TRANSALKYLATION OF DIETHYLBENZENE WITH BENZENE IN SUPERCRITICAL CARBON DIOXIDE: INFLUENCE OF STRUCTURE AND ACIDITY OF ZEOLITIC CATALYSTS.

Uguina, M.A.*[1], Rodríguez, A.[1], Capilla, D.[1], López, B.[1], Pérez, A.[1] and Cavani, F.[2]
[1]Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, SPAIN.
email: uguinama@quim.ucm.es Fax: +34 394 4114
[2] Dipartimento di Chimica Industriale e dei Materiali, INSTM, Research Unit of Bologna. Viale Risorgimento 4, 40136 Bologna, ITALY.

1 INTRODUCTION

Ethylbenzene (EB) is commercially one of the largest volume derivates of benzene. The worldwide production of EB is 23 million metric tons per year with a 4 % annual growth. The 90 % of EB world's production is employed in the manufacture of styrene, the other 10 % is used in other applications like paint solvents and pharmaceuticals [1].

EB is mostly synthesized by benzene (B) ethylation over acidic catalysts. This reaction is accompanied by the formation of many polyalkylates, mainly isomers of diethylbenzene (DEB), and also cumene, butylbenzenes and ethylene oligomers. In order to transform these by-products in more valuable ones, the transalkylation reaction between B and DEB to obtain EB is carried out. However, transalkylation requires higher acid strength and more severe reaction conditions than alkylation, which becomes unselective at those conditions [2].

Since 1950s, the synthesis of EB was performed using Friedel-Crafts catalysts like $AlCl_3$. Nevertheless, the operating costs associated with the corrosivity, safe handling and disposal of this type of catalysts as well as a higher environmental conscience during the last decades, have made the industry to move towards a zeolite based technology, making the process cleaner, less corrosive and more economically competitive.

Most of the zeolites employed suffered from fast deactivation due to coke deposition, since the size of the molecules implicated and the bulky bimolecular intermediate compound slowly diffuse out of the zeolite pore structure. Therefore large-pore zeolites, such as type Y, beta and mordenite have been reported as the ones with the best performance [3] .

In supercritical phase, density and transport properties can be continuously pressure-tuned in the critical region to obtain unique fluid properties (e.g. gas-like transport properties, liquid-like solvent power and heat capacities). These properties can favour the extraction of coke precursors from the catalyst surface and their transport out of the pores before they are transformed into consolidated coke. The advantages of using CO_2 as supercritical reaction media for optimizing catalyst activity and product selectivity have been proved for a variety of reactions including alkylation on solid-acid catalysts [4].

The effect of acidity and structure of different zeolites on the transalkylation of DEB with B using supercritical conditions has been studied. Acid commercial large pore zeolites with BEA, FAU and MOR structures and different silicon to tetrahedrical aluminium molar ratio (Si/Al_T) were employed. To select the most adequate acidity for each type of structure different discontinuous essays were done. Then, continuous tests were carried out to study the stability of the catalysts previously selected. CO_2 was used as solvent in order to work at milder reaction conditions in terms of temperature.

2. MATERIALS AND METHODS

2.1. Materials

Benzene of high purity grade (>99.7 %), provided by Merck and a mixture of 1,2-, 1,3-, and 1,4- DEB isomers with a 95 % purity, supplied by Aldrich, were used as reactants. Liquefied CO_2 of high purity was provided by Air Liquide.

2.2. Catalysts

Commercial zeolites with different topologies and Si/Al molar ratio were used in their powdered and acid forms. Beta zeolites (HB) were supplied by Zeocat, type Y zeolites (HY) by Tosoh and Mordenite (HMOR) by Engelhard. The catalysts were activated by calcination at 550ºC for 5 hours prior to the reaction.
All samples were characterised by X-ray diffraction (PHILIPS X`PERT MPD instrument) to determine their crystallinity that in all cases was 100%. Si/Al ratio was measured by X-ray fluorescence (PHILIPS PW-1480 instrument) and Al-extra framework was quantified by 27Al MAS NMR (VARIAN VXR-300 spectrometer). The acidity was determined by ammonia temperature programmed desorption measurements (ATPD). The ammonia desorption profile was deconvoluted and the area under each peak as well as its maximum temperature allows comparing the acid strength distribution of the catalysts. The physicochemical properties of the zeolites are summarized on Table 1.

Table 1. Physicochemical properties of the catalysts.

