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## ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

# Catalytic Features of the Reaction of Oxidative Cross-Coupling of Styrene and Hexene-1

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**Abstract**—The reaction of oxidative cross-coupling of styrene and hexene-1 in the medium of ice acetic acid was studied in the presence of various active phases based on palladium deposited on carbon-containing carrying agents, activated carbon, fullerenes, astralenes, and nanotubes.

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Earlier [1] it has been shown that in the case of oxidative cross-coupling of styrene and hexene-1 in the medium of ice acetic acid at 110°C and pressure 3 MPa in the presence of the $Pd_3Sb/C$ catalyst the full conversion of reagents with the 80% selectivity of 1-phenyl-1,3-octadiene formation can be reached. The choice of the catalyst nature in this case was dictated by a known and exclusive feature of palladium complexes to catalyze cross-coupling reactions [2]. At the same time the application of the catalyst containing the active intermetallic phase $Pd_3Sb$ was caused by sufficient stability and effectiveness of this system in oxidative acetoxylation reactions, which are extremely close in realization conditions to the cross-coupling reactions [3].

Positive results obtained for the cross-coupling reactions on heterogeneous catalysts for the first time have allowed expanding a search for active components of contacts based on palladium. Furthermore, the aim of the work included the study of the effect of the carrying agent nature on the final product yield, as the restriction imposed earlier [4] is caused by the exclusive feature of activated carbon not to inhibit a simultaneously passing acetoxylation reaction. The inhibiting action of other carrying agents was attributed to the capability of contact components to react with $Al_2O_3$, $SiO_2$, etc., which resulted in destruction of redox pairs like Pd-Sb, Pd-Te, Pd-Sn, Rh-Bi, Rh-Ga, and others, and thus catalysts became inactive.

In view of the fact that the work was aimed at the one-reactor performing of two reactions, cross-coupling and acetoxylation, we have also selected various carbon derivatives, supramolecular structures: fullerenes, astralenes, and nanotubes. In this case it was possible to expect a certain modification of properties of contacts, at least due to a more diffusive distribution of an active phase or to the formation of more active endohedral structures [5].

Theoretically interest to modificators of palladium is limited by *p*-elements of the IIIA–VIA groups. The fact of a high activity of palladium–tellurium–tungsten and analogous rhenium compositions for 1,3-butadiene acetoxylation [3] is practically known, therefore in application to the cross-coupling reaction an expanded experimental study is required. To reduce labor-consuming practical work and to choose faster a set of effective catalysts, and also to detect predominant physical factors responsible for successful operation of contacts, we have applied the extrapolation forecasting method [6, 7].

The essence of the method (algorithm of the binary linear qualifier with a zero threshold) consists in searching hyperplanes separating good objects from poor objects in the space of recognition criteria (they can be various physicochemical or structural properties of catalysts). A position of planes in the space of the criteria is established by initial, better experimental, data (training sample). Knowing a position of the separating plane by the criteria of experimentally not studied catalysts, it is possible to determine to which of two classes they refer, i.e. to predict above or below desirable value there will be their expected activity or any other target property.

In the present case it was accepted conventionally on the basis of the experimental data [1] that good catalysts should provide the yield of 1-phenyl-1,3-octadiene higher than 80 wt % under the standard autoclave loading and the 100% raw material conversion. Thus the basic purpose of the forecasting consisted in the determination of such combinations of promoters and compositions of catalysts, for which it is possible to expect simultaneous realization of the both conditions.

As recognition criteria we used theoretically computable characteristics of catalysts [8], which are subdivided into two groups. The first group consists of probabilities of various combinations of atoms on the surface of catalysts calculated by combinatorial formulas. The criteria connected with the electron factor of the contact action and calculated by a quantum-chemical method fall in the second group.

During mathematical handling of experimental data we have selected 8 criteria, the most influential in the solution of the problem on hand, from the system including 16 possible criteria (Table 1).

The planes completely separating catalysts from the training sample into classes by the above-mentioned values of the yield and conversion were found in the space of these criteria.

According to the fulfilled classification, the systematic forecast of binary catalysts containing palladium as an active element has been carried out. For each promoter we determined properties of 50 catalysts containing from 0 up to 100 at% of a platinum group metal with a step of 2 at%.

