.04	0.26	0.39	3.90	18.3	46
PtGe2-CI	0.22	0.12	0.22	0.33	3.90	20.0	33
PtGe3-CI	0.61	0.33	0.14	0.25	3.40	16.0	33
PtGe4-CI	1.83	0.98	0.14	0.25	3.90	16.2	17
PtGe1-SR	0.08	0.04	0.03	0.07	2.80	1.8	51
PtGe2-SR	0.22	0.12	0.04	0.08	2.20	0.88	23
PtGe3-SR	0.68	0.37	0.03	0.07	0.56	0.45	0

[a] Ge/Pt values calculated from the actual Pt and Ge content determined by AAS.
[b] Reaction rate (r_{CH}) in the CHD (r_{CH} = x/(W/F_{CH}°), where x: CH conversion, W: Pt weight in the sample, F_{CH}°: molar CH flow).
[c] Initial conversion (X_{CP}^0) in the CPH calculated by extrapolation to t = 0.
[d] Deactivation parameters (Δ_{CP}) in the CPH (Δ_{CP} = (X_{CP}^0 – X_{CP}^f)/X_{CP}^0), where X_{CP}^0 and X_{CP}^f are the conversion at t = 0 and 120 min. PtGe1-4-CI and PtGe1-3-SR catalysts prepared by CI and CSRs, respectively.

chemisorption sharply decreases even at very low modifier contents [6,8,28]. It was suggested [29,30] that Pt atoms when alloyed with Ge are in an electron-deficient state and therefore suppressed CO coverage.

Contrary to that in PtGe1-4-CI series of catalysts, the decrease of the chemisorption values is less pronounced.

Test reactions of the metallic phase. Table 2 shows the results of the test reactions: (i) reaction rates (r_{CH}) values for CHD, (ii) initial conversions (X_{CP}^0) and (iii) the deactivation parameter (Δ_{CP}) for CPH.

CHD is a structure insensitive reaction that has been carried out with the aim to get information on the number of active sites, i.e., the amount of accessible or electronically active Pt atoms and hence should not depend on Pt crystal size and geometry [8,9]. Only slight decrease of the reaction rates in CHD were observed in PtGe1–4–CI series of catalysts (see Table 2). Contrary to that, the introduction of Ge onto the Pt by CSRs resulted in pronounced decreases of the r_{CH} values. These finding indicated that the introduction of germanium by CI resulted in only very slight electronic modification of Pt, whereas a decrease in the exposed metallic area observed in PtGe1–3–SR series of catalysts can be related to the PtGe alloy formation.

With respect to the activity of these catalysts in CPH reaction (structure-sensitive reaction [5,19,22]), the CP conversion/time curves were fitted with an exponential function of the type $X_{CP} = X_{CP}^0 \times \exp(-\alpha t)$, where X_{CP} is the conversion measured in moment t. As can be seen from data given in Table 2 the Pt/C catalyst has a high values for both X_{CP}^0 and Δ_{CP}. It is necessary to mention that the trend in the decrease of X_{CP}^0 values as a function of Ge/Pt ratio is different for catalysts prepared by CI and CSRs. These results indicated that in the case of Ge–Pt/C catalysts prepared by CI technique, the X_{CP}^0 and Δ_{CP} values in CPH reaction were much higher (and also rather constant) than in PtGe1-3-SR series of catalysts. This behaviour unambiguously indicated the loss of Pt ensemble sites required for this reaction when Ge was added to Pt by using CSRs. On the other hand, the similar hydrogenolytic activity of PtGe1-4-CI series of catalysts with respect to the monometallic Pt/C strongly indicated that a major part of Ge are located either on the support or at a considerable distance from Pt that cannot break up the hydrogenolytic ensembles.

4. Conclusions

Upon using CSRs a series of Ge–Pt/C catalysts with Ge/Pt$_s$ ratio up to 0.9 were prepared. It was demonstrated that in this modification method surface species with general formula of $-Ge(C_2H_5)_{(4-x)}$ were anchored almost exclusively onto platinum. The results of blank experiment clearly indicated that the involvement of functionalized active carbon support in Ge anchoring can be excluded.

The introduction of Ge by anchoring reaction strongly reduces the number of Pt sites involved both in H_2 and CO chemisorption and test reactions. Contrary to that the modification with Ge by CI resulted in only slight alterations in catalytic activities (both in CHD and CPH) and chemisorption properties.
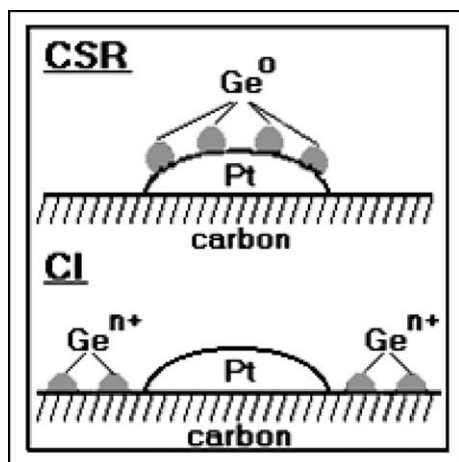
Consequently, it was demonstrated that the surface composition of supported bimetallic catalysts strongly depends on the method of their preparation. Scheme 1 shows that in Pt–Ge/C catalysts prepared by CI method the main part of Ge are located on the support. Contrary to that exclusive formation of alloy type surface entities can only be achieved by using of CSRs method.

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Scheme 1.