ETHYLBENZENE DISPROPORTIONATION ON ZSM-5: CATALYTIC BEHAVIOUR AROUND CRITICAL POINT

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INTRODUCTION

Disproportionation is an important reaction in the interconversion processes of mono-, di- and tri-alkylbenzenes, which have a wide variety of applications. This is the case of *p*-diethylbenzene, which is a high-valued desorbent used in *p*-xylene adsorptive separation process. Zeolites were used to replace the traditional Friedel Crafts catalysts in these reactions, resulting in several patents such as ethylbenzene disproportionation to *p*-diethylbenzene on ZSM-5 zeolite commercialized by Mobil [1]. The main disadvantage of using zeolites as catalysts is their deactivation caused by coke deposition [2]. Several works have been targeted to improve the process by using supercritical conditions [3, 4].

In this work, ethylbenzene disproportionation, catalyzed by HZSM-5 was studied at different reaction conditions around the ethylbenzene critical point (36 bar, 344 ºC), including supercritical phase. The spent catalysts were characterized by means of thermogravimetric and elemental analyses.

MATERIALS AND METHODS

Disproportionation reactions

Disproportionation experiments were carried out in a continuous flow equipment where pure ethylbenzene was pumped at 0.5 $cm^3 \cdot min^{-1}$, preheated and fed to a stainless steel fixed-bed reactor (17 mm i.d.), placed in an oven. Powdered HZSM-5 supplied by Zeocat with a Si/Al ratio of 25 was activated for 6 hours at 550ºC and packed into the reactor (4.5 g; bed length *ca*. 50 mm). The pressure in the equipment was managed by a pressure control valve coupled with a PID-controller. The sampling was carried out in duplicate by an on-line valve which samples at high pressure and by collecting the liquid after depressurization and subsequent condensation. Both samples were analysed by a GC with a FID detector. After the experiments, catalysts were purged of reactants and products with N_2 and cooled down to room temperature.

Catalytic experiments were performed for 3 hours of time-on-stream at different temperatures from 300 to 400ºC. Higher temperatures were not tested because secondary reactions such as ethylbenzene dealkylation become increasingly significant [5]. Pressure was varied from 1 to 60 bar, below and above the ethylbenzene critical pressure. The experimental area is shown in Fig. 1.

Deactivation experiments were performed for high values of time-on-stream at several conditions within the experimental area.
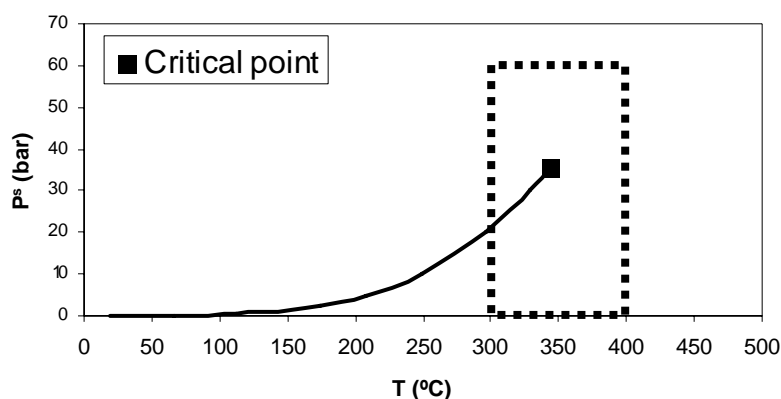
Figure 1. Experimental area

Characterization of spent catalysts

Spent catalysts were characterized by thermogravimetric and elemental analysis in order to determine coke content and its aromaticity by means of H/C ratio, respectively.

Thermogravimetric analyses were performed on a PerkinElmer STA 6000 thermobalance. The spent catalysts were preheated to 550ºC under a N_2 flow of 50 cm^3 min^{-1} and a heating rate of 10ºC min^{-1} in order to remove reactant and product residues. Afterwards, catalysts were heated to 800ºC under an air flow of 50 cm^3 min^{-1} and a heating rate of 10ºC min^{-1}. The coke content was determined from the weight loss between 550 y 800ºC, related to the weight of spent catalysts free of residue.

