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Hydrosilylation of n-alkenes and allyl chloride over platinum supported on styrene–divinylbenzene copolymer

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ABSTRACT

Catalytic performance of styrene–divinylbenzene copolymer-supported platinum catalyst of high crosslinking degree and high surface area was studied in reactions of hydrosilylation of allyl chloride, 1-octene and 1-butene. The catalyst has shown considerably greater stability of catalytic activity than classical active carbon-supported catalyst. In experiments on repeated use of catalysts, the decrease in catalytic activity for hydrosilylation of liquid double bond-containing compounds proceeding in the presence of the copolymer-supported and carbon-supported platinum was considerably smaller in the case of the former catalyst. Bimetallic Pt–Cu catalyst on polymeric support appeared to be considerably less active than monometallic catalyst.

1. Introduction

The addition of silane containing Si–H bond to multiple bonds, called hydrosilylation, is the most important way of synthesis of organofunctional silanes which have found many commercial applications, among others as adhesion promoters for inorganic material–polymer systems and modifiers of mineral surfaces [1,2]. Particularly important representatives of this group of compounds are 3-chloropropyltrichlorosilane and its alkoxy derivative. Most of the research work on hydrosilylation has been performed in homogeneous catalytic systems in the presence of transition metal complexes [3–6] or in heterogenized catalytic systems in the presence of the above complexes immobilized on surfaces of polymers [7,8], whereas only a small number of papers were devoted to hydrosilylation carried out in typical heterogeneous catalytic systems by using supported metals in their elemental form as catalysts [3–6,9]. However, it is worth to add that commercial process of synthesis of 3-chloropropyltrichlorosilane, which is the key process in the production of the whole family of silane coupling agents, is carried out on carbon-supported platinum catalysts. Easy separation of reaction products from catalyst, which is a well-known advantage of heterogeneous catalysis, has encouraged us to search for a supported metal catalyst which would be characterized by both good activity and high selectivity as well as by capability of being used several times or for a prolonged time-on-stream without significant loss of main product yield.

2. Experimental

2.1. Preparation of catalysts

The support used in this study was styrene–divinylbenzene (SDB) copolymer of particle size 0.3–0.8 mm (Aldrich). Catalysts 1%Pt/SDB and 1%Pt + 0.2%Cu/SDB were prepared by incipient wetness technique using chloroformic solutions of platinum(II) and copper(II) acetylacetonates (Ventron) as metal precursors. Reduction of the precursors was carried out in hydrogen flow (50 ml/min) for 3 h at 160 °C (the preparation of 1%Pt/SDB catalyst) or 280 °C (the preparation of 1%Pt + 0.2%Cu/SDB catalyst). Commercial catalyst (Degussa) containing 1 wt% platinum on active carbon (1%Pt/C) was used for the sake of comparison.

2.2. Characterization of catalysts

Low-temperature nitrogen adsorption isotherms were determined on an ASAP 2010 sorptometer (Micromeritics). Hydrogen chemisorption measurements were determined on the same

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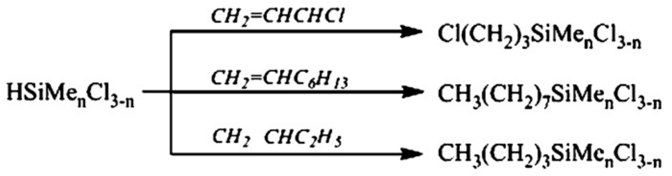

where:n = 0, 1 or 2 in the case of trichlorosilane, methyldichlorosilane and dimethylchlorosilane, respectively

Fig. 1. Simplified scheme of reactions.

instrument at 35 °C. Calculations of platinum particle size were performed assuming spherical shape of the metal particles according to the formula given in Ref. [10].

Thermogravimetric analysis was performed on a Setaram thermobalance Setsys 12 in argon flow (purity 99.999%, 30 cm^3/min) at heating rate of 10 °C/min.

Temperature programmed reduction with hydrogen (TPRH$_2$) was conducted on a Chemisorb 2705 instrument (Micromeritics) in the stream of the mixture of H$_2$ (10%) and Ar (90%) using a TCD detector. The flow rate of the mixture was 30 cm^3/min, temperature increase rate 10 °C/min and sample weight 30 mg.