Catalyst	Si/Al	% Al_T	Si/Al_T	Acidity distribution, µmol NH_3 (T_{max}, ºC)			
				Peak 1	Peak 2	Peak 3	Total
HB-13	12	80	15	92(311)	214(388)	83(538)	389
HB-38	38	88	43	43(321)	162(382)	35(550)	239
HB-75	72	100	72	9(311)	65(374)	40(550)	114
HMOR-10	10	88	12	334(408)	356(516)	52(550)	785
HMOR-23	22,5	87	14,3	227(417)	265(508)	9(550)	500
HMOR-58	54	93	58	60(348)	227(477)	18(550)	306
HY-3	3	66	4	79 (284)	240(351)	341(444)	661
HY-15	16	84	19	39 (302)	205(382)	110(521)	354
HY-40	42	83	51	10(278)	100(343)	48(540)	159

2.2. Experimental set up and procedure

2.2.1 Discontinuous Reactor.

The preliminary catalytic runs were carried out in a stainless steel batch reactor of 300 ml of capacity. Initially, the benzene and the catalyst were loaded into the reactor. Reaction temperature was achieved by a heating jacket and maintained within ± 2ºC. No benzene conversion was detected during heating step. Liquefied CO_2 was added prior to heating. As the reactor worked at autogenous pressure, the mass of the reactants and solvent at the reaction conditions was calculated previously to reach the reaction pressure within ± 5%. Once steady conditions were achieved, DEB was fed in by pressurized N_2, zero time for the reaction. After the reaction time, the reactor was cooled down and then slowly depressurized. The liquid samples were collected to be analyzed by GC in a Varian CP 3800 Gas Chromatograph, with a CP Sil 5 column (15-m length x 0.32-mm ID) and FID detector. Figure 1 shows the experimental apparatus.

2.2.1 Continuous Flow reactor.

A continuous down-flow fixed bed reactor, 1.75 cm internal diameter and 30.5 cm length was employed to determine catalysts life. The aromatic substrate was fed into the reaction system by a membrane-pump (Dosapro Milton Roy). The substrate flowrate was measured by weight in order to determine the effective contact time. Liquefied CO_2 was added from a pressurized bottle and cooled down by a compact-cold-thermostat before being pumped with an independent pump (Dosapro Milton Roy). The mixture of aromatics and CO_2 passed through a preheater before entering the reactor. Reaction temperature was achieved by a heating jacket and maintained within ± 2ºC. The reaction pressure was kept constant by a pressure control valve. Both, heating jackets and pressure valve were connected to PID controllers. Initially, the reaction mixture bypassed the reactor, and once steady conditions were reached, the reactants stream was redirected into the reactor. The product stream passed through a condensation system and the output was collected at different time on stream values to be analyzed by GC.

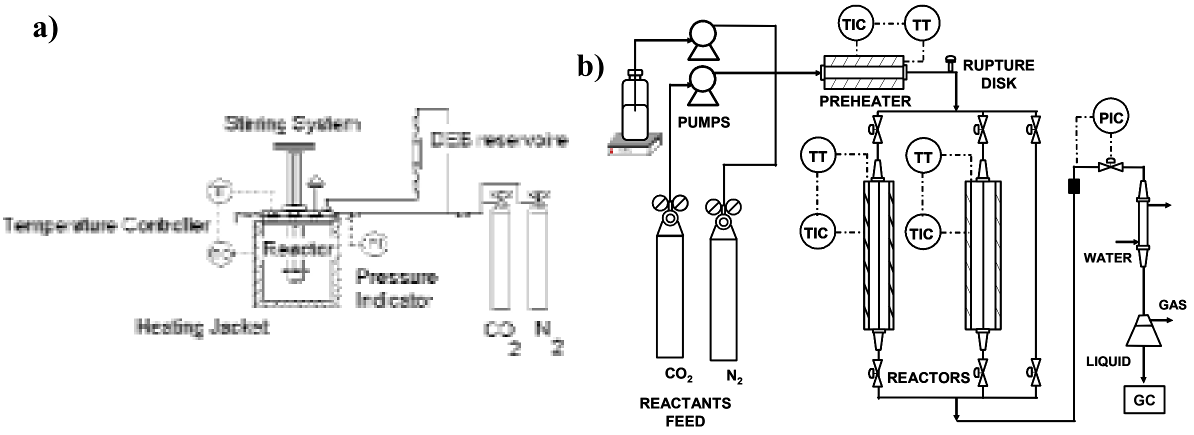

Figure 1. a) Discontinuous Flow Reactor. **b)** Continuous flow reactor

3 RESULTS AND DISCUSSION

3.1 Selection of the reaction conditions.

3.1.1 Discontinuous tests.

According to literature [2, 3], a B/DEB molar ratio ≥ 7 was necessary to reach high values of DEB conversion and to avoid the side reaction of disproportion; therefore a B/DEB of 10 was chosen.

