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CHEMICAL KINETICS
AND CATALYSIS

The Heterogeneous Catalytic Heck Reaction in an Ionic Liquid

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Abstract—The C–C cross coupling reaction between bromobenzene and styrene in the presence of Pd deposited on mesoporous acetylene soot (Pd/C) occurred in a tetraalkylammonium ionic liquid (IL) as a truly heterogeneous catalytic process. The active palladium form was not transferred into the reaction solution. Deposited palladium activation was observed when the Pd/C catalyst was preliminarily heated in the IL in the presence of dibutylamine as a base.

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INTRODUCTION

The arylation of unsaturated compounds with haloaryles by C–C cross coupling (the Heck reaction) is basic to many practically important processes of fine organic synthesis, such as the preparation of biologically active substances, vitamins, and pharmaceuticals. Palladium salts or complexes in homogeneous media are largely used as reaction catalysts. The greatest progress was achieved thanks to the use of phosphine ligands, which stabilized palladium-based catalytic systems.

The high cost of palladium phosphine complexes and the impossibility of their regeneration, however, restrain wide use of the Heck reaction on an industrial scale. At the same time, its exceptional attractiveness as a labile and multipurpose tool for chemical syntheses stimulates intense search for alternatives to homogeneous catalysts. One of such alternatives is the use of deposited Pd catalysts, which sometimes accelerate the Heck reaction no less effectively than homogeneous systems [1], but are much more efficient technologically, because they allow catalysts to be easily separated from reaction products.

As was mentioned in review [2], the mechanism of the Heck reaction in phosphine-free systems, such as heterogeneous catalytic Pd-containing systems, is such that the reaction can only occur in polar solvents of the type of dimethylformamide, N-methylpyrrolidone, etc. At the same time, these and similar traditional molecular solvents do not meet modern requirements of "green chemistry." They are mostly toxic, and their regeneration is energy-consuming and requires more expenditures than their production [3]. In this respect, ionic liquids (ILs) have obvious advantages. Ionic liquids are organic salts with melting points below 100°C and, which is of fundamental importance, zero vapor pressure up to the decomposition temperature (400–500°C). When heterogeneous catalytic reactions are performed in ILs, reaction products are fairly easily isolated from the reaction mixture by extraction, and, if it is necessary to separate a solid catalyst, by simple filtration. All these advantages allow ILs to be considered "green" solvents with a fairly broad spectrum of applications in organic syntheses [4]. Lastly, the number of chemical reactions that can be performed in ILs is much larger than that in perfluorocarbons, which are close to ILs in their ecological characteristics, and supercritical fluids [5].

However, note that, in spite of obvious advantages of ionic solvents for heterogeneous catalytic arylation of unsaturated compounds according to the Heck reaction, the number of works on the problem is very small compared with those concerned with the homogeneous catalysis of this reaction. The reason for this is twofold. On the one hand, the physical and physicochemical properties of ILs and, as a consequence, the reactivity of substrates and catalysts dissolved in them depend substantially on the composition and structure of their cationic and anionic components. The selection of various combinations of cations and anions, whose number is at present several hundreds and increases rapidly [5], allows ILs with the required solvent characteristics, including melting point, polarity, product and reagent solubilities, etc., to be designed to answer the requirements of particular chemical problems.

On the other hand, the high sensitivity of the Heck reaction to the properties of the medium requires catalytic systems, such as ILs, to be constructed carefully in each particular case [2]. For instance, C–C cross coupling in the presence of deposited Pd occurs in the tetrabutylammonium IL at a high rate, whereas the reaction does not occur at all in the IL based on imidazole [6]. With such a large number of factors influencing the process, we can hardly predict the response of the system to changes in internal and external parameters, which makes the solution to the problem "the Heck reaction in an ionic liquid" highly unstable even when parameter variations are small.

The purpose of this work was to solve a comparatively narrow problem. We wished to determine the special features of C–C cross coupling between bromobenzene and styrene in the presence of nanodisperse Pd deposited on a carbon carrier (mesoporous hydrophilized soot) in a tetraalkylammonium IL, tributylhexylammonium *bis*-triflylamide, as a solvent.

