THE INFLUENCE OF STRUCTURE AND ACIDITY OF ZEOLITIC MATERIALS ON THE TRANSALKYLATION OF DIISOPROPYLBENZENE WITH BENZENE IN SUPERCRITICAL CARBON DIOXIDE.

Sotelo[a], J.L., Calvo[a]*, L., Pérez[a] A., and Capilla[a], D.

[a] Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad
Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, SPAIN.
Phone: +34 91 3944185 Fax: +34 91 394 4114 email: lcalvo@quim.ucm.es

Cavani[b], F., Bolognini, M.
[b] Dipartimento di Chimica Industriale e dei Materiali, Viale Risorgimento 4, 40136 Bologna,
ITALY.

INTRODUCTION

Monoalkylbenzenes (isopropylbenzene and ethylbenzene) are important intermediates for the synthesis of large-scale chemical commodities, i.e phenol (from isopropylbenzene) and styrene (from ethylbenzene). The synthesis of isopropylbenzene (cumene, CUM) by benzene (B) isopropylation over acidic catalysts is usually accompanied by the formation of polyalkylates, mainly isomers of diisopropylbenzene (DIPB). From an industrial point of view, transformation of these by-products into valuable products is interesting. Thus, dialkylates can be transformed to CUM by further reaction with B (transalkylation).

The installed capacity of cumene through transalkylation is around 700.000-1.000.000 tons per year, depending on the zeolite technology adopted in the alkylation section, and it is expected to grow as the producing plants change into zeolite based technology.

Due to the size of molecules, and due to the fact that the mechanism of the transalkylation reaction is known to involve a bulky bimolecular compound as the reaction intermediate, zeolitic materials belonging to the large-cavities class have been primarily investigated and claimed [1,2,3]. The hydrogen form of Beta (H-B), Y (H-Y) and ZMS zeolite types were specifically disclosed in several patents [4,5,6].

On the other hand, transalkylation reactions proceed on strong Brönsted acid sites [7], which are function of the framework Al content. The presence of extra-framework Al can decrease the catalytic activity of the zeolite. Theoretical models developed to explain relations between acidity and framework composition suggest that, as framework Al decreases, the fraction of "isolated" Al atoms increases resulting in a raise in the acid strength of the active sites [8]. Accordingly, the relation between the Si/Al ratio, responsible of the number and strength of the active sites, and the catalytic activity of the zeolites can be described by curves with a maximum, where the catalyst performance is the best.

Adsorption/desorption and pore-transport are key parameters influencing the activity and product selectivity in the transformation of alkylaromatics in porous catalysts. With conventional media (gas or liquid phase), it is difficult to achieve the desired combination of fluid properties for optimum system performance. In contrast, 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), which may overcome limitations of heterogeneously catalysed reactions. Formed intermediates and coke-precursors may desorb faster from solid catalysts due to their higher solubility and improved mass transfer in supercritical medium. Damages of the catalysts by “hotspots” in exothermic reactions may be reduced as consequence of enhanced heat transfer [9].

The aim of this work was to investigate the influence of structure and acidity of zeolitic materials on the transalkylation of DIPB with B in supercritical carbon dioxide. Thus, H-B, H-Y and H-Mordenite (H-MOR) commercial zeolites with different aluminium contents (e.g. Si/Al molar ratio) were compared in terms of yield and selectivity.

MATERIALS AND METHODOLOGY

Materials. All reagents were analytical grade from Aldrich. The diisopropylbenzene was used in its para-form. Catalysts were obtained from commercial providers in powdered form. Their source as well as their properties are shown on Table 1. They were activated by calcination at 550ºC for 5 hours, stored in a dessicator until weighted and charged to the reactor.

Table 1: Nomenclature and characteristics of employed catalysts.

