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Oxidative dehydrogenation of ethylbenzene with carbon dioxide on alkali-promoted Fe/active carbon catalysts

T. Badstube [a], H. Papp [a], P. Kustrowski [b] and R. Dziembaj [b]

[a] *Institut für Technische Chemie, University of Leipzig, Linnestrasse 3, 04103 Leipzig, Germany*

[b] *Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland*

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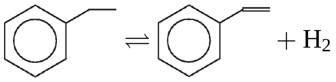
The catalytic behavior of iron supported on activated carbon was investigated in the oxidative dehydrogenation of ethylbenzene. CO_2 was applied as oxidant. High ethylbenzene conversion (>70%) and selectivity towards styrene (>90%) were observed at 550 °C. Apart from styrene, benzene, toluene, carbon monoxide and water were formed as products.

Keywords: oxidative dehydrogenation of ethylbenzene, carbon dioxide, active carbon, alkali promoter, iron oxide

1. Introduction

The oxidative removal of hydrogen (e.g., by oxygen) being formed in equimolar ratio with styrene during catalytic dehydrogenation of ethylbenzene (EB) shifts the equilibrium to the product side. Earlier efforts concerning the oxidative dehydrogenation of EB were reviewed by Emig and Hofmann [1] and up-dated by Cavani and Trifirò [2]. The active carbonaceous deposits on the acidic catalysts seem to act as the active centres for the oxidative dehydrogenation. This was first proposed by Alkhazov et al. [3] and has been elaborated by Emig and Hofmann [1] to a concept of islands of condensed chinoic compounds oxidizing hydrogen in the ethyl group of the adsorbed EB. This concept has been supported by a series of spectroscopic studies, e.g., aroxyl radical surface species were confirmed by ESR [4,5], and antrachinon-like species by XPS and/or SIMS [6–8].

H_2 from the dehydrogenation reaction can also be removed by the reverse water–gas shift reaction. The thermodynamic analysis of the complex system



(1)

$$H_2 + CO_2 \rightleftharpoons H_2O + CO \qquad (2)$$

gave promising results [9]: at 600 °C and a molar ratio of $CO_2/EB = 9$, the equilibrium conversion of ethylbenzene (EB) reaches 90%, while in the case of a water-diluted reaction mixture only 70% conversion is achieved under the same conditions. This suggests a potential improvement of the present technology by using CO_2 instead of H_2O.

The addition of CO_2 and H_2O at the same time into the dehydrogenation reactor showed, however, a decrease in the catalytic activity of iron-based catalysts [10,11].

The only experimental results on EB dehydrogenation with an excess of CO_2 and without H_2O were recently published by Suzuki et al. [12]. They used active carbon catalysts impregnated with iron, alkaline and alkaline-earth nitrates. The observed EB conversions and styrene yields were, however, much lower than those observed in the present work. Suzuki et al. [12] proposed a mechanism with Fe^{3+} ions acting as the active centres. Fe^{3+} ions oxidize two hydrogen atoms in the ethyl group converting the EB molecule into a styrene molecule. The resulting Fe^{2+} ion is reoxidized by CO_2. Though the final products, CO and H_2O, are the same as in case of the water–gas shift reaction, a real oxidative dehydrogenation is postulated.

The aim of our work was to investigate the oxidative dehydrogenation of ethylbenzene with CO_2 as oxidant using alkali-promoted iron oxide active carbon catalyst.

2. Experimental

2.1. Catalysts

Active carbon (Chemviron-Carbon GmbH) containing 0.2 wt% of ash was activated with 90% HNO_3 at 90 °C for 1 h (D-90). Then it was impregnated by an incipient wetness technique with an aqueous solution of iron(III) nitrate which was adjusted to obtain 5 wt% of Fe in the sample. It was then dried in air at 180 °C for 2 h. Subsequently, portions were impregnated by an incipient wetness technique with water solutions of alkaline (Li, Na, K) or alkaline-earth (Be, Mg, Ca) nitrates in the molar ratio $M : Fe = 0.1$. The obtained samples were again dried with the same procedure.

2.2. Characterization measurements

The specific surface areas of the samples before and after catalytic tests were determined by the BET method (N_2 adsorption at 77 K) in an ASAP 2000 (Micromeritics). The obtained isotherms were analyzed by the Horvath–Kawazoe method and the pore distribution was determined.

TG/DTG/EGA measurements were performed in a STA 409 (Netzsch GmbH) equipped with a QMS 200 (Balzers) with the following conditions: 50 mg sample, 75 $cm^3\,min^{-1}$ of He, 10 °C min^{-1} from 20 up to 600 °C, with corundum as standard material.

