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NOTES

Bi–K–Graphite Intercalation Compound as a New Catalyst for Styrene Synthesis

Several methods of styrene synthesis have been elaborated. Many of them involve oxidative dehydrogenation of ethylbenzene with atmospheric oxygen (*1–3*). The catalysts of the reaction of oxidative dehydrogenation of alkyloaromates to vinyl monomers (including the conversion of ethylbenzene into styrene) are, as a rule, compound metal oxides (*4*). Besides these, other catalysts of this reaction are aluminum oxide modified in various ways (*5, 6*), aluminosilicates (*7*), and metal phosphates of groups IIA, IIIA, VA, and VIIIA (*8*). During the reaction, carbon deposits are formed on these catalysts. The deposits are products of further conversion of styrene. In this reaction, catalytic abilities are assigned to these deposits, which has a well developed specific surface (*9*). The catalytic activity of condensed aromatic binders, an organic redox system with a quinone group in the reactions of oxidative dehydrogenation, is also known (*10*).

The above analysis induced investigations of the catalytic properties of graphite intercalated by metals. Graphite shows an amphoteric character and its electronic interaction with various metals has been proved (*11*). In the present work attempts to apply the catalytic system K–Bi–graphite in the reaction of oxidative dehydrogenation of ethylbenzene have been undertaken.

It is well known that electron donor–acceptor (EDA) compounds such as graphite intercalation compounds (GICs) exhibit activity in several reactions, for example in the reaction with hydrogen and catalytic synthesis of ammonia (*12, 13*).

Boersma (*14, 15*) lists many applications of metal-GICs as catalysts for hydrogenation, dehydrogenation, isomerization, alkylation, hydrodealkylation, dimerization, polymerization, ammonia synthesis, and Fischer–Tropsch synthesis. Intercalates of graphite containing two intercalated metals are a very interesting group of so-called "synthetic metals." Preparation and properties of such systems as MT_xC_{4n}, where T = Hg, Bi, Tl; $x = 0.55 - 1.5$; M = K, Rb, Cs (*16–21*) have been investigated. They were prepared as an M–T alloy (e.g., KHg, KBi or RbHg) by heating these metals in a mixture under reduced pressure to obtain a liquid phase. Afterwards, graphite was added and the alloy was heated again for a longer time (e.g., 10 days to obtain K–Bi–graphite). By controlling the temperature and duration of the reaction, various compounds can be obtained. The compounds $KHgC_4$ and $KBi_{0.6}C_4$ show high organization of layers, while the others show a type of irregularity.

McRae *et al.* (*16*) give the distances of interplanar spacings for all the compounds of MT_xC_{4n} type at 245 K then known. The α and β phases separated from the compounds of the same chemical composition can be distinguished. The thermal stability of MT_xC_{4n} is higher than that of the free alloys M–T. The compounds are stable in air. Another unclear problem is the electronic structure and the direction of electron transfer (*22*). It is certain that the system possesses free "extra" electrons. This property gives the opportunity of applying these compounds in conductive systems and catalysis. The latter branch of application seems to be a better prospect.

Intercalate K–Bi–graphite was obtained by applying a method different from those described above; heating the components under nitrogen atmosphere in a reactor made of Pyrex. The mixture of potassium

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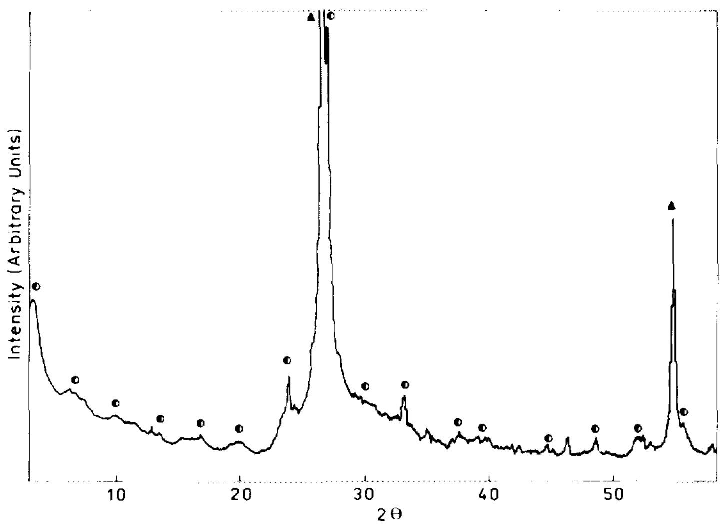

FIG. 1. X-ray diffraction pattern of K–Bi–graphite sample. Peaks marked by ◐ were assigned to K–Bi–GIC, and by ▲ to graphite.

and bismuth was heated for 72 h at 320°C, forming K–Bi alloy. Next, specially purified powdered natural (Sri Lanka) graphite (plates of size 1–20 μm by 30–100 μm) was added. The mixture was heated further for 264 h at 380°C.