Catalyst	**Supplier**	**Si/Al**	**Al4**	**Si/Al4**	**Cristallinity**	**Total acidity**	**Fraction and strength of acid sites (%)**		
		molar ratio	*(%)*	*molar ratio*	*(%)*	*(μmol NH3)*	*Weak*	*Medium*	*High*
H-B 12	Zeocat	12	80	15	100	389	24	55	21
H-B 38	Zeocat	38	88	43	100	239	18	68	15
H-B 75	Zeocat	75	100	72	100	114	8	57	35
H-Y 3	Tosoh	3	66	4	100	661	12	36	52
H-Y 16	Tosoh	16	84	19	100	354	11	58	31
H-Y 42	Tosoh	42	83	51	100	159	6	63	31
H-MOR 10	CVB	10	88	12	100	785	43	45	7
H-MOR 45	CVB	45	97	46	100	316	7	82	11
H-MOR 54	CVB	54	93	58	100	306	20	74	6

Apparatus and Methodology. The experimental work was conducted using a 300 ml-capacity batch reactor. To start up an experiment, the benzene and the catalyst were loaded into the reactor. Then, liquefied CO_2 was added from the bottle at its vapor pressure. Reaction temperature was achieved by a heating jacket and maintained within ± 2ºC. No benzene conversion was detected during heating up phase. The reaction pressure, as defined by the initial volume of the solution and the temperature, varied within ± 5% from the pre-established value. Once steady conditions were achieved, the transalkylation agent was fed in by pressurized N_2. That time was taken as zero time for the reaction. Following the prescribed reaction time, pressure was slowly reduced and the mixture was cooled down. The liquid samples were collected to be analyzed by GC.

Analytical procedures. A Varian CP 3800 Gas Cromatograph, equipped with a CP Sil 5 column (15-m length x 0.32-mm ID) and a FID detector was used to quantify the products in liquid samples.

Catalysts characterization. Catalysts were characterized by means of (i) Atomic Absorption or X-ray fluorescence, to determine the effective Al and Si content, (ii) RMN to distinguish the extra-frame Al fraction, and (iii) X-ray diffraction to determine the crystallinity of the samples. The evaluation of acid sites distribution was done by ammonia adsorption and desorption under programmed temperature (TPD). Typical conditions for ammonia TPD were the following: Pretreatment at 550°C for 120 min; Adsorption: pulse of 10% ammonia/He at 200°C till saturation; Evacuation: He flowing for 1 h at 200°C; Desorption: heating 10°C/min from 200°C to 550°C, holding till complete desorption. Deconvolution of TPD profile was done in 3 Gaussian peaks.

RESULTS AND DISCUSSION

Prior to decide the operating conditions, it was necessary to define the supercritical state where a single and homogeneous phase occurs. Since no experimental data were available, the P-V-T behavior of the reaction mixture was estimated. Thus, the phase diagram was simulated using the Predictive Redlich Kwong Soave (PSRK) equation of state with the Hoderbaum-Gmehling mixing rule which uses the Gibbs excess energy. Only the major components were used for the simulation, that is the reactants and main product. This meant four component mixtures. The critical point of the mixtures was obtained at the point where the liquid and gaseous phase become identical.

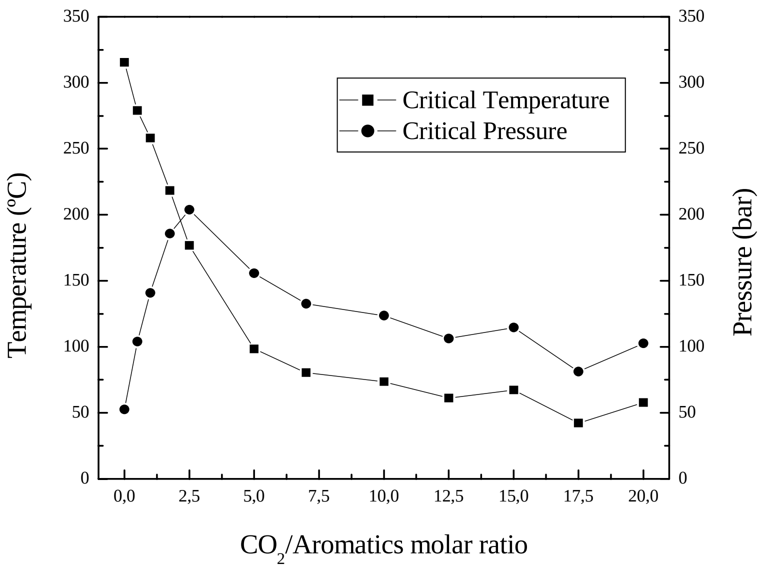

Figure 1: Effect of CO_2/aromatics molar ratio on critical pressure and temperature of the mixtures.