2.3. Catalytic tests

The catalytic tests were performed in a quartz continuous-flow reactor (6.0 mm i.d.) with 100 mg catalyst in a fixed bed. The EB flow was controlled by a Bronkhorst fluid flow controller, and evaporated in a controlled evaporation system (Bronkhorst).

Two gas chromatographs were used for chemical analysis of the educts and products. One of them (Shimadzu GC-14B) was equipped with a capillary column HP-1 (12 m, 0.2 mm i.d., and 0.33 μm film of polydimethylsiloxan). It was used to separate the liquid products. The second GC (Shimadzu GC-8A) was equipped with three packed columns: 1 m × 1/8″ Porapak T (for water determination), 1 m × 1/8″ Carboxen 100 (for CH_4 and CO_2) and 5 m × 1/8″ Molsieve 5A (for H_2, O_2, N_2 and CO).

Preliminary tests showed the beginning of noticeable EB cracking in the gas phase at 580 °C. Therefore, all catalytic tests were carried out between 350 and 550 °C. The catalysts were first outgassed in a He stream at 350 °C. Then, the catalytic tests started at 350 °C using the following conditions: total flow 100 $cm^3\,min^{-1}$, 3 vol% of EB, a molar ratio of $CO_2 : EB = 10 : 1$, and He as carrier gas. After three GC analyses, in 20 min intervals, the reaction temperature was increased by 50 °C, and the next GC measurements began, etc. – up to 550 °C.

The above experiments were carried out for all catalysts. The three best catalysts were then tested with the following $CO_2 : EB$ molar ratios: 0, 1, 5, 10, 20.

3. Results and discussion

3.1. Specific surface areas and pore distributions

The obtained results are collected in tables 1 and 2. The pure activated carbon showed a high specific surface area (950 $m^2\,g^{-1}$), which was changed only slightly (800–850 $m^2\,g^{-1}$) after impregnation and initial calcination. It is obvious that the micropore walls accounted for about 97% of the total specific surface area. The most abundant pores had a diameter from 4 to 5 Å. According to Horvath–Kawazoe, the volume of micropores amounted to about 92% of the total pore volume in the catalyst grains.

After the catalytic tests the specific surface area decreased due to carbonaceous deposits. For K-, Na- and Ca-promoted catalysts the changes were smaller than for Li- and Mg-promoted catalysts. The appropriate changes in the micropores volumes are from 93 to 83% and from 92 to 62%, respectively.

3.2. Thermal analysis

All catalysts lost adsorbed water at about 100 °C. At about 200 °C, the decomposition of nitrates was observed combined with an increase in the masses 14, 28, 30 and 44. NO_2 evolved oxidized the carbon matrix with the formation of surface oxidic groups and led to a desorption of CO or CO_2. A part of carbon dioxide is adsorbed by alkali

Table 1
Surface area and pore volume for the catalysts before the catalytic tests.

Catalyst	Total specific surface area (m^2/g)	Microporous area (m^2/g)	Volume of micropores (cm^3/g)	Total pore volume (cm^3/g)
D-90	955	919	0.5481	0.6038
5% Fe/D-90	832	807	0.4798	0.5211
5% Fe/D-90 + Li	847	823	0.4872	0.5258
5% Fe/D-90 + K	811	786	0.4650	0.5045
5% Fe/D-90 + Na	894	866	0.4828	0.5244
5% Fe/D-90 + Be	838	812	0.4816	0.5231
5% Fe/D-90 + Ca	854	826	0.4892	0.5339
5% Fe/D-90 + Mg	802	777	0.4598	0.4980

Table 2
Surface area and pore volume for the catalysts after catalytic tests (5.5 h).

Catalyst	Total specific surface area (m^2/g)	Microporous area (m^2/g)	Volume of micropores (cm^3/g)	Total pore volume (cm^3/g)
5% Fe/D-90 + Li	271	209	0.1235	0.1490
5% Fe/D-90 + K	252	237	0.1405	0.1747
5% Fe/D-90 + Na	322	308	0.1724	0.1987
5% Fe/D-90 + Be	293	249	0.1466	0.1655
5% Fe/D-90 + Ca	273	255	0.1522	0.1869
5% Fe/D-90 + Mg	159	125	0.0721	0.1164

Table 3
Results of catalytic tests for all catalysts (CO_2/EB = 10).

