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# Styrene from toluene by combinatorial catalysis

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## Abstract

The side-chain alkylation of toluene with methanol is one alternative technology to produce styrene that has been given attention in the last few years. In the literature basic materials has been proposed as catalyst for the reaction but the real number of tested catalysts is very small and few preparation parameters have been taken into account. In this work a combinatorial approach has been used to explore the possibilities of basic zeolites to carry out such reaction. To do this, the following catalyst variables have been studied: nature of zeolite, framework composition, nature and content of compensating cation and method of incorporation (exchange, impregnation). The results obtained confirm the requirements of both basic and acid sites in the catalysts and show the compromise between these two functions. The study carried out shows that zeolite-based catalysts are still poor reactive to give the styrene/ethylbenzene yields required for converting this process in a real alternative to the existing one, based on the alkylation of benzene with ethylene, followed by the dehydrogenation of ethylbenzene to styrene.

*Keywords:* Toluene alkylation; Styrene; Combinatorial methodology; High-throughput screening; Discovery algorithm

## 1. Introduction

Styrene is an industrially important chemical that is used for production of plastics and rubbers. This molecule is industrially produced by two subsequent reactions: the alkylation of benzene with ethylene to produce ethylbenzene and its dehydrogenation to styrene. There is a potentially interesting alternative route for production of styrene, which involves the direct side-chain alkylation of toluene with methanol. Indeed, back in 1967, Sidorenko et al. [1] showed that alkali exchanged zeolites were active catalysts for this reaction. Since then, a large number of papers and patents have been published and some of the earlier ones are given here as reference [2–18]. It was known that basic catalysts direct the alkylation of toluene to the formation of chain-alkylated products, while acid catalysts produce ring alkylation [2]. More specifically, basic zeolites such as Cs-X, Rb-X and Cs-Y give side-chain alkylation [1], and the selectivity to styrene can be improved by adding B, P, Cu or Ag to the basic zeolite [3–5]. Also, small quantities of alkali-hydroxide particles entrapped within the alfa cavities of faujasite, strongly increase the alkylation in the side-chain of alkylaromatics [6–8]. Other basic solids such as magnesium oxide and hydrotalcite have also been used as toluene alkylation catalysts [19].

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With respect to the mechanism of the side-chain alkylation reaction, it is generally accepted that formaldehyde produced via dehydrogenation of methanol is the alkylating agent, and this is the controlling step of the whole process [1,10]. NMR and IR in situ studies together with quantum chemical calculations [23] have strongly improved the knowledge about the details of the mechanism of the reaction. It has been established that the key requirements for a successful side-chain alkylation catalyst are: (i) sufficient base strength to generate the alkylating agent (formaldehyde); (ii) enough amount of weak Lewis acid sites able to stabilize sorbed toluene and polarise its methyl groups; (iii) a balanced sorption stoichiometry of the two reactants. In other words, a good balance between the acid–base properties of the catalyst should be achieved.

Despite the relatively deep mechanistic knowledge achieved, a side-chain alkylation catalyst giving high conversion and selectivity has not been reported up to now and there is room for improving the design of such type of catalysts.

In this paper, we report a case study concerning the application of a combinatorial methodology to the selection of a catalytic material for the side-chain alkylation of toluene. The catalytic parameters space has been constrained to the area of basic zeolites. The zeolite systems have been selected as potentially suitable for tuning the basicity–acidity characteristics of the catalysts and for favouring the bimolecular reaction owing to the reactant proximity within the micropores.

Specifically, the catalysts are composed of zeolites (X, Y, Beta, ZSM5 and L) exchanged and/or impregnated with alkali and alkali-earth and have been prepared in parallel by means of a robotic system. These catalysts were screened in a high-throughput fixed bed continuous reactor system on an iterative manner while learning when proceeding.