It follows from the analysis of data for 5000 compositions of catalysts that in the case of palladium contacts it is hardly possible to obtain catalysts meeting the above requirements in the case of promoting by a single element (Fig. 1), as there are no fields of overlapping for compositions satisfying the both criteria: 100% conversion at the yield of a target product greater than 80%.

For each of ternary systems the forecast was carried out for 200 catalysts, which correspond to points of a concentration triangle forming a uniform net (Fig. 2). In the case of ternary compositions fields of a satisfactory overlap of criteria for the Pd–Te–Sb and Pd–Sb–Bi systems were detected. This fact at least points to the absence of a negative influence of tellurium and bismuth on the Pd–Sb phase of the catalyst, which seems to be positive at the following combination of Pd–Sb and Rh–Bi systems at the realization of the cross-coupling and acetoxylation reaction in the same reactor.

**Table 1.** Indexes of significance of the criteria used for classification of catalysts in relation to the 1-phenyl-1,3-octadiene yield

| Criterion | Index of significance, relative units, at the 1-phenyl-1,3-octadiene yield as compared to theoretical, % | | |
|---|---|---|---|
| | 80 | 85 | 90 |
| Fraction of centers with a configuration: | | | |
| $AA_6$[a] | 0.01 | 0.01 | 0.01 |
| $AA_3X_3$ | 0.01 | 0.01 | 0.01 |
| $AX_6$ | 0.01 | 0.01 | 0.01 |
| Fermi level energy | 0.35 | 0.45 | 0.36 |
| Charge on a central atom | 0.30 | 0.35 | 0.41 |
| Energy of adsorption on active centre: | | | |
| carbon | 0.80 | 0.86 | 0.88 |
| oxygen | 0.60 | 0.73 | 0.80 |
| Charge on adsorbed | 0.50 | 0.52 | 0.51 |

[a] Notation $AA_nX_m$ corresponds to a center containing an active metal atom (A) surrounded by the same atoms and by *m* promoter atoms (X).

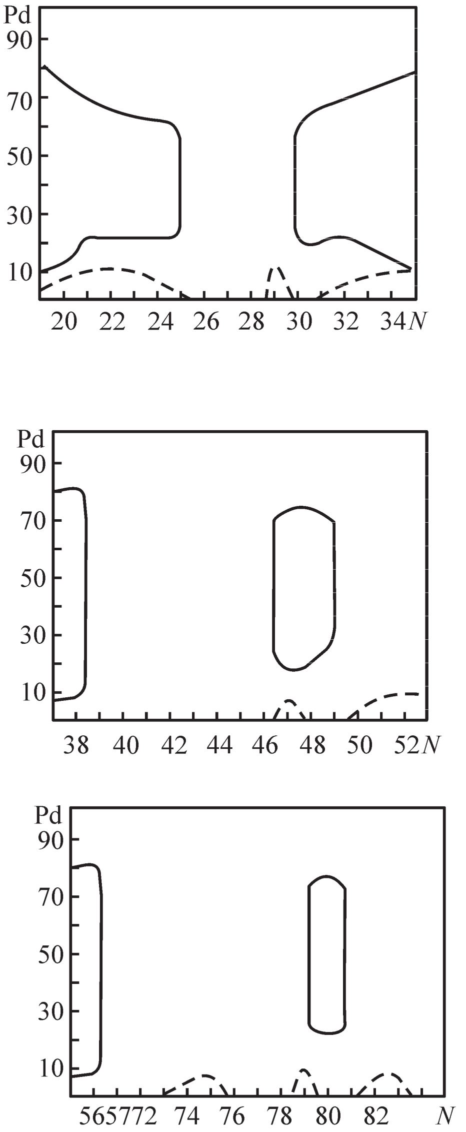

**Fig. 1.** Results of the forecast of catalytic properties of binary catalysts: compositions depending on Pd yield (at. %) are contoured by a shaped line, those on Pd conversion (at. %)- by a solid line. *N* is the number of an element in the periodic system.