The results showed that as CO_2 proportion increased, the critical temperature decreased while the critical pressure showed a maximum (Figure 1). The CO_2 content was chosen so that the critical pressure was relatively low. Thus, catalysts screening tests were conducted at a 100:10:1 CO_2:Benzene:Diisopropylbenzene molar ratio. For this mixture, critical pressure was 125 bar. Based on this prediction, supercritical tests were run at 130 bar. On the other hand, the critical temperature of the mixture was 74ºC; however, working at those temperatures, the p-DIPB conversion was negligible. Higher temperatures were necessary for rate acceleration. Consequently, the catalysts performance on cumene production was investigated at 200ºC.

Apart from the reactants and cumene, other byproducts were followed in the liquid samples. Seven major products were identified by mass spectroscopy, including toluene, ethylbenzene, n-propylbenzene, secbutylbenzene, m-diisopropylbenzene, diphenylbenzene and 1-ethyl, 3-isopropylbenzene. Except for the last two compounds (that were difficult to find commercially or handle) the others were analyzed in all samples. Typically, detected products accounted for more than 99% mass fraction in the effluent. The isomerization product, m-diisopropylbenzene was found to be the major byproduct. Thus, product yield and selectivity were calculated taking only into account the transalkylation and isomerization products. Mass balance ranged from 92% to 100%. Average uncertainty in reported data was typically ± 8%.

Three types of acid zeolites were used as catalysts: Y, Beta and Mordenite with different acidity degree. All of them had a cristallinity degree higher than 95%. A catalyst/aromatic substrate weight ratio of 5% was used. The results of their performance on the transalkylation of p-DIPB with B to produce CUM are shown on Figures 2 to 4. Reaction time was two hours while agitation speed was 500 rpm. Reactivity was insignificant in blank tests.

For H-Y zeolites, the best result was achieved in the case of H-Y 16, yielding a conversion degree to cumene of 77%. This sample had an 84% framework aluminum and a total acidity equivalent to 354 μmol NH_3 with only an 11% weak acid sites. H-Y 3 gave a high conversion due to its high acidity but presented lower selectivity than H-Y 16. This can be due to the high fraction of weak acid sites associated to the presence of extra-frame aluminum (34%) and to the effect of Faujasite (FAU) structure on the acidity of the protons bonded to Al atoms. H-Y 42 showed lower conversion and selectivity due to its low number of active sites.

In the case of Beta structure, the highest conversion and selectivity (90% and 69%, respectively) were found with H-B 12, containing an 80% of framework aluminum and 389 μmol NH_3. H-B 75 showed higher selectivity than H-B 38 because of the higher fraction of strong acid sites of the former or to the higher degree of framework aluminum of the latter one.

For Mordenite (MOR) structure, it can be observed that the structural acidity was much higher than in the case of Beta or Y zeolites. Thus, the best result (71% cumene yield) was found for H-MOR 45, with 97% of framework aluminum and 316 μmol NH_3 which only contained 7% weak acid sites. H-MOR 54 showed lower conversion and selectivity. This could be explained because the presence of higher amount of extra-framework aluminum species and the higher fraction of weak acid sites. H-MOR 10 gave a high conversion due to its high acidity. However, this sample presented lower selectivity than H-MOR 45 because of the high fraction of weak acid sites and to the effect of MOR structure on the acidity of the protons bonded to Al atoms.

The isomerization product (m-DIBP), in thermodynamic equilibrium ratio (2/1 m/p-DIPB molar ratio) was reached in the cases in which transalkylation occurred in high extent. On the contrary, for transalkylation reaction the equilibrium was not always achieved. This suggests that the acid strength required for transalkylation reaction is higher than needed to equilibrate the mixture of isomers, or that the nature of the catalyst make the isomerization to proceed faster than the transalkylation. This occurs specially at high temperatures, because isomerization is characterized by higher activation energy than transalkylation [1,2].

CONCLUSIONS

This work was devoted to investigate the behavior of different zeolite materials on the synthesis of cumene by benzene transalkylation in supercritical conditions. The impact of acidity degree was also studied, discovering that the optimum Si/Al molar ratio was different in each type of zeolite. For H-B and H-Y zeolites, it was found to be about 12 and 16, respectively, where total acidity was within 350 to 500 μmol NH_3, and the aluminum atoms were strongly incorporated in the structure of the zeolite. This same acidity degree was reached at a Si/Al ratio around 45 for MOR zeolite structure, indicating that the acidity of Al atoms was different depending on the solid structure. As a result of the presence of extra-frame Al-containing species, the catalytic activity decreased, explaining the detrimental effect on cumene production for samples containing higher Si/Al ratios than the optimum.