A D8 advance diffractometer (Bruker) was used to obtain XRD patterns. Platinum content in catalysts after their use in hydrosilylation of allyl chloride and 1-octene with trichlorosilane was determined on a Varian Vista-MPX spectrometer (ICP-OES).

2.3. Reactions studied

Trichlorosilane (>99%) was purchased from Unisil Ltd., Tarnów and subjected to distillation under argon prior to use. Allyl chloride (Zachem, Poland) of >98% purity was also distilled before being used. 1-octene (Fluka), 1-butene (Aldrich), methyldichlorosilane (Fluka), dimethylchlorosilane (Fluka) and benzene (POCh, Poland) were used as received.

Table 1
Surface area and pore size of catalysts and supports.

Sample	Surface area (m^2/g)	Average pore diameter (nm)	Pore volume (cm^3(STP)/g)
SDB (no treatment)	1172	2.6	0.77
SDB after 3 h in CHCl$_3$	1151	2.6	0.74
SDB after 3 h at 280 °C	1031	2.7	0.68
1%Pt/SDB	1120	2.6	0.73
1%Pt/SDB + 0.2%Cu/SDB	987	2.7	0.66
Active carbon support (C)	1281	1.9	0.61
1%Pt/C	1206	1.9	0.57

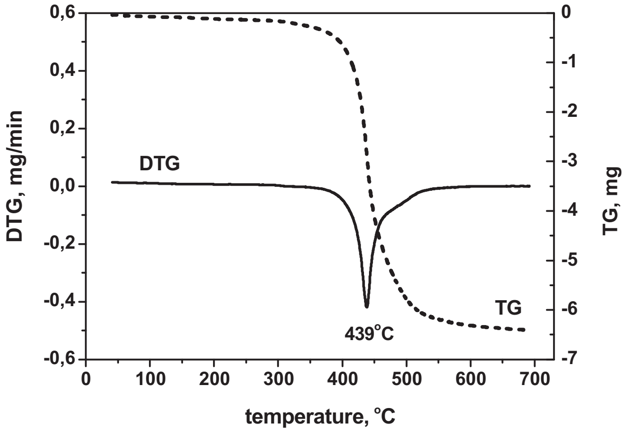

Fig. 3. TG and DTG curves of Pt/SDB catalyst.

The addition of trichlorosilane to allyl chloride and 1-octene as well as the addition of methyldichlorosilane and dimethylchlorosilane to 1-octene was carried out at 60 °C for 3 h in batch reactors in the form of headspace vials sealed with silicon/PTFE septa and aluminum crimp seals. The reactors were loaded with catalysts in the amount corresponding to 2 × 10^{-4} mol of Pt per 1 mol of trichlorosilane. Hydrosilylation of allyl chloride was carried out in benzene