## 2. Experimental

### 2.1. Description of the search strategy

#### 2.1.1. Catalyst parameters

Basic zeolites can be obtained essentially by ionic exchange or impregnation (or by combination of both methods) of basic cations on neutral zeolites. Most of the preparation parameters for the zeolites modification have a strong effect on the catalytic activity. The investigation strategy consisted of combining the most usual parameters of the synthesis: (i) nature of zeolites (medium-large pore zeolites at different $SiO_2/Al_2O_3$ molar ratio, neutralized with $Na^+$ or $K^+$; in particular, NaZSM5, NaY, NaX, NaBeta and KL), (ii) mixture of the above zeolites (100 wt.%, 75–25 wt.% or 50–50 wt.%), (iii) preparation method (ionic exchange and/or impregnation), (iv) loading of the basic cation for the impregnation procedure (0.5, 1.0, 1.5 or 2 wt.%), (v) nature of basic cation chosen among alkali and alkali-earth elements (Li, Na, K, Rb, Cs, Mg, Ca, Sr and Ba) and (vi) cation precursor (highly soluble in water and easily decomposed by thermal treatment, as nitrate, acetate and hydroxide).

Binary combinations of zeolites are here considered; in that case some synergism/interaction between them may occur, not only from the point of view of the intrinsic catalytic activity but also of performance of the basic cation exchange/impregnation during the preparation.

These basic materials are very sensible to air pollutants (e.g. $CO_2$) and moisture. At the same time, the procedure applied to decompose the precursors of the basic cations affects notably the final basic strength of the active sites. For these reasons, the calcination was performed before reaction directly in the reactor under controlled atmosphere (see Section 2.3).

#### 2.1.2. Test parameters

According to the literature [4,6–9,20–22,24], temperature, feed composition and space velocity influence greatly the catalytic performance. Therefore, the following experimental conditions were selected: (i) gas phase reaction at atmospheric pressure; (ii) temperature range of 380–500 °C; (iii) toluene/methanol molar ratio from 0.1 to 5, often with inert dilution (i.e. He/mixture ca. 5/1); (iv) WHSV of 1–10 $h^{-1}$.

In order to simplify the comparison among the catalytic performances of these materials, a well-defined set of conditions were applied for the screening of all samples (see Section 2.3). These conditions were chosen to minimize the secondary reactions of methanol, including water and coke formation. The selectivity to the most interesting products (styrene and ethylbenzene from basic catalysis and xylenes from acid one) are referred to the conversion of the reactant present in lower amount (i.e. methanol).

### 2.1.3. Evolutionary strategy

The following parameters have been selected for the screening: five zeolites, nine basic cations, three types of cation precursors (nitrate, acetate and hydroxide, the latter only for the alkali cations), three preparation methods (ionic exchange, impregnation and their combination), four cation loadings and two binary mixtures of zeolites (50–50 and 25–75 wt.%). The number of calculated combinations within for this parameter space is larger than 250.000. A strategy for the design of libraries are therefore crucial to reduce strongly the number of tested materials in order to speed up the discovery of new active catalysts.

Recently, an evolutionary strategy was successfully applied to the design of libraries resulting in the discovery and optimisation of new mixed oxides catalysts [25]. In the present work all selected parameters of the synthesis are discrete and therefore a new genetic algorithm (GA) able to operate with qualitative data on the basis of binary coding had to be developed (Fig. 1). The catalysts were described as 100 disjunctive variables (also called descriptors). These variables can be categorized in three groups: preparation variables, interaction variables and additional aggregated variables.

In addition, the genetic algorithm was hybridised with a knowledge-based system (KBS) which enables to extract, update and validate knowledge from all the tested catalysts. This learning method is based on the extraction of equivalence classes, which accumulates strategic information on the whole search space previously explored. It also allows to monitor efficiently the browsing–exploitation ratio or, in other words, the chemist can guide the design of catalysts generation either to cover as much as possible the whole parameter space or to focus on well-defined area (defined by selected parameters) which have been revealed as promising by the KBS. Details on the hybrid algorithm can be found elsewhere [26].