The investigations of the reaction of oxidative dehydrogenation of ethylbenzene were performed in a continuous flow quartz reactor. The catalyst used was Bi–K–GIC (weight 5.8g, diameter of grain size 0.4–1.2 mm). Catalyst crumbs were made by pressing the powder with a hydraulic press at 6 MPa. This solid was lightly crushed and separated using a steel sieve. The tests were made under atmospheric pressure. As an oxygen carrier atmospheric air was used. The products of the reaction were analyzed by gas chromatography.

Figure 1 shows the X-ray diffraction powder pattern of a K–Bi–graphite sample. The decrease in the intensity of reflection (002) of graphite (335 pm) in comparison with the intensity of reflection of pure graphite is considerable (from 117 to 76 × 10^3 c.p.s.). In addition, new reflections appear, the most intense of them having interplanar distance 330.52 pm. This corresponds to reflection (008) by a periodical structure of identity period $d_{001} = 2640$ pm. The diffractogram shows a series of reflections of values 2640 pm (001); 1320 pm (002); 880 pm (003); 660 pm (004); 528 pm (005); 440 pm (006); 377 pm (007); 330 pm (008); 293 pm (009); 264 pm (0010); 220 pm (0012); 203 pm (0013); 188 pm (0014); 176 pm (0015); and 165 pm (0016). Reflections (008) and (0016) are the most intense. The above interplanar distance $d_{\mathrm{l}} = 1320$ pm corresponds to the sum of the α-phases of K–Bi–GIC stage 2–5 and graphite; e.g., 994 pm + 335 pm = 1329 pm (*23*). The system is a mixture of graphite and the intercalate compounds K–Bi–graphite. The presence of a clear stratified system is confirmed by micrographs taken with a scanning electron microscope (Jeol JSM-6100) (Fig. 2). There is visible stratification of graphite plates along the direction (001). The total chemical composition of the sample used, marked with the method of X-ray fluorescence, is $KBi_{0.904}C_{6.65}$.

The results of the exploratory application of Bi–K–GIC as a catalyst for the reaction

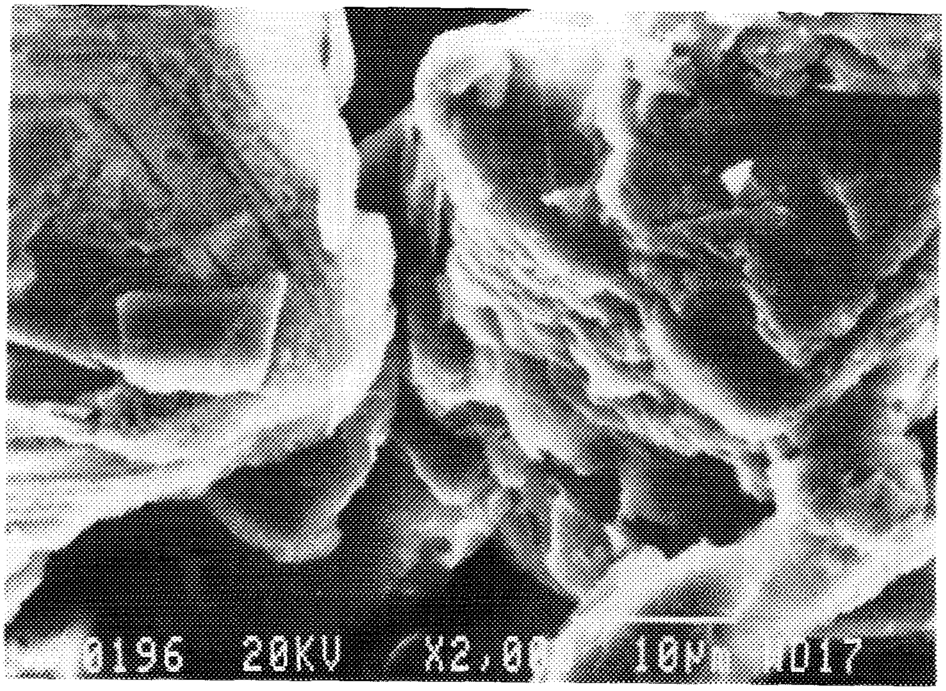

FIG. 2. Scanning electron micrograph of K–Bi–graphite sample.