In order to determine the H/C ratio of coke deposited on spent catalysts, zeolite was treated with 40% HF to dissolve the siliceous matrix and release the trapped coke. Elemental analysis of the extracted coke was performed on an LECO CHNS-932 microanalyzer. H/C ratio values from 0.4 to 0.7 indicate that coke is polyaromatic[6].

RESULTS

Effect of temperature and pressure on the properties of reaction media

Temperature and reactant concentration are the most important factors influencing the reaction kinetics. Since experiments were performed in a wide range of pressure and temperature, it is important to analyze their effect on the properties of reaction media. Density, which changes drastically with temperature and pressure, has a direct influence on the reactant concentration. Thus, density is expressed in terms of concentration in this work, as mol L^{-1}. Fig. 2 shows the evolution of ethylbenzene density with pressure for the selected temperatures, calculated by means of Peng Robinson equation of state. The density increases sharply at temperatures below critical value due to the phase change from gas to liquid. Above the critical temperature, the increase of density is caused by the change from gas to supercritical conditions. The closer the temperature to the critical point, the greater and more pronounced the increase of density.
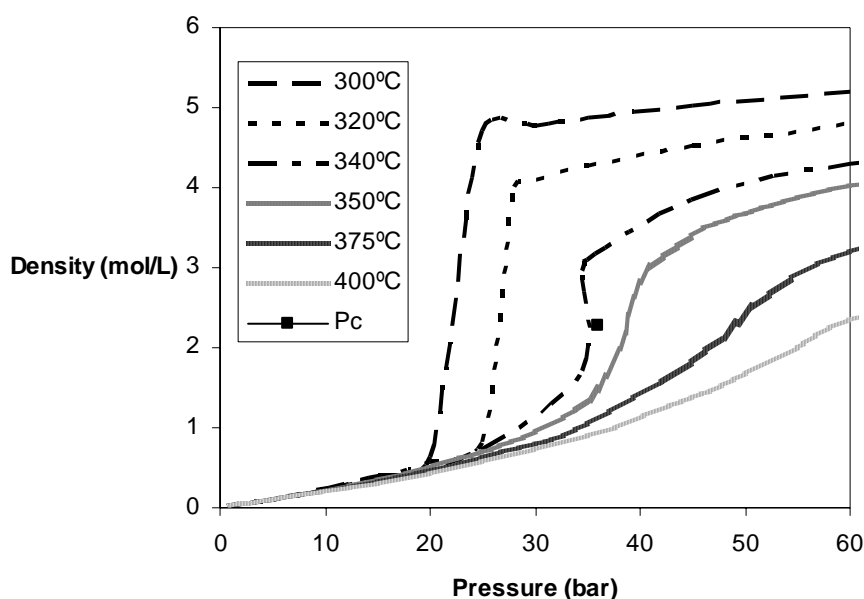
Figure 2. Evolution of density of ethylbenzene with pressure at several temperatures.

Catalytic experiments

The results of the catalytic experiments are shown in Fig. 3 as ethylbenzene conversion versus pressure at different temperatures. Conversion improves significantly with pressure at all temperatures in gas phase, due to the increase of density and concentration with pressure. The maximum conversion at each temperature is obtained when reaction media changes from gas to liquid or supercritical phase depending on temperature (below or above the critical value). The reason is that the density at liquid and supercritical conditions is higher than the density in gas phase. At liquid or supercritical conditions, conversion does not practically vary with pressure.
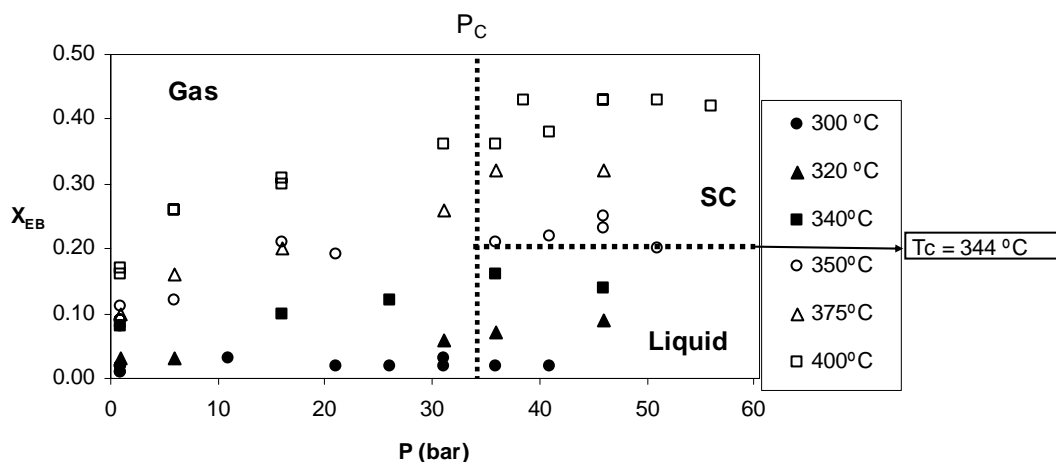