EXPERIMENTAL

The Preparation of Tributylhexylammonium bis-Triflylamide

Tributylhexylammonium *bis*-triflylamide [Bu_3HexN][NTf_2], where NTf_2 is the anion of the composition $(CF_3SO_2)_2N^-$, was selected as a solvent for the Heck reaction because of an optimum combination of its characteristics, namely, a low melting point (+19°C), high solubility of the initial reagents (bromobenzene and styrene) and bases (di- and tributylamine), moderate solubility of the main (stilbene) and side (biphenyl) products, and immiscibility with hydrocarbons (cyclohexane and *n*-decane) and water. In addition, the viscosity of this IL, fairly high at room temperature, which substantially complicates filtration, can be decreased substantially by the addition of small amounts of acetone.

[Bu_3HexN][NTf_2] was synthesized as follows. Tributylamine dried over sodium metal and distilled at a reduced pressure (75–77°C, 3 torr) was quaternized with hexyl bromide (a 20% excess) in boiling acetonitrile for 18 h. After reaction termination, the solvent was distilled off at a reduced pressure, and the residue was two times washed with hexane to remove unreacted hexyl bromide; traces of organic solvents were removed by heating to 80°C at 3 torr.

Tributylhexylamine obtained this way (30 g) was dissolved in distilled water (100 g). A stoichiometric amount of lithium triflylamide was added to the solution. An oily layer of the "raw" IL immediately formed at the bottom of the reaction vessel. This layer was separated from the solution, washed with a 0.5% solution of lithium triflylamide and two times with distilled water. The IL obtained, tributylhexylammonium *bis*-triflylamide, was dried by heating at 2–3 torr until gas release ceased.

The Preparation of Palladium Deposited on a Carbon Carrier

The initial material for the preparation of a mesoporous carbon carrier was acetylene soot AS100. To hydrophilize its surface, it was treated with a mixture of H_2SO_4 and HNO_3 at 90°C. Such a modified carrier with a specific surface area of 260 m^2/g consisted of mechanically strong fractal agglomerates whose mean size was 0.5 μm. The agglomerates were in turn formed from primary nanoparticles with a size of about 30 nm. The surface of the carrier was amorphous carbon with inclusions of structurally ordered graphite-like domains.

Pd/C catalysts were prepared by the reduction of Pd(II) hydroxide preliminarily deposited on the surface of the carrier from an alkaline solution under ultrasonic stimulation conditions. AS100 soot (1.0 g), water (28 ml), and $NaHCO_3$ (227 mg) were loaded into a flask placed in an ultrasonic water bath. The mixture was heated at 80°C for 40 min under intense stirring with ultrasonic stimulation. Next, Na_2PdCl_4 (0.510 mmol) and water (22 ml) were added to the hot suspension during 2 min, the mixture was heated for 1.5 h more, and an aqueous solution of formaldehyde was added to it. The mixture was heated for 1 h under ultrasonic stimulation conditions and for 30 min with ultrasound switched off. The product was then filtered, washed on a filter six times with 15 ml portions of demineralized water and once with doubly distilled water, dried in a vacuum (12 torr) at 80°C, and then heated in a vacuum (10^{-3} torr) at 250°C for two hours. The content of palladium in the Pd/C catalyst sample was 5 wt %.

Procedures for Physicochemical Studies

The content of palladium in the samples was determined by X-ray spectral fluorescence analysis on a Carl Zeiss Jena VRA-30 spectrometer. The characteristics of the structure of the carbon carrier and metal nanoparticles incorporated into it were obtained by electron diffraction on an EMR-102 instrument at an accelerating voltage of 75 keV. The specific surface area and the volume of pores and their mean size were determined using low-temperature adsorption of nitrogen according to Brunauer, Emmett, and Teller on a Micrometritics ASAP 2000N sorption meter. The morphology of deposited palladium metal particles was controlled by high-resolution transmission electron microscopy on a Tecani G2 30 S-TWIN microscope at an accelerating voltage of 300 keV and by small-angle X-ray scattering on AMUR-K and HECUS System-3 units.

Catalytic Experiments

The reaction of bromobenzene with styrene was performed in a static system at 140°C and atmospheric pressure. Unless otherwise stated, experiments were performed as follows. IL (10 ml), bromobenzene (10 mmol), styrene (15 mmol), base (sodium acetate or dibutyl- or tributylamine) (20 mmol), and Pd/C catalyst in the amount corresponding to 0.03–0.4 mol % Pd based on initial bromobenzene were placed into a Schlenck flask. A flow of dry argon was bubbled through the mixture for 15 min. The reactor was then closed and immersed into an oil bath preliminarily heated to 140°C, while the mixture was vigorously stirred. Samples (1 ml) were periodically taken for analyses from the reaction mixture containing unreacted initial substances and reaction products.