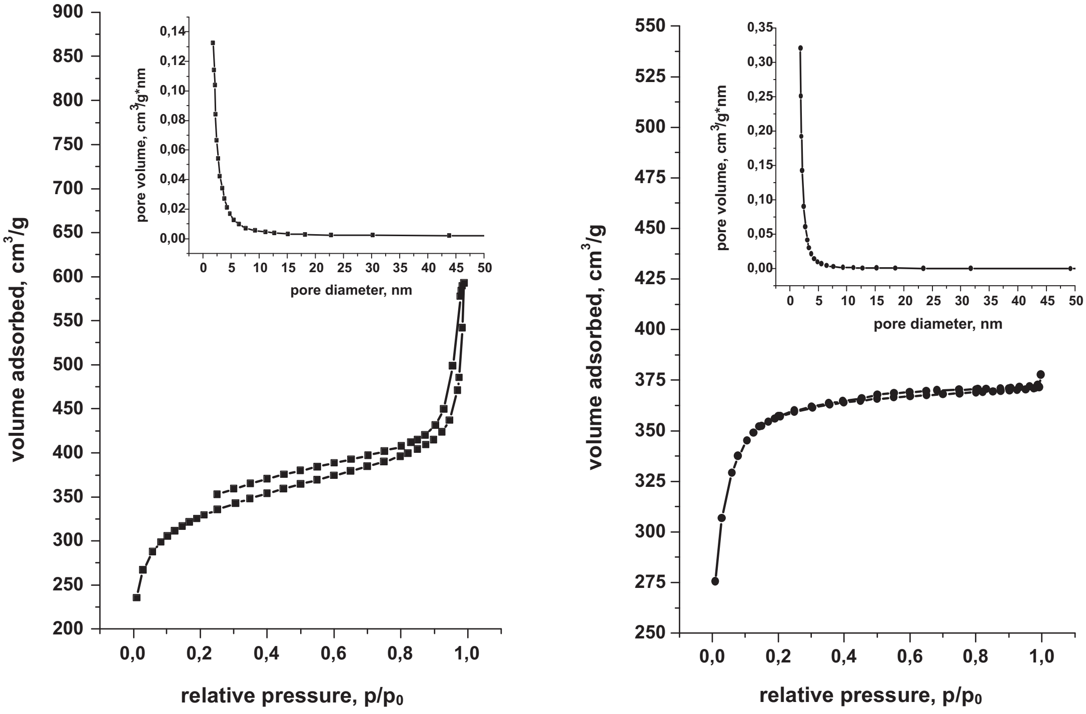

Fig. 2. Low-temperature nitrogen adsorption–desorption isotherms and pore size distributions (inserts) for 1%Pt/SDB (left) and 1%Pt/C (right) catalysts.

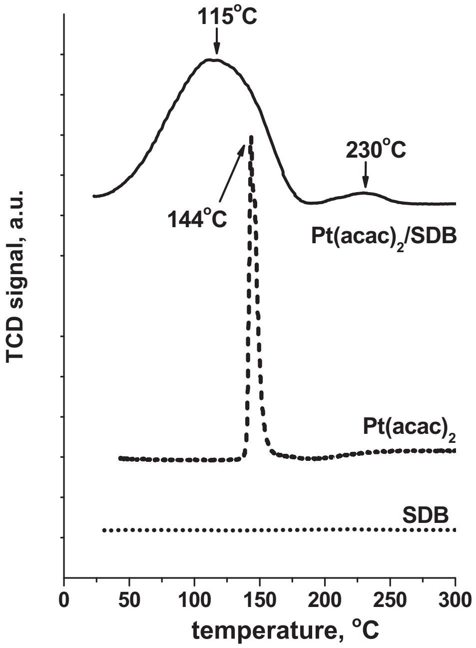

Fig. 4. TPRH$_2$ profiles of SDB copolymer, platinum precursor Pt(acac)$_2$ and SDB-supported precursor Pt(acac)$_2$/SDB.

solvent (volume ratio of reactants to benzene was 1), whereas that of 1-octene without a solvent. Reaction products were analyzed on a Perkin–Elmer Auto System XL gas chromatograph using a DB-5 capillary column of 30 m in length and 0.53 mm in diameter. When catalytic performance during repeated use of a catalyst was investigated, the post-reaction mixture was removed by using a syringe inserted through headspace vial septum and benzene or 1-octene (in the case of hydrosilylation of allyl chloride and 1-octene, respectively) was injected several times in order to wash the catalyst and then reactants were introduced to begin the next run of reaction.

Hydrosilylation of 1-butene was performed at 140 °C in a flow reactor (40 cm in length, 1 cm in diameter, catalyst load: 1 g) by passing 1-butene (10 ml/min) through a thermostated saturator filled with trichlorosilane. Reaction products were analyzed in the way described above.

Schemes of the reactions studied are shown below (Fig. 1).

3. Results and discussion

Strongly hydrophobic nature of the SDB support [11] and good solubility of acetylacetonates in chloroform were the reason for employing the latter compound as a solvent for metal precursors. This choice required, however, the determination of chloroform effect on the texture of SDB resin. The styrene–divinylbenzene copolymer used in our study was distinguished by very well-developed porosity as evidenced by its high surface area and pore volume (Table 1). From textural point of view, the SDB resin differs from activated carbon used in our study as a support in the 1%Pt/C catalyst, although their common feature is that both of them are characterized by high surface area of about 1200 m^2/g (Table 1).