In order to improve the learning process, additional information (here called additional aggregated variables, Table 1) were added to the catalysts encoding, namely: $SiO_2/Al_2O_3$ molar ratio, pore size, number of member ring (i.e. number of tetrahedra constituting the channel structure of the zeolite), cation charge, crystal ionic radius, atomic radius and electronegativity. In the case study, the learning proceeded on two classes of catalysts defined as “bad” and “good” according to an objective function (Eq. (1)). This function was chosen to give more importance to the production of styrene (desired product of reaction) and a lower one to ethylbenzene (obtained by consecutive hydrogenation of styrene, but anyway indicative of basic catalysis). Despite the limited number of experiments, we were able to confirm most of empirical rules found by the described algorithm by classical frequency and contingency table studies.

$$y = \tfrac{3}{4}\text{yield (styrene)} + \tfrac{1}{4}\text{yield (ethylbenzene)} \qquad (1)$$

The first generation containing 32 catalysts was designed on a random manner with a statistical

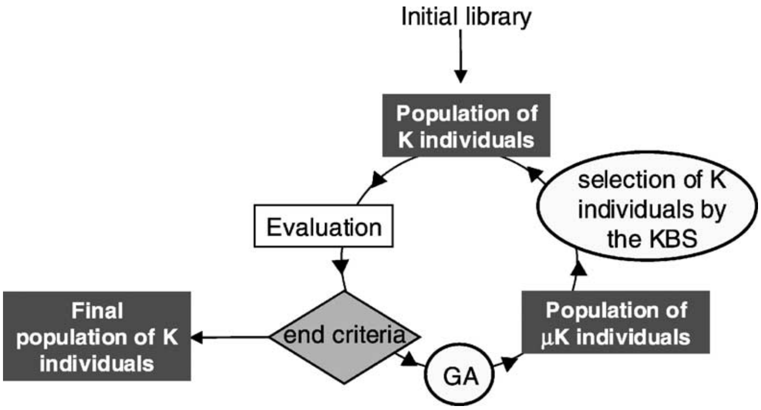


Fig. 1. Diagram of the evolutionary strategy.

Table 1
Physico-chemical characteristics of alkali and alkali-earth cations and zeolites

| Zeolite type | Pore size (Å) | Number of member ring | $SiO_2/Al_2O_3$ molar ratio | | | |
|---|---|---|---|---|---|---|
| KL | 7.1 | 12 | 6.0 | | | |
| NaZSM5 | 5.5 | 10 | 23 | | | |
| NaY | 7.4 | 12 | 5.6 | | | |
| NaBeta | 5.5–7.0 | 12 | 25 | | | |
| NaX | 7.4 | 12 | 1.1 | | | |
| Cations | Crystal ionic radius (Å) | Atomic radius (Å) | Electronegativity ($\chi$) | Line number | Ionisation energy I (II) (kJ/mol) | Charge (+) |
| Li | 0.68 | 2.05 | 0.98 | 2 | 513.3 | 1 |
| Na | 0.97 | 2.23 | 0.93 | 3 | 495.8 | 1 |
| K | 1.33 | 2.77 | 0.82 | 4 | 418.8 | 1 |
| Rb | 1.47 | 2.98 | 0.82 | 5 | 403.0 | 1 |
| Cs | 1.67 | 3.34 | 0.79 | 6 | 375.7 | 1 |
| Mg | 0.66 | 1.72 | 1.31 | 3 | 737.7 (1450.7) | 2 |
| Ca | 0.99 | 2.23 | 1.00 | 4 | 589.7 (1145.4) | 2 |
| Sr | 1.12 | 2.45 | 0.95 | 5 | 549.5 (1064.2) | 2 |
| Ba | 1.34 | 2.78 | 0.89 | 6 | 502.8 (965.2) | 2 |

partitioning of the parameters space (equal frequency of zeolites, preparation methods, elements and precursors type) in order to allow an easier recognition of relevant parameters.

### 2.2. Catalysts preparation

Samples of same generation were prepared in a truly parallel fashion by using the robotic system Zinsser SOPHAS, able to carry out all the liquid handling steps under inert atmosphere. First, 0.6 g of zeolites or binary mixture of zeolites were placed manually in 8 ml glass vials which were supported on 4 × 8 racks. To assure the adequate mixing of binary combinations, the rack was shacked for 1 h.