Catalyst	Conversion of EB (%)	Selectivity (%)		
		Benzene	Toluene	Styrene
Reaction temperature = 350 °C				
D-90	0	0	0	0
5 wt% Fe/D-90	4.1	0	0	100
5 wt% Fe + Li/D-90	4.0	0	0	100
5 wt% Fe + Be/D-90	4.7	0	0	100
5 wt% Fe + K/D-90	4.0	0	0	100
5 wt% Fe + Ca/D-90	3.8	0	0	100
5 wt% Fe + Mg/D-90	4.1	0	0	100
5 wt% Fe + Na/D-90	4.6	0	0	100
Reaction temperature = 450 °C				
D-90	0	0	0	0
5 wt% Fe/D-90	33.0	1.7	2.9	95.4
5 wt% Fe + Li/D-90	30.9	1.7	1.9	96.4
5 wt% Fe + Be/D-90	33.5	2.0	2.0	96.0
5 wt% Fe + K/D-90	32.4	1.6	1.5	96.9
5 wt% Fe + Ca/D-90	31.8	1.2	1.5	97.3
5 wt% Fe + Mg/D-90	31.1	1.3	2.1	96.6
5 wt% Fe + Na/D-90	34.3	1.1	1.2	97.7
Reaction temperature = 550 °C				
D-90	9.5	0	0	100
5 wt% Fe/D-90	60.7	3.1	4.7	92.2
5 wt% Fe + Li/D-90	75.0	2.2	3.3	94.5
5 wt% Fe + Be/D-90	67.3	2.8	4.7	92.5
5 wt% Fe + K/D-90	66.4	0.7	2.4	96.9
5 wt% Fe + Ca/D-90	58.3	1.5	3.5	95.0
5 wt% Fe + Mg/D-90	57.2	2.2	4.0	93.8
5 wt% Fe + Na/D-90	68.3	1.0	2.4	96.6

oxides with the formation of carbonates, which were then decomposed at temperatures higher than 500 °C.

3.3. Catalytic results

The catalytic results obtained for all catalysts are collected in table 3. The pure active carbon D-90 showed a very low activity, only at 550 °C a yield of styrene of 9.5% was obtained. Impregnation with Fe and promotion with alkali or alkali-earth ions led to a strong increase in styrene yields (54% for the Mg-promoted catalyst and 71% for the Li-promoted catalyst at 550 °C, cf. figure 1). The other promoters gave results between the above mentioned values. It should be stressed that high selectivities to styrene (from 92 to 97%) were obtained at rather high EB conversions (from 58 to 75%). The tested catalysts showed also higher selectivity to toluene than to benzene.

The catalysts were covered during catalytic tests by carbon deposits shown by a 15–20 mg weight increase (table 4).

The best three catalysts (5 wt% Fe/AC promoted by Li, Na and K) were chosen for further tests, with various molar ratios of $CO_2 : EB$, otherwise under identical conditions.

A strong increase in the yield of styrene was observed with an increase in the amount of CO_2 in the reaction mixture (cf. figure 2) up to a CO_2/EB ratio of 10. At a CO_2/EB ratio of 20 a decrease in catalytic activities of all tested samples was observed – the highest one for the Li-containing catalyst. The reason for this fact may be the formation of inactive metal carbonates on the surface of the catalysts in the presence of large amounts of CO_2.

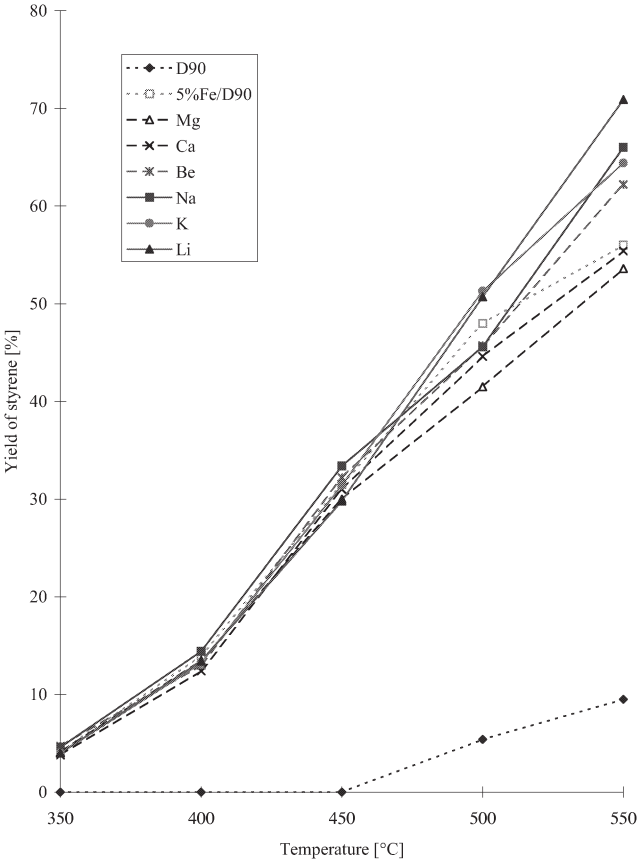


Figure 1. The comparison of styrene yields obtained on differently promoted catalysts as a function of reaction temperature.

Table 4
Weight of catalysts (mg) before and after catalytic reaction.