Average pore diameter of the former (2.6 nm) is in the lower range of mesopores and the shape of nitrogen adsorption isotherm (Fig. 2, left) indicates that both micro- and mesopores contribute to the total porosity of SDB polymer-supported catalyst, whereas the latter is a microporous solid of average pore diameter equal to 1.9 nm and has nitrogen adsorption isotherm of type I (Fig. 2, right), according to IUPAC classification of isotherms [12]. In the case of the active carbon-supported catalyst, its pore size distribution is shifted towards smaller diameters compared to Pt/SDB. A 3-h contact of the SDB resin with chloroform results in a small decrease in surface area (by less than 2%), while 3-h heating at 160 °C after contact with CHCl$_3$ causes loss of surface area by 4.4%. The highest decrease in surface area (by 15.8%) was observed after reduction of metal acetylacetonates for 3 h at 280 °C. Therefore we can conclude that the porous system of SDB resin is quite resistant to heating at 160 °C,

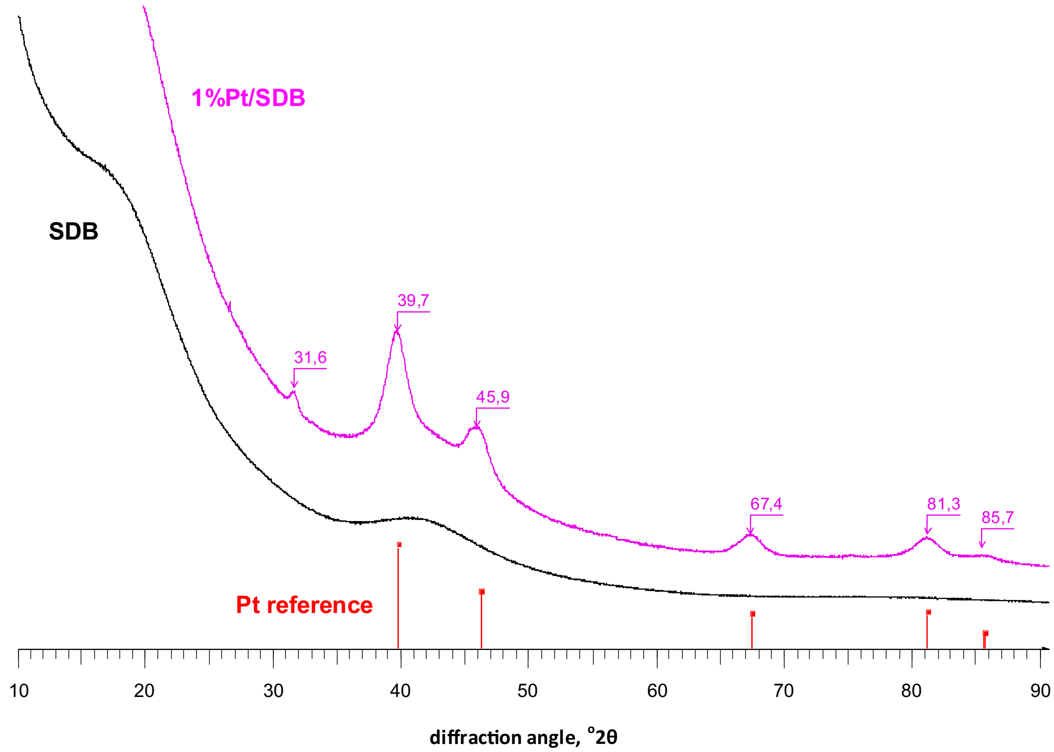

Fig. 5. X-ray diffraction patterns of 1%Pt/SDB catalyst and SDB support.

i.e., the temperature at which platinum(II) acetylacetonate decomposes to platinum metal in flowing hydrogen, but heating at 280 °C (reduction temperature of copper(II) acetylacetonate) results in the collapse of some pores. It is likely that at the latter temperature, fragments of some pore walls begin to be removed from the polymer which is reflected by faster TG curve dropping at about 300 °C (Fig. 3). On the ground of thermogravimetric analysis of another SDB sample, Wu and Chang [11] concluded that it was stable below 200 °C and suggested that the application of Pt/SDB catalyst should be limited to 160 °C for extra margin of safety against textural damage. The peak on DTG curve (Fig. 3) that appears at 439 °C indicates the maximum rate of mass loss, but onset of the copolymer decomposition occurs clearly below the mentioned temperature. Thus it can be concluded that the temperature of Pt/SDB catalyst preparation (160 °C) and catalytic reaction temperatures (60 and 140 °C) are safe for the above catalyst, whereas reduction temperature of the mixture platinum(II) and copper(II) acetylacetonates at 280 °C can be too high.