Chromatographic and NMR Spectral Analyses

The reaction mixture was analyzed by gas-liquid chromatography. A sample was extracted with cyclohexane containing 1 vol % *n*-decane as an internal reference, and the filtrate was analyzed. Analyses were performed on a CHROM-5 chromatograph equipped with a katharometer and a 2 m metallic column 3 mm in diameter packed with Chromaton N-Super (0.6–1.2 mm) with 3 wt % SP-2000 phase under the conditions of two-step temperature programming, from 100 to 150°C (heating rate 10 K/min) and from 150 to 250°C (heating rate 12 K/min). The instrument was calibrated against solutions of bromobenzene, styrene, biphenyl, and stilbene in cyclohexane with an internal reference.

The degree of initial reagent (bromobenzene and styrene) conversions was determined by comparing their contents in the initial mixture and in the samples taken during the catalytic reaction. The yields of reaction products, stilbene and diphenyl, were calculated as ratios between their contents in the samples and the theoretically possible amount equivalent to the content of bromobenzene in the initial mixture.

The reaction mixture was analyzed for palladium by the MALDI-TOF method. ^{1}H NMR spectra were used to qualitatively analyze the initial and regenerated IL; the spectra were recorded on an MSL-400 Bruker instrument at a 400.13 MHz frequency.

RESULTS AND DISCUSSION

The Morphology of Pd Metal in Carbon Carrier Mesopores

According to the transmission electron microscopy and small-angle X-ray scattering data, reduced palladium in the samples 0.5% Pd/C, 5% Pd/C, an 20% Pd/C formed nanosized crystals with the unit cell parameter 0.389 nm, which corresponded to massive Pd metal. The mean size of Pd particles in all the three samples was ~4–5 nm, and the size of 90% of metal particles did not exceed 10 nm. Note that the metal particle size and carrier pore diameter distribution curves were closely similar, which was evidence that Pd nanocrystals predominantly formed within carbon carrier mesopores.

Such a sterically hindered formation of the active metal phase determines its nanostructured character on the one hand and, on the other, makes the whole volume of mesopores accessible to not very large catalytic reaction substrates. This allows carbon carrier mesopores with ultradisperse palladium metal particles in them to be treated as peculiar nanoreactors functionally similar to stabilized Pd metal sols catalyzing the Heck reaction [7].

The Kinetics of the Heck Reaction between Bromobenzene and Styrene

The kinetic curves shown in Fig. 1 are the experimental dependences of the conversion of bromobenzene and the yields of stilbene and biphenyl on reaction duration obtained for various initial reaction mixture compositions and various experimental conditions. First note that the use of sodium acetate (NaOAc) and tributylamine (Bu_3N) as reagents binding HBr in the IL gives closely similar results (Figs. 1a and 1b). These bases only differ in the yields of the side product. In the presence of NaOAc, biphenyl is formed in very small amounts, within errors in gas-liquid chromatography measurements.

Conversely, when we pass from tributylamine to less basic dibutylamine (Bu_2NH), the kinetics of the reaction changes substantially (Fig. 1c). The reaction turnover frequency increases more than twofold, and the number of reaction turnovers during 10 h also increases two times. It follows that the effectiveness of binding hydrogen bromide does not depend on reagent basicity; that is, it is determined by the kinetic rather than thermodynamic factor. At the same time, these results are substantially different from those obtained by Köhler et al. [8]. In that work, the Heck reaction was performed in molecular solvents (N-methylpyrrolidone and N,N-dimethylacetamide), and the number of reaction turnovers for Pd deposited on activated carbon was 3 times larger in the presence of NaOAc than in the presence of Bu_3N as a base.

Such discrepant results can hardly be explained by differences in the properties of the carbon carriers, acetylene soot in this work and activated carbon in [8]. To interpret these results, it must be borne in mind that the reaction system was heterophase in both experiments. It consisted of the liquid phase containing dissolved reagents and products and the solid with the catalytically active component immobilized in its narrow pores.