Figure 3. Effect of pressure on ethylbenzene conversion at several temperatures.

On the other hand, the temperature has the expected effect on reaction kinetics, conversion increases as temperature does till the thermodynamic equilibrium is reached. Thus, the maximum conversion, near the thermodynamic equilibrium, was obtained at 400 ºC and pressures above the critical value (supercritical conditions). These results can be explained as a combination of the high density of the reaction media and the high temperature. However, the high values of density in liquid phase do not lead to high conversions due to the low temperatures, inherent in these conditions.

Characterization of coke

Table 1 shows the coke content of the catalysts (CC) and its H/C ratio, obtained from the characterization of spent catalysts tested at several reaction conditions, as an example.

Table 1. Results of the characterization of the coke deposited (TOS = 3 h)

T (ºC)	P (bar)	CC (%)	H/C	X (%)	S (%)	Phase
300	1	0.7	-	2	96	Gas
300	46	0.4	-	3	99	Liquid
340	1	0.4	-	7	92	Gas
340	46	0.7	-	15	93	Liquid
350	1	0.7	-	9	94	Gas
350	46	0.9	-	25	92	SC
400	1	1.8	0.64	16	75	Gas
400	46	6.2	0.55	40	70	SC

At 400 ºC and 46 bar (supercritical conditions), conversion as well as coke deposition show the highest values. Thus, it seems to be a close relation between the progress of the main reaction and coke formation and deposition. However, it is important to analyze deeply the results obtained in the critical point vicinity (temperature from 340 to 350ºC and 46 bar). At these conditions, conversions obtained are equal or higher than that obtained in gas phase (400 ºC, 1 bar), which is the conventional reaction media. The high density of media near the critical point determines high conversion values in spite of the fact that temperature is lower than the corresponding to gas phase. Thus, the evolution of coke content with time-on-stream was studied in the vicinity of the critical point. The results are shown in Table 2.

Table 2. Comparison of coke content in the critical point vicinity (TOS = 18 h)

T (ºC)	P (bar)	CC (%)		Phase
		TOS=3h	TOS=18h	
340	46	0.7	0.7	Liquid
350	46	0.9	0.9	SC
400	1	1.8	2.9	Gas

It can be observed that in the critical point vicinity, coke content is negligible and is not affected by the increase of time-on-stream, both in liquid and supercritical phase. However, the coke content continuously increases with time-on-stream at gas phase.

Especially, at 350ºC and 46 bar, conversion is greater than that obtained in gas phase and coke deposition does not occur. These results can be explained considering that the temperature is not high enough to favour coke formation reactions. It can also be explained considering that supercritical reaction fluid possesses a larger ability of coke extraction than gas phase [4].

CONCLUSIONS

In the ethylbenzene disproportionation reactions, the highest conversion is obtained at 400ºC and 45 bar in supercritical phase, due to the combination of the high density of the media and the high reaction temperature. However, the content and aromaticity of the coke deposited in these conditions are also the highest, caused by the combined influence of pressure and temperature.
Near the critical point, it is possible to profit from the high density of the media, working at relatively low temperatures. In these conditions coke deposition is insignificant.

ACKNOWLEDGEMENTS

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