Temperatures of reduction of platinum(II) and copper(II) acetylacetonates to metals (160 and 280 °C, respectively) were chosen on the ground of $TPRH_2$ profiles of the above metal precursors. The profile of $Pt(acac)_2$ is characterized by the presence of clearly marked large peak at 144 °C. The peak is quite narrow – its onset temperature is 140 °C and the return to baseline occurs at 160 °C (Fig. 4). After supporting $Pt(acac)_2$ on SDB, the profile changed, most likely due to interactions between the precursor and the support. The peak became broader and its flat maximum shifted to 115 °C, however, it descended to the baseline only at about 180 °C (Fig. 4). At about 200 °C the profile began to ascend again and a small broad peak appeared with a maximum at 230 °C. On the ground of $TPRH_2$ of $Pt(acac)_2$/SDB it was concluded that hydrogen consumption proceeds in two stages: (1) reaction with $Pt(acac)_2$ (the large peak at a lower temperature), and (2) reaction at a higher temperature with products of partial decomposition of platinum acetylacetonate (small peak with maximum at 230 °C). Although the platinum precursor was not fully reduced at 160 °C, a comparison of peak areas brings to the conclusion that the amount of unreduced platinum(II)-containing species is very small. A similar conclusion can be drawn on the ground of X-ray diffraction patterns (Fig. 5) which point to the presence of Pt^0 as proved by a very good agreement between reflections recorded for the catalyst sample and those for platinum reference material. An additional reflection that requires a comment is the weak signal at 31.6° 2Θ which can be a result of changes occurring in the polymeric support during decomposition of platinum precursor in hydrogen flow. The SDB resin is an amorphous material as indicated by the absence of reflections in the 2Θ range of 10–90° (Fig. 5), except for a small peak at about 40° 2Θ that probably originates from the diffraction of X-ray radiation on the sample holder. However, a small amount of platinum species other than metallic platinum particles can be present, even though they remained undetected by X-ray technique. Another evidence that the reduction to Pt^0 took place at 160 °C, was provided by hydrogen chemisorption experiments (Table 2). On the surface of SDB copolymer platinum is present in the form of considerably larger crystallites than those on the surface of active carbon where platinum dispersion is over 8 times higher than on the former catalyst. The volume of irreversibly bound hydrogen, i.e., that which remains on platinum particles after evacuation of catalyst sample at the same temperature at which chemisorption experiment was carried out, and its ratio to reversibly bound hydrogen are considerably higher in the case of Pt/C catalyst (Table 2). Large contribution of hydrogen reversibly adsorbed to the total amount of hydrogen adsorbed on Pt/SDB catalyst can suggest that the surface of this catalyst can be partly covered with carbonaceous species formed from the acetylacetonate precursor of platinum. If there is a relationship between the strength of hydrogen chemisorption and that of substrates of hydrosilylation reactions, then one can suppose that weaker chemisorption observed on Pt/SDB contributes to better performance of copolymer-supported catalyst. However, this is not the only factor influencing catalytic activity for hydrosilylation and this problem will be discussed later.

Table 2
Results of hydrogen chemisorption measurements on catalysts studied.

Catalyst	1%Pt/SDB	1%Pt/C
Platinum dispersion (%)	8.0	67.0
Average crystallite size (nm)	5.0*	1.7
Metallic surface area (m^2/g) sample	0.2	1.7
Total volume of hydrogen adsorbed (cm^3(STP)/g)	0.047	0.385
Volume of irreversibly adsorbed hydrogen (cm^3(STP)/g)	0.006	0.198
Volume of reversibly adsorbed hydrogen (cm^3(STP)/g)	0.041	0.187
Ratio of irreversible hydrogen to reversible hydrogen	0.146	1.059

* Calculated from XRD line broadening.

