

CARBON DIOXIDE AS OXIDIZING AGENT FOR ETHYLBENZENE DEHYDROGENATION WITH METAL DOPED Fe SUPPORTED ACTIVE CARBON CATALYSTS

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Introduction

The main industrial method to produce styrene (S) is the catalytic dehydrogenation of ethylbenzene (EB). The process is usually realized at high temperature above 600°C with an excess of water vapor in the presence of a hematite catalyst promoted mainly with potassium oxide [1]. The dehydrogenation reaction is strongly endothermic, it consumes a high amount of energy, and thermodynamics limit the conversion of ethylbenzene to approximately 50-60 %.

Many disadvantages of the equilibrium process can be eliminated by insertion of an oxidizing agent (e.g. oxygen) instead of water vapor into the reaction system. Alkhazov et al. [2] showed that carbonaceous deposits which form in the first hours of reaction on the surface of acidic catalysts act as the active centers for the oxidative dehydrogenation. This was confirmed by many authors by using carbon molecular sieves with which a conversion of 80% of ethylbenzene with selectivity towards styrene of 90% at 350°C was achieved [3].

A considerable amount of ethylbenzene is, however, totally oxidized to carbon oxides when using oxygen as oxidizing agent. The attempt of using CO₂ as oxidant together with H₂O gave negative results. A decrease in the catalytic activity of iron oxide based catalysts was observed [4].

Sugino et al. [5] used iron oxide supported active carbon impregnated with alkaline and alkaline earth nitrates as catalysts in ethylbenzene dehydrogenation with CO₂ in the absence of water. The catalytic results of their experiments were very promising. We found similar or even better results for promoted iron oxides supported on active carbon [14]. Here we report about the catalytic activity of different carbonaceous supports doped with transition metals and additional promoted with alkali metals.

Experimental

Pyrolyzed polyacrylnitril (PPAN) and polycarbonate (PC) were obtained through the carbonization of polymer material:

- PPAN (flow of Ar (1 l/min) at 500°C for 3 h)
- PC in Ar at 600°C for 3h

The samples of active carbon (AC) were initially activated with 90% HNO₃ at 90°C for 1h:

- AC-A90 (Hajnowski Przedsi biorstwo)
7.1 wt % of ash
- AC-B90 (Merck)
4.9 wt % of ash
- AC-C90 (Chemviron-Carbon GmbH)
3.0 wt % of ash
- AC-D90 (Chemviron-Carbon GmbH)
0.2 wt % of ash

The active phases were added first by an impregnation (incipient wetness technique) with aqueous solutions of transition metals and subsequently impregnated with aqueous solutions of alkaline and alkaline earth metal nitrates respectively [6]. The catalysts were dried in air at 180°C for 2h.

The catalytic tests were carried out in a fixed bed, quartz flow micro reactor system. The effluent of the reactor was analyzed using a Shimadzu GC system consisting of a FID for hydrocarbons and a TCD for permanent gases. The preliminary studies of the catalyst performance was carried out in the temperature range between 350 and 550°C. The catalytic tests were performed under the following conditions: 100 mg catalyst, total flow 100 ml/min, 3 vol. % ethylbenzene, molar ratio carbon dioxide/ethylbenzene 10:1 and helium as carrier.

Results

The pyrolysed polyacrylnitril (PPAN) and polycarbonate (PC) loaded with different transition metals (Fe, Ni) were almost inactive, even at the highest tested temperature (550°C) only traces of styrene (a yield of less than 5 %) were observed. An additional impregnation with alkaline or alkaline earth metal nitrates (Ca, K) of the PPAN and PC catalysts did not lead to higher yield of styrene.

The active carbon supports loaded with 5 wt. % of iron gave a significantly higher yield of styrene. The yield of styrene increased with the decrease of ash content. The catalytic activity for A90, B90 and C90 did not differ much (yield of styrene: 11-15 %) at 550°C like the ash content of the supports. The catalytic activity was

significantly higher for the active carbon D90 with the lowest content of ash with a conversion of ethylbenzene of 66 % and a yield of styrene of 55 % at 550°C (Fig.1).