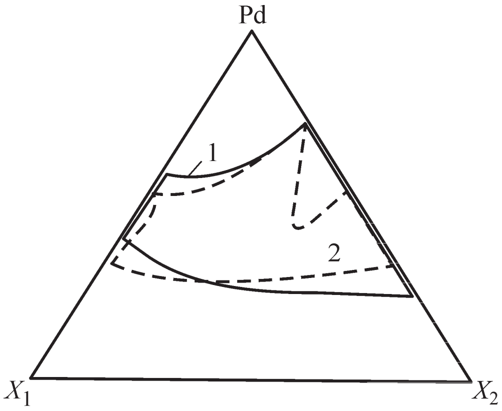

**Fig. 2.** Results of the forecast of catalytic properties of ternary catalysts: (*1*) Pd-Te-Sb, (*2*) Pd-Te-Bi.

The analysis of the mathematical data handling allowed us to obtain information about dominance of indexes of significance of the criteria used for classification of catalysts.

It follows from Table 1 that the criterion of the energy of carbon adsorption on an active center exerts the greatest effect. The energies of oxygen adsorption on an active center, the charge on adsorbed oxygen, and the Fermi level energy are arranged further. A significance of the charge on a central atom agrees with the connection detected earlier [9] between the catalytic activity of a platinum group atom and the effective positive charge on palladium in coupled redox systems.

To check the results of the extrapolation forecast, we have carried out a series of experiments aimed at a con-

**Table 2.** Oxidative cross-coupling of styrene and hexene-1 on palladium catalysts. Temperature 100°C, air pressure 3 MPa, reaction duration 3 h

| Active phase | Yield of 1-phenyl-1,3-octadiene, wt % | Selectivity of 1-phenyl-1,3-octadiene formation, % |
|---|---|---|
| Pd–Sb | 81.0 | 81.0 |
| Pd–Bi | 77.8 | 77.9 |
| Pd–Te | 75.8 | 75.7 |
| Pd–Ge | 80.4 | 80.3 |
| Pd–As | 77.1 | 77.0 |
| Pd–Ga | 74.5 | 74.5 |
| Pd–Tl | 90.0 | 89.9 |
| Pd–In | 76.6 | 76.5 |
| Pd–Sn | 74.7 | 74.6 |
| Pd–Te–Sb | 87.3 | 87.1 |
| Pd–Sb–Bi | 79.4 | 79.3 |
| Pd–Te–Bi | 83.5 | 83.4 |
| Pd–Te–W | 26.0 | 99.0 |
| Pd–Te–Re | 17.4 | 78.3 |

firmation or a refutation of the high efficiency of theoretically predicted ternary compositions, and also some binary compositions, in the cross-coupling of styrene and hexene-1 (Table 2).

An examination of the data of Table 2 allows us to draw the following conclusions. It is possible to reach a higher yield of 1-phenyl-1,3-octadiene in the presence of certain binary compositions than in the presence of the $Pd_3Sb$ system. However, it is difficult to find an explanation to this fact at the present stage of the study, as ordinary correlations, for example, with electronegativity of the second elements, were not observed. We can assume that in this case connection of the catalytic activity and physical properties of elements entering into a composition has a more complicated character, i.e. is multi-parameter. These data agree with the results of the extrapolation forecast with the only exception for the Pd–Tl composition. Apparently, this fact can be explained by an easier electron transfer from thallium on palladium in the redox-process of autoneogenesis of the initial oxidized palladium form in a catalytic cycle. However the capability of thallium to catalyze a cross-coupling reaction in the absence of palladium seems more significant, which should lead at least to the additive effect in the Pd–Tl system. However the check of this supposition is hampered by the stoichiometry of the reaction in the presence of only one of the specified elements. It is curious that $Pb^{4+}$ ions are also capable to catalyze this reaction, which seems to be connected with the well-known lead poisoning of palladium.

The study of ternary compositions (Table 2) gave results, which also agree with the extrapolation forecast data. So, two compositions were found, which exhibit a higher catalytic activity than their separate pairwise combination with palladium atoms. At the same time no special catalytic properties of W and Re was revealed in respect to the cross-coupling despite a similarity of the reaction under study and the acetoxylation (the same coupling reaction) of unsaturated hydrocarbons.