To establish the operating conditions of the catalytic tests, it was necessary to calculate the critical point of the different reactants mixtures in order to define the supercritical (SC) phase. Since no experimental data were available, the critical points of the different reaction mixtures were simulated with ASPEN PLUS® Simulation Engine, by using a predictive equation of state. Previous simulations showed that Predictive Redlich Kwon Soave equation (PSRK) was the most accurate one.

Different simulations were done varying the CO_2 to aromatics molar ratio (CO_2/Ar). The results showed that as CO_2 proportion increased, the critical temperature decreased while the critical pressure showed a maximum (Figure 2). The CO_2 content was chosen so that the critical pressure was the lowest one without an excessive aromatics dilution. Thus, catalysts screening tests were conducted at a CO_2/Ar of 10, at which the minimum critical pressure is reached (124 bar).

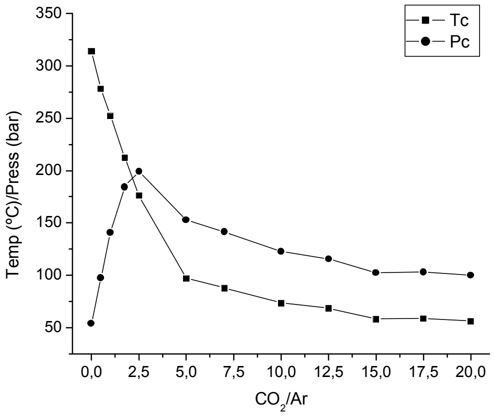

Figure 2. Evolution of the critical point for the feed mixture B/DEB = 10 with the CO_2/Ar molar ratio

Nevertheless, to be sure of working at SC conditions, a pressure slightly higher than the critical one, 130 bar, was chosen. Temperature was established in 200 ºC, far away from the critical value (74 ºC), due to kinetic requirements. The reaction time was two hours since not complete conversion was achieve, making possible the comparison among catalysts. The mass of catalyst was 5 % of (B+DEB) mass in the reaction mixture to assure an excess with respect to the aromatic ring.

3.1.1 Continuous tests.

All the continuous flow tests were done at the same experimental conditions: 130 bar , 300 ºC and a contact time (W/F) of 7 min. As in the discontinuous tests, a B/DEB and CO_2/Ar molar ratios equal to 10 were used.

3.2 Effect of the catalysts structure and acidity

3.2.1 Discontinuous essays

Figure 3 shows the catalytic performance of all the samples essayed, as EB yield and EB selectivity. It can be observed that all the catalysts tested showed a high selectivity to EB always higher than 98% without noticeable differences among them. However, the EB yield is affected by the structure as well as by the acidity of the samples.

The highest EB yield corresponded to the FAU structure as result of its opened structure as it can be expected. However, the BEA structure showed the lowest value of this parameter. This cannot be only explained by the different pore sizes of these structures as all these zeolites possess 12-MR pore openings. Furthermore, BEA structure has three–dimensional interconnecting channels system whereas MOR structure is characterized by one-dimensional channels. So, as the structural advantage of the beta zeolites should lead to higher EB yield than mordenites, the acidity of the different catalysts have to be taken into account.

Table 1 shows that the total acidity decreased when Si/Al molar increased as it can be expected. Related to acid strength distribution, it can be observed that the deconvolution of the ATPD profiles in the MOR samples lead to peaks at higher maximum temperatures than the other ones, that can be assigned to higher strength of acid sites. In the case of zeolites with BEA structure, H-B 13 presented the highest EB yield (27 %) due to its higher total acidity (389 µmol NH3) as compared with the other samples. On the other hand, for zeolites with MOR structure, the highest EB yield (37 %) was obtained with HMOR- 23. This zeolite had an acidity of 500 µmol NH3, lower than the acidity of HMOR-10 (750 µmol NH3), but the strongest acidity (higher T_{max}). Results for zeolites with FAU structure showed that HY-15 had an EB yield of 61 % and, as in the case of HMOR-23, its acidity (354 µmol NH3) was lower than HY- 3 one (661 µmol NH3) but it also had the highest amount of strong acid sites.

Comparing the best catalysts of each structure, HB-13, HMOR-23 and HY-15, it can be observed that HY-15 presented the highest EB yield. Similar results were found on literature [3]. The optimum Si/Al relationship is different for each structure, being very similar for the cases of HY-15 and HB-13, both of them with three-dimensional structure. Zeolite HMOR-23 with a one-dimensional structure of channels required the highest acidity.