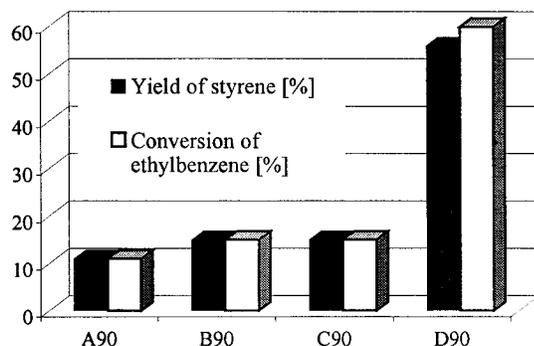


Fig.1: Comparison of the catalytic activity obtained on 5% Fe on active carbon at 550°C

The influence of the amount of iron oxide on D-90 (1, 5 and 10 wt. %) on the catalytic activity was tested.

The highest activity was observed for the catalyst containing 5 wt. % Fe which possessed the highest selectivity towards styrene as well (Fig. 2). The amount of by-products rose with temperature and reached 4.7% of toluene and 3.1 % of benzene at 550°C.

For the catalyst with 10 wt. % iron we noticed at 550° C a higher conversion of ethylbenzene (66 %) with a yield of styrene of 50 % but also significantly higher selectivities to benzene and to toluene of 10.2 % and 13.4 % respectively. Only 1 wt. % of iron on the sample led to lower catalytic activity (conversion of EB: 32 %, yield of styrene: 29 %). The same behavior was observed for the other three active carbon samples (A90; B90, C90). The conversion of ethylbenzene and also the yield of styrene was lower for samples with 1 % and 10 % of iron respectively.

Iron oxide was substituted by other transition metal oxides. Cobalt oxide and Nickel oxide on D90 showed no activity, Copper oxide and Chromium oxide showed lower activity than the Fe containing catalysts. Chromium oxide supported D90 showed during the catalytic test at 550°C a styrene yield of 10.2 % followed by a decrease to 4.3 % with time-on-stream. Copper oxide on D-90 behaved similarly; a yield of styrene of 11.7 % at 550°C and decrease to 4.6 % with time-on-stream after 60 minutes.

Promotion of the 5 wt.% Fe on D90 with alkali (Li, Na, K) or alkali earth ions (Be, Ca, Mg) (atomic ratio metal to Fe: 1:10) led to strong increases in conversion of ethylbenzene and in yields to styrene. We observed that alkali metals were better promoters than alkaline earth metals. The activity of the catalysts promoted with different alkali metals did not differ much. High

catalytic conversion (Li: 75 %, K: 66 %, Na: 68 %) of ethylbenzene with high selectivity towards styrene (> 90 %) was obtained at 550°C.

We investigated also catalysts with atomic ratios of M (M = Li, Na or K) to Fe: 0.05, 0.1 and 0.2, and a constant content of iron (5 wt %). All three alkali metals showed the same behavior. The molar ratio of alkali metal to iron of 1:10 led to the highest catalytic activity. The yield to styrene decreased after varying the molar ratio to 1:5 (Li: 44 %, Na: 46 %, K: 48 %) or 1:20 (Li: 51 %, Na: 54 %, K: 55 %) respectively.

All three alkali promoted catalysts were tested with the following molar ratios of CO₂:ethylbenzene: 0, 1, 5, 10, 20. All three catalysts showed a similar behavior. A strong increase in the yield of styrene was observed with an increase in the amount of carbon dioxide in the reaction mixture. A ratio of 10:1 led to the highest activity. At a CO₂/EB ratio of 20 a decrease in catalytic activities of all tested samples was observed.

Addition of small amounts of water, hydrogen peroxide or oxygen respectively into the reaction system did not increase the catalytic activity.

Conclusions

Among the investigated catalysts active carbon is definitely the best material as support and iron oxide the best active phase. The catalyst with 5 wt. % Fe on D90 achieved a styrene yield of 56 % at 550°C. Additional impregnation with alkaline metal nitrates led to higher yields of styrene. The best catalytic results we found for a molar ratio of alkaline metal to iron 1:10 and a molar ratio CO₂:EB of 10.

References:

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