In the following stage of the work it seemed expedient to study the effect of the carrying agent nature on catalytic properties of the above-chosen contact, i.e. to consider a significance of the carbon allotropy. To solve this problem, we have chosen such carrying agents, as astralenes, nanotubes, and fullerene $C_{60}$. The results obtained (Table 3) point to the fact that the nature of carbon allotropy definitely influences activity of cross-coupling catalysts, increasing selectivity of the reaction by 1.4–3.5%. Moreover, the effect is noticeable at the formation of catalysts with the use of astralenes with particles of a polyhedral structure made by flat defect-free graphite surfaces connected by boundary defect fields of preferentially pentagonal structure.

Somewhat greater yield of products of the cross-coupling reaction with such catalysts, apparently, can be explained by a greater specific surface area and, hence, accessibility of contact active centers. Furthermore, preparation of catalysts using supramolecular structures often results in the formation of contacts containing nanostructured active phases, which have either enhanced reactivity or catalytic properties unknown earlier [10].

The study of kinetics of the reaction of styrene and hexene-1 cross-coupling has shown that the reaction order with respect to styrene is zero and with respect to hexene-1 it comes nearer to one. It means that hexene does not participate in a limiting stage of the process. Then, on the basis of common reasons and the published data on arylation of olefins [2], we can generally present the reaction mechanism as follows:

$$\mathrm{Cat} + C_6H_5CH{=}CH_2 \leftrightarrow \mathrm{Cat}(\pi\text{-}C_6H_5CH{=}CH_{2)},$$

$$\mathrm{Cat}(\pi\text{-}C_6H_5CH{=}CH_2) \leftrightarrow \mathrm{Cat}(\sigma\text{-}C_6H_5CH\text{-}CH)^- + H^+,$$

$$\mathrm{Cat}(\sigma\text{-}C_6H_5CH\text{-}CH)^- + 1\text{-}C_6H_{12} \rightarrow \text{products} + H^+,$$

**Table 3.** Effect of the allotropy of carbon-containing carrying agents on $Pd_3Sb$ catalytic properties. Temperature 100°C, air pressure 3 MPa, reaction duration 3 h

| Carrying agent | Yield of 1-phenyl-1,3-octadiene, wt % | Selectivity of 1-phenyl-1,3-octadiene formation, % |
|---|---|---|
| Recuperation activated carbon AR-5 | 81.0 | 81.0 |
| Astralene (stacking of 40-50 graphene sheets) | 82.4 | 82.3 |
| Nanotubes (armchair structure) | 84.5 | 84.3 |
| Fullerene $C_{60}$ | 82.1 | 82.0 |

$$2H^+ + SO_2 \rightarrow H_2O.$$

In the first stage styrene π-coordination is observed, and then hydrogen is replaced to form a σ-organometallic compound. Further a transfer of the styroyl group on hexene-1 occurs probably by the intercalation–detachment mechanism (the last stage is fast). Air oxygen present in the reaction medium binds freed protons (from styrene and olefin) in water, making the reaction irreversible.

The first stage of the mechanism, alternative to the mechanism with the primary olefin coordination, was confirmed by the IR spectrum of the catalyst after its treatment with an equimolar mixture of styrene and hexene-1: absorption bands characteristic of stretching vibrations of *sp*$^3$ hybridized carbon atoms and bending vibrations of a C–H bond in alkenes were absent from the IR spectrum. At the same time absorption bands responsible for stretching (1490 cm$^{-1}$) and bending (695 cm$^{-1}$) vibrations of the C=C group of chemisorbed styrene and ν(C–H) were observed in the IR spectrum at 3010–3025 cm$^{-1}$.

It is assumed [11] that one of coproducts, 1,1'-buta-1,3-dien-1,4-diylbenzene, formed in the reaction course (the product of styrene dimerization) is formed also from the specified organometallic intermediate, however the presence of an alkene in the reaction zone essentially suppresses this reaction.

## EXPERIMENTAL

The $^1$H NMR spectra were recorded on a Bruker-300 device in $CDCl_3$ at a spectrometer working frequency of 300.152 MHz without additional standards with binding frequency to a deuterated solvent signal.

The IR spectra were measured on a UR-20 device in KBr tablets.

Chromatographic analyses were carried on a “Khrom-42” device with a flame ionization detector and a glass column 2.5 m × 3 mm with an attachment filled by 3.5% OV-225 on varaport-30 (100-120 mesh). Gas carrier was nitrogen (30 cm$^3$ min$^{-1}$), temperature raise from 70 up to 230°C according to the program 3 deg min$^{-1}$, temperature of an evaporator 300°C.