As distinct from molecular liquids, ionic liquids are characterized by the presence of nanosized structured regions, which has very serious consequences for diffusion processes in these media. Moreover, it was shown in [9] that polar and nonpolar domains were structurally separated in nanostructured regions of ILs with nonsymmetric alkyl substituents. As a consequence, ILs show dual behavior, they behave as low-polarity media with respect to nonpolar molecules, whereas the transport of polar and ionic particles of similar sizes is sub-

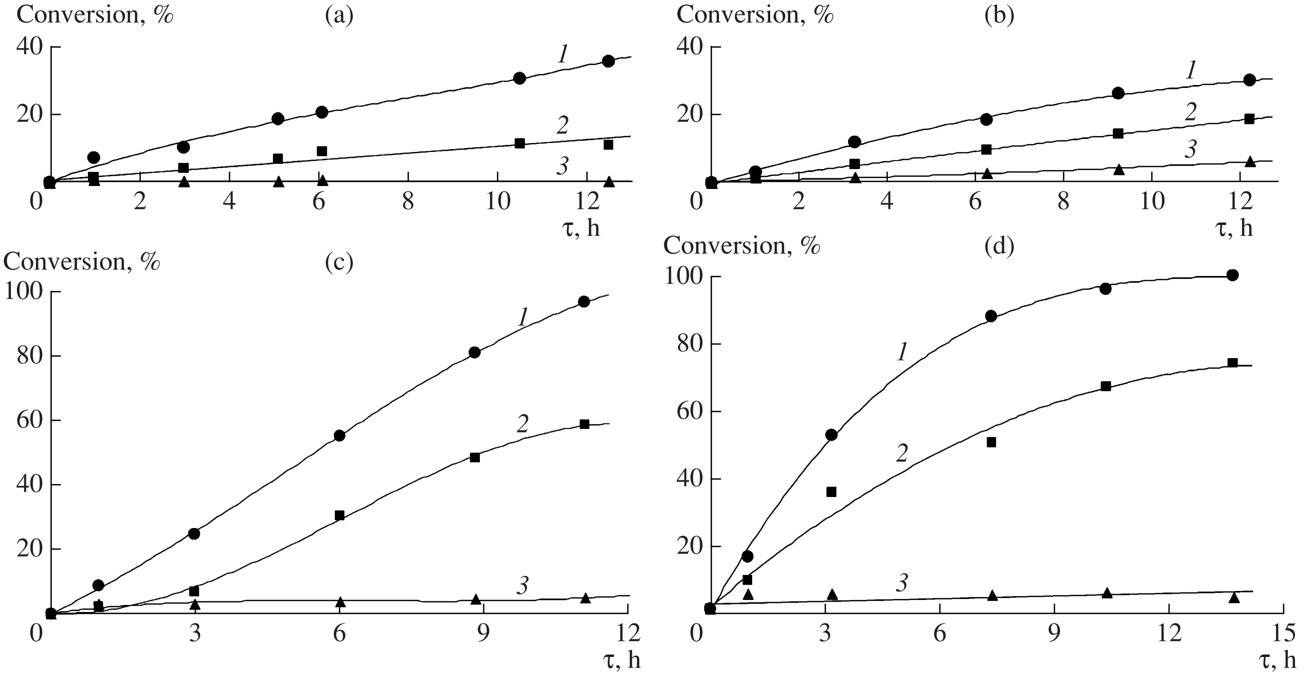

Fig. 1. Dependences of (*1*) bromobenzene conversion, (*2*) stilbene yield, and (*3*) biphenyl yield on reaction duration. Reaction conditions: 0.1 mol % Pd, base (a) sodium acetate, (b) tributylamine, (c) dibutylamine, and (d) dibutylamine with preliminary catalyst activation in the IL in the presence of dibutylamine.

stantially decelerated in them. This is likely the main factor in the kinetics of liquid-phase heterogeneous catalysis in ionic solvents. Indeed, the viscosity of ionic liquids is 1–2 orders of magnitude larger than that of molecular liquids. Accordingly, the effective diffusion coefficients of dissolved molecules are 1–2 orders of magnitude smaller in them. For this reason, when a liquid-phase heterogeneous catalytic reaction is performed in an ionic solvent, it is quite possible that the diffusion transfer of reagents and products in catalyst pores filled by the IL rather than chemical transformation becomes the limiting reaction stage.

Clearly, a key question is that of whether the reaction occurs on the surface of the catalyst by the classic heterogeneous catalysis scheme or it is quasi-homogeneous, that is, occurs in the volume of the solvent. This question has repeatedly been discussed in the literature, but no unambiguous answer to it was given [1]. Moreover, the experimental data obtained for different heterogeneous catalysts and different solvents are fairly discrepant. For instance, it was convincingly shown in [8] that the rate of the Heck reaction in molecular solvents was determined by the concentration of active Pd-containing particles in the liquid phase; these particles were formed in the interaction of initial aryl halide with deposited palladium and were transferred into solution but again became deposited on the surface of the carrier after reaction termination. In other words, the solid Pd/C catalyst in this reaction is only a source of palladium, but is inactive itself.