of oxidative dehydrogenation of ethylbenzene into styrene were satisfactory. The data concerning activity and selectivity in relation to styrene, carbon oxides, benzene, and toluene in the studied range depending on the control parameters: temperature, load, ethylbenzene/oxygen molar ratio, and volume concentration of ethylbenzene were obtained. Table 1 shows the dependence of selectivity and conversion of ethylbenzene on temperature for two typical experimental conditions. It should be emphasized that the reaction was performed in a reactor with a large postcatalytic volume (a reactor planned for some other purposes was adapted), which, under the conditions of the reactions at high temperatures and in homogeneous phase, gave the results of high degree of conversion and full oxidation (24).

Table 2 gives a conventional presentation of the results, which show a typical influence of the other parameters: as a result of an increase of air and nitrogen feed (rise of total load), the amount of carbon oxides grows and the ethylbenzene/oxygen molar ratio particularly unfavorably influences the selectivity to styrene.

To sum up, the properties of GICs suggest that they may have interesting applications

TABLE 1

Dependence of Conversion of Ethylbenzene on Temperature

Temp. (°C)	Conversion (%)						Selectivity to styrene (%)
	Styrene	Benzene	Toluene	CO_2	CO	Total	
530	3.9	0.4	0.0	2.7	0.1	7.1	54.9
560	7.2	0.8	0.0	3.9	0.1	12.0	60.0
580	13.7	2.8	0.9	5.4	0.1	22.9	59.8
600	18.8	4.7	2.8	5.7	0.2	32.2	58.4
600[a]	17.0	2.8	2.8	7.9	0.2	30.7	55.4
625[a]	23.9	5.6	3.5	9.2	0.2	42.4	56.4
655[a]	30.5	10.1	7.6	10.7	0.2	59.1	51.6

Note. Feed: ethylbenzene 2.8 g/h; nitrogen 0.8 dm^3/h; air 1.7 dm^3/h; [a] air 2.6 dm^3/h.

TABLE 2

Dependence of Selectivity and Conversion on Control Parameters

Conc. of ethyl benzene (% vol.)	Total load (dm^3/gh)	Ethyl benzene /oxygen molar ratio	Temp. (°C)	Total conv. (%)	Product selectivity (%)				
					Styrene	Benzene	Toluene	CO	CO_2
20.6	0.54	1.9	600	32.2	58.4	14.6	8.7	17.7	0.5
16.0	0.69	1.2		30.7	55.4	9.1	9.1	25.7	0.7
16.0	0.69	1.2	655	59.1	51.6	17.1	12.9	18.1	0.4
9.6	1.14	1.3		56.4	57.4	13.8	11.7	16.0	1.1
9.6	1.14	1.3	675	68.4	41.8	23.4	18.1	15.3	1.3
6.9	1.60	0.8		71.0	36.8	17.7	16.6	26.8	2.1

in catalysis. This fact was confirmed by our attempts to apply K–Bi–GIC as a catalyst for the reaction of oxidative dehydrogenation of ethylbenzene. The reaction occurs with 56% conversion and 40% selectivity under the conditions defined above. The introductory results predict higher values after more attempts are made in a reactor system which will be better adapted for this purpose.

On the basis of our results we can confirm that only the phases of K–Bi–graphite play an active role in the catalytic step because free graphite is inactive, Bi–graphite cannot be obtained, and in K–graphite there occurs decomposition of intercalated potassium.

The characterization of the K–Bi–graphite and the stage of intercalation is rather complicated, particularly after the dehydrogenation of ethylbenzene. The above problem requires studies *in situ* and should be subjected to further investigations. At the present time, we can only suppose that the reaction proceeds rather at the external surface of the intercalated graphite because the size of ethylbenzene is somewhat larger than the interlayer distance of the K–Bi–graphite compounds.

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