Reactions of oxidative cross-coupling and acetoxylation were normally carried out in a periodic mode in a stainless steel autoclave. Into a glass of 0.05 l capacity 30 ml of ice acetic acid, 0.8–0.9 g of a powdery catalyst, and a rated amount of reagents were loaded; the autoclave was sealed hermetically, electric heating was switched on, and after reaching a desired temperature air was fanned up to necessary pressure, stirring was switched on, and the experiment was carried out, as a rule, up to exhaustion of reagents (chromatographic monitoring).

Spectral characteristics of the mixture of geometrical isomers of (*Z,E*)-1-phenyl-1,3-octadiene correspond to the data of [12]: IR spectrum (in a thin layer), cm$^{-1}$: 1640, 1595, 1490, 985. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 t (3H, *J* 7.1), 1.25–1.45 m (4H), 2.05–2.20 m (2H), 5.87 d.t (1H, *J* 7.1, 15, PhC=C–C=CH), 6.21 d.t (1H, *J* 11.2, 11.6, PhC=CH), 6.30 d (1H, *J* 11.6, PhCH=C), 6.60 d.d (1H, *J* 11.2, 15, PhC=C–CH=C), 7.15–7.40 m (5H, arom).

**Table 4.** Main technical characteristics of supramolecular carrying agents

| Parameter | Astralenes | Nanotubes | Fullerene $C_{60}$ |
|---|---|---|---|
| Carbon content, no less than, % | 99.99 | 99.99 | 99.99 |
| Density, g cm$^{-3}$: | | | |
| bulk | 0.6–0.8 | 0.6–0.8 | 0.6–0.8 |
| true | 2.2 | 2.0–2.1 | – |
| Average size, nm: | | | |
| particles | 80–150 | 20–3000 | 10–20 |
| pores | 20–60 | 2–4 | – |
| Extent of graphitization, no more than | 0.2 | 0.02 | 0.02 |
| Thermobaric stability (3000°C), no less than, kbar | 50 | – | – |
| Interlayer distance, nm | 0.342 | 0.342 | – |
| Sorption with respect to $CCl_4$, no less than, mg g$^{-1}$ | 50 | 200 | – |
| Electrical resistance (at 120 Pa), no more than, Ω m | $2.5 \cdot 10^{-4}$ | $1.5 \cdot 10^{-4}$ | $2 \cdot 10^{-4}$ |
| Current density of cold emission (1000 V m$^{-2}$), no less than, mA cm$^{-2}$ | 1 | 10 | – |

Catalysts were prepared by a pretreatment of 10 g of AR-5 activated recovery carbon or other carbon-containing materials with a 15% nitric acid aqueous solution, evaporating the mixture on a water bath up to disappearance of a liquid phase. A rated amount of components of the contact in the form of nitrates, chlorides, or oxides was dissolved in a mixture of 30 ml of water, 45 ml of nitric acid, and 25 ml of hydrochloric acid, and then resulting solution was poured out on 10 g of the carrying agent and evaporated to dryness. The prepared catalyst was calcinated in a reactor at 150°C for 1–1.5 h, then temperature was increased up to 200°C, a hydrogen current was blown in (10–20 $l\ h^{-1}$), and the reduction was carried out at 500–550°C within 1 h; the reactor was cooled under the presence of a reducing agent.

Carbon-containing carrying agents corresponded to the characteristics given in Table 4.

## CONCLUSIONS

(1) The extrapolation forecast by the pattern recognition method has shown that it is hardly to select a more effective catalyst than $Pd_3Sb$ among binary compositions of the type palladium-metals of the periodic system with atomic numbers from 22 up to 80. On the contrary, among ternary compositions systems with additionally introduced tellurium can be more active phases.

(2) The study of the effect of carbon allotropy on catalytic properties of contacts has shown that astralene (stacking of 40–50 graphene sheets), nanotubes (armchair structure), and fullerene $C_{60}$ are more effective carrying agents than activated carbon.

(3) It was shown that chemisorption of styrene, but not of alkene, takes place in the primary chemical act. On this basis a preferable mechanism of the oxidative cross-coupling reaction was proposed.

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