It was shown in [10] that the imidazole IL as a medium for performing the Heck reaction in the presence of palladium deposited on SiO_2 caused the transfer into solution of larger amounts of active Pd compared with molecular dimethylformamide. Accordingly, this increased the rate of the reaction. At the same time, when similar heterogeneous catalysts such as Pd/C, Pd/SiO_2, Pd/Al_2O_3, and Pd/$Mg(OH)_2 \cdot Al(OH)_3$ and the tetrabutylammonium IL are used, palladium is transferred into the liquid phase in small amounts, and such solubilized palladium does not catalyze the Heck reaction [11]. Clearly, the heterogeneous or homogeneous character of the Heck reaction is determined in each particular case by the mechanism and conditions of deposited Pd activation. The generally accepted activation mechanism includes the oxidative addition of aryl halide to Pd(0) with the formation of a soluble form of Pd(II). The interaction of palladium with this reagent is considered the only method for Pd activation, whereas other reaction mixture components, that is, the polar solvent and the base, are assumed to play a secondary role of stabilizing agents [8, 12].

The results obtained in this work, however, show that the nature of the IL solvent substantially influences the activation of the Pd/C catalyst of the Heck reaction. The kinetic curves shown in Figs. 1c and 1d were obtained using two different regimes for performing the process. In the first case (Fig. 1c), the reaction was performed by the introduction of all reaction mixture components into the tetraalkylammonium IL solvent, including bromobenzene, styrene, dibutylamine, and the Pd/C catalyst. The kinetic curves obtained in this experiment are not typical of heterogeneous catalytic reactions. They contain a distinct inflection point, and the rate of the reaction shows no tendency to decrease even at deep reagent transformation degrees and almost coincides with the initial reaction rate. Such a shape of kinetic curves is obvious evidence of reaction acceleration with time, that is, of catalytic component activation in interactions with the reaction medium.

In the second experiment (Fig. 1d), the Pd/C catalyst was heated at 140°C for several hours in the IL solvent in the presence of only Bu_2NH. After this, bromobenzene and styrene were introduced and the reaction was performed in the usual way. After such a preliminary activation in the presence of amine, the initial rate increased more than twofold, the kinetic curves did not contain inflection points, and the effectiveness of the catalytically active particle was constant as follows from the shape of the kinetic curves. Note that the effect of preliminary activation in the presence of Bu_2NH is the stronger the larger the excess of amine over palladium. In a control experiment, when the Pd/C catalyst was preliminarily heated in the IL in the absence of amine, no activation of the catalytic system was observed.

The activation effect is fully retained when the reaction is repeatedly performed in the same reaction system, even without the removal of reaction products from it. This is of importance for the understanding of the mechanism of Pd/C catalyst activation in the IL. After a 100% conversion of bromobenzene (see Fig. 1d), standard amounts of bromobenzene, styrene, and dibutylamine were again introduced into the system, and the reaction began in the second cycle at the same rate as in the first one.

An additional argument in favor of the suggestion made above according to which both the activation of palladium and the chemical reaction proper in the tetraalkylammonium IL, as distinct from molecular solvents and the imidazole IL, occurred in catalyst mesopores rather than in solution volume is the following observation. The Heck reaction did not occur in the IL in which Bu_2NH and the Pd/C catalyst were heated at 140°C and from which the catalyst was removed by filtration; that is, no Pd-containing particles were present in the filtrate, which was also substantiated by its mass spectrometric analysis. These data do not rule out the possibility of the activation of deposited palladium by the oxidative addition of aryl halide to it, but this reaction in the tetraalkylammonium IL requires the presence of the amine component. At the same time, the occurrence of the Heck reaction, at least in the system studied in this work, inside catalyst pores is obvious.

CONCLUSIONS

To summarize, the experimental results obtained in this work are evidence in favor of the truly heterogeneous mechanism of the Heck reaction between bromobenzene and styrene catalyzed by palladium deposited on mesoporous soot. The presence of amine in the IL at the stage of the preliminary activation of the Pd/C catalyst is a necessary condition for creating a stationary concentration of active centers on which the Heck reaction occurs. At the same time, the question of the sequence in which the oxidative addition of aryl halide to palladium and amine ligand addition to the complex formed take place requires additional studies.

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