Synthesis of palladium catalysts for cross-coupling reactions using porous amorphous aromatic polymers as supports

Bakhvalova Elena Sergeevna

Relevance of the research. It is known that the properties of heterogeneous catalysts depend on the composition and structure of active centers, but the nature and structure of the support are also important. Recently, different polymers have been developed that can act as supports of catalytic systems. Despite, their diversity, the issue of increasing the activity and stability of polymer-based catalysts for Pd-catalyzed cross-coupling reactions is still open. The advantage of polymer supports is the possibility of their design for the features of a specific reaction.

The aim of the work is to develop palladium catalytic systems using amorphous porous polymers and to study the transformation of the Pd-containing phase during the cross-coupling reaction depending on the functional groups in the support composition.

Research objectives:

1. obtaining and characterization experimental samples of porous amorphous aromatic polymers by one-stage synthesis of non-functionalized monomers, as well as monomers containing functional groups and heteroatoms, and their combinations at varyiation of the solvent nature, the amount of polymerization catalyst and cross-linking agent;
2. synthesis of Pd-containing catalysts using the obtained porous aromatic polymers as supports and study of the effect of introducing functional groups into the polymer samples on the distribution of the metal catalyst in the polymer matrix;
3. testing the synthesized polymer samples containing Pd^{II}, as well as Pd^{0} nanoparticles (NPs), in Suzuki, Sonogashira and Heck cross-coupling reactions and study of the stability of the selected catalyst samples;
4. study of the effect of the conditions of the Suzuki cross-coupling reaction (stirring rate and temperature) on the activity of Pd-containing catalysts;
5. carrying out the Suzuki cross-coupling reaction under conditions of competing substrates with different types of substituents to identify peculiarities of the catalytic process.

Scientific novelty of the work:

- using a single-stage cross-linking by the Friedel-Crafts reaction, porous amorphous aromatic polymers were synthesized; the influence of the nature of monomers and their combinations, the amount of polymerization catalyst and the amount of cross-linking agent on the properties of the obtained samples was also studied;
- nitration and sulfonation of naphthalene-based polymers was carried out in order to synthesize polymer matrices containing functional groups. Data were obtained on the

influence of functional groups on the porosity of polymers, wettability with selected solvents, stability, and distribution of palladium in the polymer matrix;

- data were obtained on the activity and stability of new samples of Pd-containing polymer-based catalytic systems in Suzuki, Sonogashira and Heck cross-coupling reactions;

- for the Suzuki and Sonogashira reactions, the dependence of the activity of catalytic systems on the size of Pd NPs formed during the reduction process was revealed. It was established for the first time that the activity passes through a maximum corresponding to the mean NPs diameter of 10 nm;

- the Suzuki cross-coupling reaction was studied under conditions of competing substrates with different types of substituent in the presence of ligand-free catalysts based on palladium acetate or Pd^0 NPs stabilized in the "pores" of a sulfonated amorphous aromatic polymer based on naphthalene. It was found that 4-bromoanisole and 4-iodoanisole in the presence of the reduced catalyst accelerate each other without changing the cross-coupling mechanism, and 4-bromonitrobenzene in combination with 4-bromoanisole after a short acceleration at the beginning of the reaction leads to a complete stop of the conversion of 4-bromoanisole. The stop of the conversion of 4-bromoanisole can be prevented by adding sodium salts, which probably accelerate the transmetallation stage.

The practical significance of the work. The proposed method for preparing catalytic systems using amorphous porous polymer supports can find application not only for cross-coupling reactions, but also for other processes.

Thesis to be defended:

- approach to creating Pd-containing catalytic systems for cross-coupling reactions using porous amorphous aromatic polymers;

- data on the effect of synthesis conditions on the properties of polymers obtained by single-stage cross-linking via the Friedel-Crafts reaction;

- data on the behavior of the obtained palladium ligand-free catalysts in model cross-coupling reactions of Suzuki, Sonogashira, and Heck;

- patterns of transformation of the Pd-containing phase during preliminary treatment of catalytic systems, as well as during cross-coupling reactions depending on the synthesis conditions of the supports: the nature of the monomers and the presence of functional groups.