Catalyst	Before	After
D-90	104	95
5 wt% Fe/D-90	102	115
5 wt% Fe + Li/D-90	99	117
5 wt% Fe + Be/D-90	100	117
5 wt% Fe + K/D-90	100	120
5 wt% Fe + Ca/D-90	100	117
5 wt% Fe + Mg/D-90	99	115
5 wt% Fe + Na/D-90	100	114

Changing the molar ratio of CO_2 to EB changed the selectivities towards benzene, toluene and styrene as well. In the absence of carbon dioxide, benzene appeared only at the highest temperature (550 °C) with a selectivity of 2–3%. Increasing amounts of CO_2 caused a decrease in benzene production, however, it appeared already at lower temperatures, e.g., at 400 °C at a molar ratio $CO_2 : EB = 20 : 1$. The selectivity towards toluene was the highest when no CO_2 was added and reached about 5% (for the Li- and K-promoted active-carbon-supported iron) at 550 °C. Traces of toluene were detected at 400 °C. Increasing ratios of CO_2 to EB caused a gradual decrease in selectivity towards

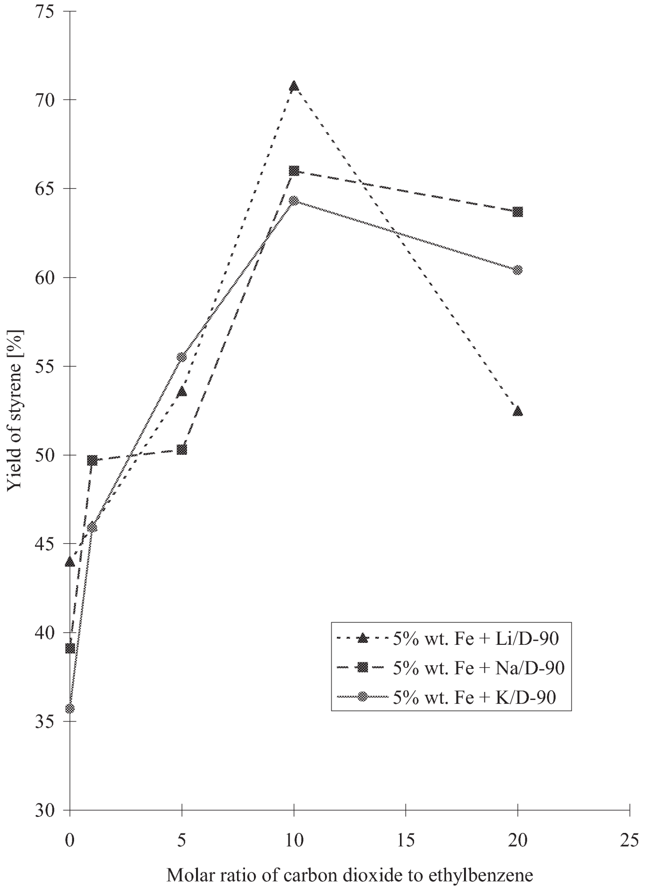


Figure 2. Styrene yields observed on the best three catalysts vs. the molar ratio of CO_2 to EB at 550 °C.

toluene, but for the ratio 20 : 1 it increased again. This tendency is opposite to the behavior of the styrene selectivity which was the smallest in the absence of CO_2 and increased up to a CO_2/EB ratio of 10 and then it decreased again.

No correlation between the molar ratios of reactants and the amount of deposited coke on the surface of catalysts was observed.

A constant molar ratio 0.8 of CO to H_2O produced during the oxidative dehydrogenation of EB was observed except for very low dehydrogenation rates (low temperature and molar ratio of CO_2 : EB). A comparison of this result with the postulated mechanisms shows in principle accordance with the water–gas shift reaction [9] as well as with the redox mechanism of the EB oxidation by Fe^{3+} from ferrite phase, succeeded by reactivation of the oxidation centres by CO_2 in the next step [12].

4. Conclusion

Alkaline-promoted active-carbon-supported iron catalysts are very active in the oxidative dehydrogenation of EB to styrene in the presence of carbon dioxide. The best results were obtained at 550 °C for a Li-promoted catalyst with a conversion of EB of 75% and a selectivity towards styrene of nearly 95%. These results are similar to those obtained with industrial catalysts which perform the dehydrogenation process with an excess of water.

The main product of the dehydrogenation reaction with CO_2 was styrene, but the following by-products were detected – benzene and toluene. The selectivity towards toluene was always higher than towards benzene. We observed also the formation of carbon monoxide and water, which were produced with a constant molar ratio of about 0.8. The weight of the catalysts increased up to 20% during the reaction due to deposition of the carbon.

Using too large an excess of CO_2 ($CO_2/EB > 10$) was harmful for the styrene yield. The most favourable molar ratio of CO_2 to EB was 10 : 1.

Acknowledgement

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