The performance of SDB-supported platinum catalyst was studied in several hydrosilylation reactions and compared to that of active carbon-supported platinum catalyst. We have chosen Pt/C as a reference catalyst because it found a commercial application and kinetics and mechanism of hydrosilylation of allyl chloride with trichlorosilane were described by Marciniec et al. [13], who deduced kinetic equation derived from catalytic model by assuming quasi-stationary concentrations of adsorbed substrates and desorption of products. In hydrosilylation of allyl chloride, the activity of 1%Pt/SDB during the first two runs was lower than that of the active carbon-supported catalyst of the same metal loading. However, in the next three runs the yield of the reaction main product, i.e., 3-chloropropyltrichlorosilane (CPTS), was maintained on the level of 70% in the case of 1%Pt/SDB catalyst, whereas in that of 1%Pt/C a progressing decrease in the CPTS yield was observed. The activity of 1%Pt/SDB catalyst appeared to be very stable during all five runs and, beginning from the third run, it surpassed that of carbon-supported catalyst (Fig. 6).

Somewhat similar situation was observed in another hydrosilylation reaction proceeding in the liquid phase, i.e., the addition of trichlorosilane to 1-octene yielding octyltrichlorosilane (OTCS). Although in this case the yield of OTCS was initially roughly the same, later the extent of catalyst deactivation, expressed by the reduction in the OTCS yield, appeared to be by 13% greater for 1%Pt/C, which again points to a higher stability of catalytic activity of SDB-supported catalyst (Fig. 7). This arises a question about the origin of gradual deactivation of the catalysts, therefore to

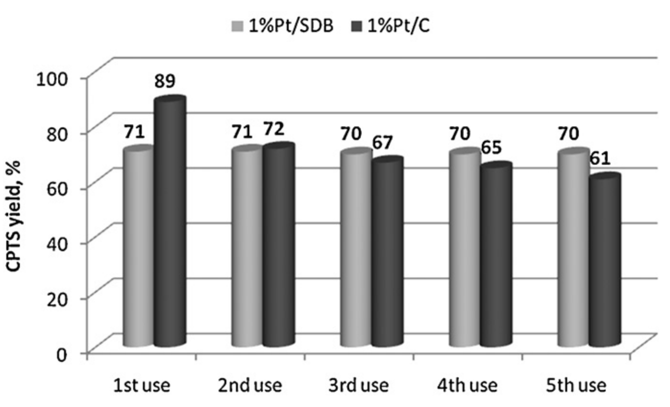

Fig. 6. The effect of repeated use of the same catalysts sample in the reaction of trichlorosilane addition to allyl chloride.

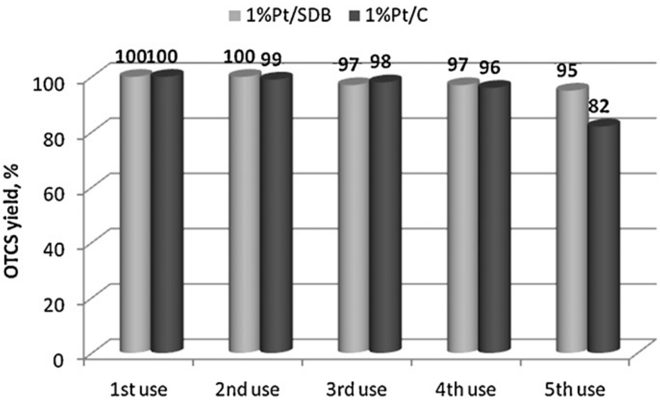

Fig. 7. Results obtained when using the same catalyst sample in subsequent runs of 1-octene hydrosilylation.

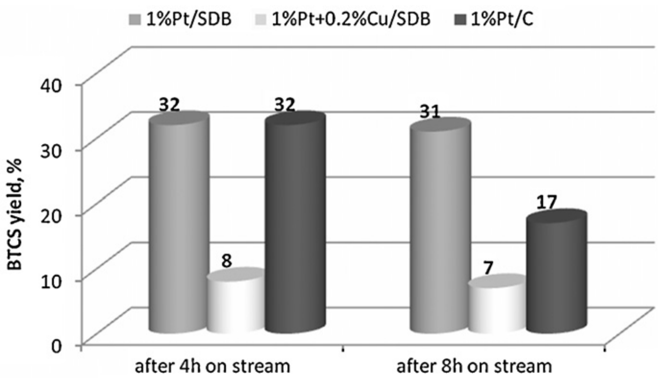

Fig. 8. The effect of time-on-stream on the activity of SDB- and active carbon-supported metallic catalysts for hydrosilylation of 1-butene.

answer it analyses for platinum content in the catalysts after five runs (i.e., after 15 h in the reaction medium) were performed on an inductively coupled plasma optical emission spectrometer. Results of the analyses were quite similar for the both catalysts. Platinum contents in the Pt/SDB catalyst after its use in reactions of trichlorosilane with allyl chloride and 1-octene were 0.78 and 0.77%, respectively, while in the Pt/C catalyst 0.79 and 0.80%, respectively. This means that about one fifth of platinum was leached, which should reflect upon catalytic activity, but in spite of comparable loss of platinum, the effect of the decrease in the activity was greater in the case of active carbon-supported catalyst.

