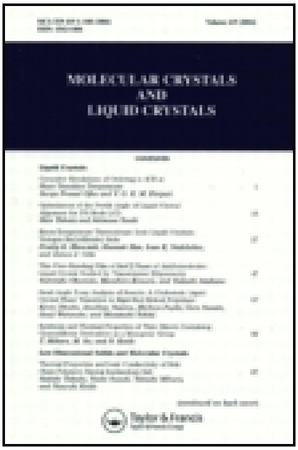

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METAL-GRAPHITE INTERCALATION COMPOUNDS AS NEW DEHYDROGENATION CATALYSTS

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Abstract The Pb-GICs and K-Bi-GICs as new catalysts for the reaction of oxidative dehydrogenation of ethylbenzene have been studied. The reaction occurred on Pb-graphite with 36.5% selectivity to styrene and 62.5% conversion (at 720°C and the feed: ethylbenzene - 3 g/h, water - 15 g/h and air - 6 dm^3/h). The exploratory results of the application of K-Bi-GICs at 600°C were: selectivity to styrene of 58.4% with conversion of 32.2% (ethylbenzene - 2.8 g/h, nitrogen - 0.8 dm^3/h, air - 1.7 dm^3/h).

INTRODUCTION

The industrial production of styrene is based on the catalytic equilibrium dehydrogenation of ethylbenzene in gaseous phase, in endothermic reaction (-120 kJ/mol)[1]. Several other methods of styrene synthesis were elaborated. Many of them involve an oxidative dehydrogenation of etylbenzene, in particular with the use of atmospheric oxygen[2]. Using oxygen in the reaction changes the energetic effect of dehydrogenation to exothermic (+142 kJ/mol).

The typical catalysts of the reaction of oxidative dehydrogenation of alkyloaromatics to vinyl monomers are based on metal oxides. The group of oxide catalysts is composed of a wide range of metal oxides deposited on various typical substrates, often together with alkaline metal oxides or rare earth oxides.

Beside the compound metal oxides, a separate group of catalysts for this reaction is: aluminium oxide modified in various ways, aluminium silicates, metal phosphates of IIA, IIIA, VA and VIIIA group. During the reaction, carbon deposits are formed on these catalysts. The deposits are the oxygenic products of further conversion of styrene. In this reaction, catalytic abilities are assigned to these deposits[3], having well developed specific surface.

The catalytic activity of condensed aromatic binders (such as organic redox systems with a quinone group) in the oxidative dehydrogenation reactions is known[4].

Electron interaction like metal oxides can be generated in graphite intercalation compounds. Graphite shows amphoteric character and its electron interaction with various metals has been proved[5]. It is known that EDA compounds exhibit activity in several reactions[6]. There are many applications of metal-GICs as catalysts for various reactions[7].

The analysis induced investigations of the catalytic properties of graphite intercalated by metals in the reaction of oxidative dehydrogenation of ethylbenzene. In this study the Pb-GICs and K-Bi-GICs as new catalysts of the reaction have been used.

EXPERIMENTAL

Reactor

The investigations of the reaction of oxidative dehydrogenation of ethylbenzene were performed in continuous flow quartz reactor of internal diameter 24 mm and length of 330 mm with a central thermocouple well. The schematic sketch of the apparatus is presented in Figure 1.

A sample of the catalyst was placed in the lower part of the reactor. An electrical jacket with automatic temperature control was used to heat the reactor. The temperature of the catalyst was controlled by a thermocouple placed in a tube situated centrally in the reactor. Air, ethylbenzene and nitrogen or water were introduced in the upper part (filled with quartz grains) of the reactor which served as evaporator and mixer for the reagents. After passage through the catalyst layer, the products were cooled and liquid components were separated from the gases in a separator.

Activity tests were performed at atmospheric pressure. Air was used as a source of oxygen.

Analysis of the reaction products

The reaction products were analyzed by gas chromatography. The analysis of hydrocarbons was performed with a GCHF 18.3 chromatograph with thermal conductivity detector and 1 m-long column with dimethyl glycol adipate +3% H_3PO_4 deposited (20%) on Chromosorb W. The last 2 cm of the column

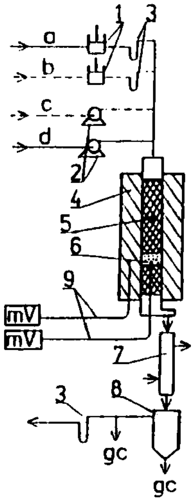

FIGURE 1. Schematic diagram of the experimental apparatus. a-air; b-nitrogen; c-water; d-ethylbenzene; 1-membrane pump; 2-micro-dose pump; 3-flow meter; 4-electrical heater; 5-evaporator and mixer; 6-reactor; 7-cooler; 8-separator; 9-temperature control; gc-gas chromatograph

were filled with molecular sieve 5A. Temperature of the column was programmed to 80° and 120°C (for removal of water). Hydrogen was the carrier gas.

The CO and CO_2 content of the output gas was determined in a N-502 chromatograph with thermal conductivity detector and 9.5 m-long column with dimethylsulpholane deposited on Sterchamol to the amount of 28%, and a second column, 1 m-long with the molecular sieve 13X. The temperature of the columns was 25°C; the carrier gas was hydrogen.

Catalyst

A sample of Pb-graphite was prepared by heating natural (Sri Lanka) powdered graphite (platelets of size: 1-20 μm by 30-100 μm) mixed under nitrogen atmosphere with shavings of metallic lead (pure for analysis). Heating was carried out in a steel reactor heated at a temperature of ca. 700°C for 336 hours. After completing the reaction, unreacted lead was separated using a steel sieve of mesh 70-140 (100-200 μm). The sample was then rinsed with concentrated nitric acid.