Afterwards the stability of these three catalysts was tested on the continuous essays

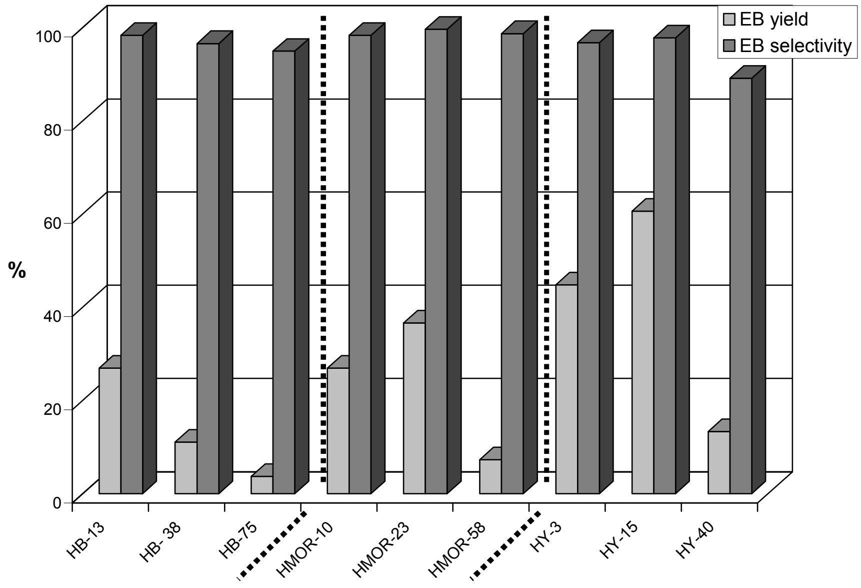

Figure 3. Effect of the acidity of BEA **a)** MOR **b)** and FAU **c)** structures on their performances.

3.2.2 Continuous essays.

The results obtained on the stability tests are shown on Figure 4. It can be observed that HB-13 had the lowest initial EB yield but its loss of activity during 75 hours was only a 20 %. On the other hand, HY-15 and HMOR-23 presented a high initial EB yield but a high deactivation rate.

The high initial EB yield of HMOR-23 was due to its high acidity and high amount of strong acid sites, however its structure of one-dimensional channels favoured the deactivation by coke deposition. The coke was deposited outside of the pores and impeded the access of the substrates to the inner acid sites. As it is a one-dimensional structure with no interconnection among the pores, the pore blockage conducts to a fast deactivation [5].

On HY-15 the high initial EB yield can be due to its high number of strong acid sites and its fast deactivation a consequence of the big cavities in the interconnection of the channels called “super cages”. These cages allow the formation of big poliaromatic compounds and the consequent deposition of coke onto the acid sites placed in them. The high initial deactivation rate observed during the first 20 hours of reaction was a consequence of both the coke deposition and the saturation of the super cages. Afterwards only the more external acid sites were accessible to the reactants.

HB-13 was the catalyst with the highest stability during the 80 hours of the test. The BEA structure allowed the transalkylation reaction in the space around the acid sites but not the formation of coke by condensation of poliaromatics due to steric limitations. Similar results were found on literature [6,7].

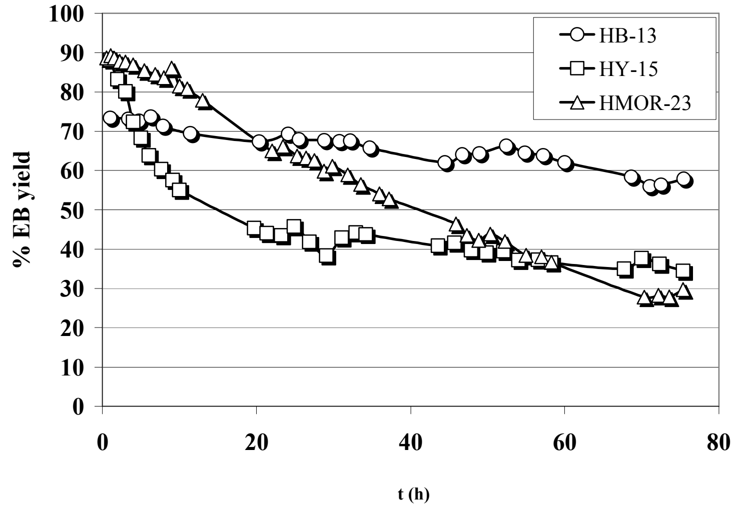

Figure 4. Effect of the zeolites structure on their stability.

4. CONCLUSIONS.

From all the catalysts essayed, the highest EB yield was obtained by HY-15 (61 %), followed by HMOR-23 (37 %) and finally HB-13 (27 %). In the stability test, both HY-15 and HMOR-23 presented high initial EB yields due to their higher acidity, but also showed a high deactivation rate because of their structure. All these facts evidence the importance of the combined role played by acidity, acid sites distribution and structure on the transalkylation reaction, showing that HB-13 has the best structure–acidity relationship for this reaction at SC conditions.

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