Catalytic performance of Pt/SDB and Pt/C was also compared in hydrosilylation of 1-octene with methyldichlorisilane and dimethylchlorosilane. The yield of the former reaction product, i.e., octylmethyldichlorosilane (octyl-MeSiCl$_2$), carried out in the presence of 1%Pt/SDB, appeared to be almost twice as high as that proceeding in the presence of 1%Pt/C (Table 3). When the second methyl substituent at silicon atom was present in the reaction substrate molecule, the yield of octyldimethylchlorosilane (octyl-Me$_2$SiCl) obtained on polymer-supported catalyst was still high, whereas active carbon-supported catalyst showed no activity (Table 3).

The stability of catalytic activity of SDB-supported Pt catalyst manifested itself even more clearly in hydrosilylation of 1-butene to butyltrichlorosilane (BTCS). It results from Fig. 8 that the above catalyst practically maintained its activity after doubling time-on-stream, while the yield of BTCS on active carbon-supported catalyst decreased almost by a factor of 2 with the extension of time-on-stream from 4 to 8 h. Recent reports on promoting effect of copper and some other metals observed in hydrosilylation of different compounds [14,15] were the reason for including bimetallic platinum–copper catalyst in our study. Unfortunately, 1%Pt–0.2%Cu/SDB catalyst appeared to be considerably less active for the addition of trichlorosilane to 1-butene than monometallic 1%Pt/SDB catalyst (Fig. 8). The difference in the catalytic performance of carbon- and oxide-supported Pt–Cu catalysts [14,15] and SDB-supported Pt–Cu catalyst results probably from already mentioned textural changes occurring in the latter case during reduction at 280 °C. It is also likely that the temperature of 280 °C that appeared to be too high for the stability of SDB porous system was, however, too low to result in the effective interaction between platinum and copper. Therefore, contrary to carbon- and oxide-supported Pt–Cu catalysts [14,15], which were reduced at a considerably higher temperature, no synergistic effect of the two metals was observed.

Table 3
The performance of Pt/SDB and Pt/C catalysts in hydrosilylation of 1-octene with dimethylchlorosilane and methyldichlorosilane.

Catalyst	Octyl-MeSiCl$_2$		Octyl-Me$_2$SiCl	
	Yield (%)	Selectivity (%)	Yield (%)	Selectivity (%)
1%Pt/SDB	89	100	83	100
1%Pt/C	48	100	0	–

60 °C, 3 h, [CH$_2$–CH–]:[HSi]:[cat] = 1.1:1:2 × 10^{-4}.

A comparison of platinum particle sizes (Table 2) with average pore diameter (Table 1) brings to a conclusion that in the case of Pt/SDB platinum is located on external surface of the catalyst (at least to a large extent) which makes the access of reactants to the metal particles easy and in such a case vigorous stirring of reaction mixtures virtually eliminated diffusion limitations. However, in the case of Pt/C, internal diffusion problem does exist and this fact makes Pt/SDB catalyst better from the point of view of practice. A direct comparison between Pt/SDB and Pt/C catalysts and giving one clear reason for the differences observed in their catalytic performance are difficult because a number of factors can influence their catalytic behavior. The crucial one seems to be metal particle size, but such factors as support reactivity (SDB has no functional groups on its surface), its hydrophobicity, textural properties, strength of substrate chemisorption, etc., can play some role as well.

4. Conclusion

Although hydrosilylation can by catalyzed by metals supported on a number of different supports, the preferred support, both in the open and patent literature, was active carbon. Results of this study permit the conclusion that SDB copolymer makes also a very good support material since Pt/SDB catalyst was more active for some hydrosilylation reactions than Pt/C catalyst.

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