For the preparation of K-Bi-GICs the following procedure was used[8]. A binary K-Bi alloy was prepared by reaction of metallic potassium with metallic bismuth at 320°C for 72 h in a Pyrex ampoule filled with nitrogen. Powdered Sri Lanka graphite was then added and the temperature raised to 380°C was applied for 264 h.

Catalyst crumbs were made by pressing the powder with a hydraulic press at 6 MPa. The solid was lightly crushed and separated using a steel sieve.

The Pb-graphite catalyst (weight 0.83 g, diameter of grain size 0.38-0.43 mm) was diluted with quartz (of the same grain size) in the weight ratio 1:5.

The other catalyst used was a sample of K-Bi-GICs (weight 5.8 g, diameter of grain size 0.4-1.2 mm).

RESULTS

It should be stressed that the reaction was performed in a reactor with large postcatalytic volume (a reactor planned for another purpose was adopted) which, in the conditions of the reactions at high temperatures and in homogeneous phase, gave results of high degree of conversion and full oxidation[9].

The chemical composition and phase contents of the samples were determined using X-ray powder diffraction methods and X-ray fluorescence spectroscopy. The Pb-graphite and Bi-K-graphite catalysts were mainly composed of graphite and phases of periodical structure characteristic of graphite intercalated compounds[8].

The oxidative dehydrogenation of ethylbenzene to styrene was performed in the presence of Pb-graphite of lead content equal to 34,8 %wt. Table I shows the dependence of conversion of ethylbenzene on temperature under the given conditions (feed: ethylbenzene 3 g/h; water 15 g/h; air 6 dm^3/h).

The Pb-GICs sample showed a catalytic activity at high temperatures. For so small a sample, i.e. with a large total load (32 dm^3/gh), these conditions must have been destructive in spite of the presence of water with the substrates. Even if Pb-graphite were treated only as a catalyst precursor with a high dispersion of metal (in the material, graphite functions both as an amphoteric support and a diluting agent), the results encouraged further experiments on a larger sample with an intercalate of another metal as a catalyst of the investigated reaction. Graphite with intercalated bismuth and potassium (total chemical composition $KBi_{0.90}C_{6.65}$) was employed for this purpose. The results were satisfactory.

TABLE I Dependence of ethylbenzene conversion on temperature over Pg-graphite sample (in %).

Temp.	Conversion						Selectivity
[°C]	styrene	benzene	toluene	CO_2	CO	total	to styrene
680	7.8	1.7	0.9	8.5	5.0	23.9	32.6
690	14.8	2.5	1.3	10.5	7.0	36.1	41.0
700	19.6	3.9	2.0	12.0	9.5	47.0	41.7
710	22.5	5.2	3.0	13.0	12.0	55.7	40.4
720	22.8	6.4	4.3	14.0	15.0	62.5	36.4

Figure 2 and Table II present the dependence of selectivity and conversion of ethylbenzene on temperature (nitrogen used as diluting agent).

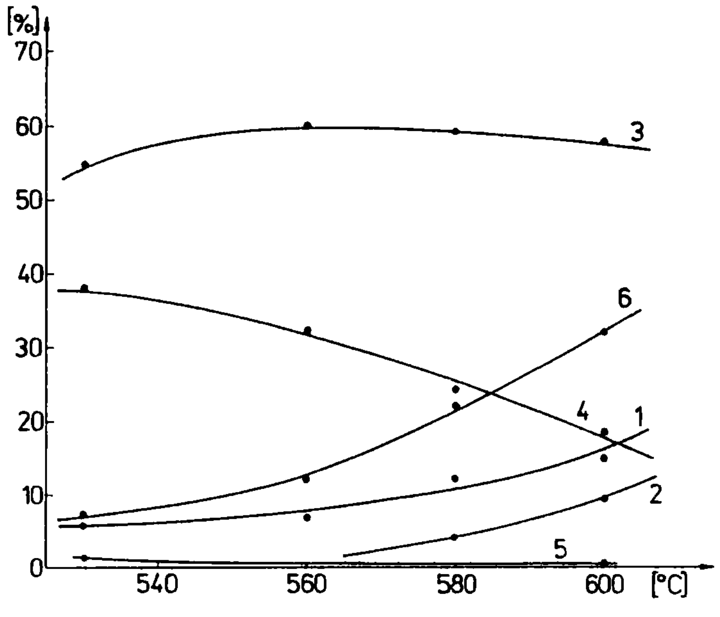

FIGURE 2. The dependence of selectivity on temperature over K-Bi-graphite sample.
1 — benzene; 2 — toluene; 3 — styrene; 4 — CO_2 ;
5 — CO; 6 — total conversion.
(Initial concentrations: ethylbenzene 20.6 %vol.; oxygen 10.9 %vol.; total load 0.54 dm^3/gh.

TABLE II Dependence of selectivity on temperature over K-Bi-graphite sample (in %).

Temp. [°C]	styrene	Product selectivity benzene	toluene	CO_2	CO	Total conversion
600	55.4	9.1	9.1	25.7	0.7	30.7
625	56.4	13.2	8.3	21.7	0.5	42.4
655	51.6	17.1	12.9	18.1	0.4	59.1

The initial concentrations: ethylbenzene 16.0 %vol.; oxygen 13.0 %vol.; total load 0.69 dm^3/h.

SUMMARY

The confrontation of properties of metals and graphite presages interesting applications, for example in catalysis. This was confirmed by the application of Pb-GICs and K-Bi-GICs as catalysts for the oxidative dehydrogenation of ethylbenzene. The first results presage obtaining even higher values by using a reactor system better adapted to this purpose.

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