At the most favorable Si/Al ratio, the three type of zeolites yielded equilibrium conversion (about 85%) and similar cumene yield and selectivity, around 70% and 80%, respectively. Based on these results, it is difficult to decide which one would perform better at industrial scale. Therefore, it is necessary a deeper study on deactivation rate and other aspects (e.g., behavior against pressure, byproducts formation) to choose the more adequate zeolite structure for this reaction.

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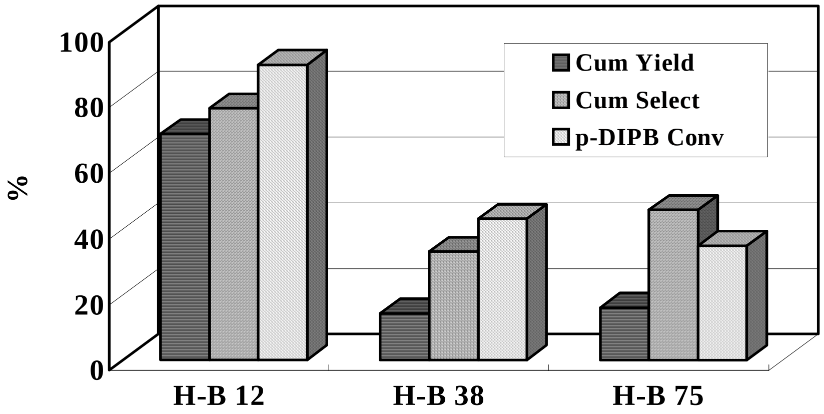

Figure 2: Effect of acidity degree of Beta zeolites on p-DIPB conversion, and CUM yield and selectivity.

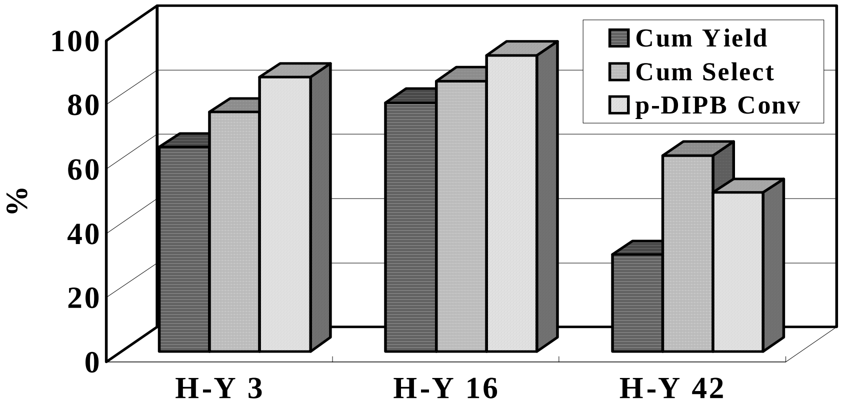

Figure 3: Effect of acidity degree of Y zeolites on p-DIPB conversion, and CUM yield and selectivity.

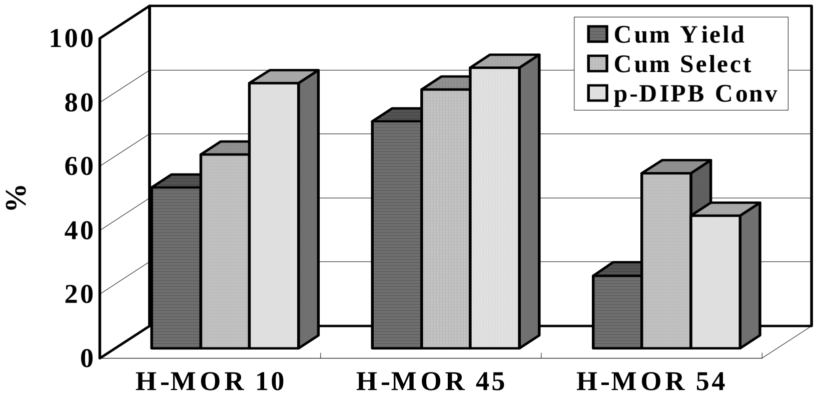

Figure 4: Effect of acidity degree of Mordenite zeolites on p-DIPB conversion, and CUM yield and selectivity.