For the ionic exchange procedure, 5 ml of aqueous solution of the basic cation precursor ($[M] = 0.06–0.2$ M) was added to the zeolites. The suspensions were then shacked for 2 h at 25 °C. After a short sedimentation of the powders down to the vials, the suspensions were filtered from the top with needles equipped with filters. The wet unwashed solids were dried under $N_2$ stream at 120 °C for 12 h. For the wetness impregnation, the desired amount of the basic cation precursor in aqueous solution ($[M] = 8$ g/l, $V_{tot} = 5$ ml), was added to the zeolites to get the desired loading. After 2 h shaking at room temperature, the water was evaporated under nitrogen at 120 °C for 12 h. For samples prepared both by ionic exchange and impregnation, the ionic exchange was performed first.

In Table 2 all materials and their preparation variables are listed. The materials are named with consecutive numbers (from 1 to 96), divided in three generations of 32 samples. The preparation variables of each material are reported in the same line of the sample in the rows of the corresponding generation (e.g. the preparation variables of sample 64 can be found in the last row of the table corresponding to the second generation).

### 2.3. Catalytic test

High-throughput catalytic tests were carried out by means of a multiple continuous reactor system [27], which allows to test 16 catalysts in parallel. In this automated system, the measurement and/or control of temperature, pressure, flow of nitrogen feed (gas) and liquid mixture feed is carried out in each of 16 microreactors, individually.

The calcination was performed prior to reaction in the same reaction system at 520 °C under $CO_2$ free air (50 ml/min flow) for 1 h and under nitrogen (110 ml/min flow) for 2 h. The reaction conditions for the catalytic testing were: 450 °C, atmospheric pressure, toluene/methanol molar ratio = 5, nitrogen/mixture

Table 2
Composition and preparation procedure of the three generations screened

| Sample | Zeolites | | | | Cations | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Type 1 | % | Type 2 | % | Exchange | Precursor | Impregnation | Precursor | % |
| First generation | | | | | | | | | |
| 1 | NaZSM5 | 100 | | | Li | Nitrate | | | |
| 2 | NaX | 100 | | | Cs | Acetate | | | |
| 3 | NaY | 100 | | | Ca | Hydroxide | | | |
| 4 | Naβ | 100 | | | Sr | Nitrate | | | |
| 5 | NaZSM5 | 100 | | | | | K | Hydroxide | 0.5 |
| 6 | NaX | 100 | | | | | Rb | Hydroxide | 1 |
| 7 | NaY | 100 | | | | | Ca | Nitrate | 1.5 |
| 8 | Naβ | 100 | | | | | Sr | Acetate | 2 |
| 9 | NaZSM5 | 100 | | | K | Hydroxide | Ca | Nitrate | 0.5 |
| 10 | NaX | 100 | | | Mg | Acetate | Cs | Acetate | 2 |
| 11 | NaY | 100 | | | Ca | Nitrate | Cs | Hydroxide | 1.5 |
| 12 | Naβ | 100 | | | Ba | Hydroxide | Mg | Nitrate | 1 |
| 13 | KL | 100 | | | Li | Acetate | K | Acetate | 1 |
| 14 | KL | 100 | | | Na | Nitrate | Li | Hydroxide | 0.5 |
| 15 | KL | 100 | | | Rb | Nitrate | Li | Nitrate | 2 |
| 16 | KL | 100 | | | Sr | Acetate | Na | Acetate | 1.5 |
| 17 | NaZSM5 | 25 | NaX | 75 | K | Acetate | | | |
| 18 | NaZSM5 | 50 | NaX | 50 | Rb | Hydroxide | | | |
| 19 | NaY | 75 | NaX | 25 | Mg | Nitrate | | | |
| 20 | Naβ | 25 | KL | 75 | Ba | Acetate | | | |
| 21 | NaZSM5 | 50 | NaY | 50 | | | Ba | Hydroxide | 1.5 |
| 22 | NaX | 75 | NaY | 25 | | | Rb | Nitrate | 2 |
| 23 | NaY | 25 | KL | 75 | | | Cs | Acetate | 2 |
| 24 | Naβ | 50 | KL | 50 | | | Sr | Hydroxide | 1 |
| 25 | NaZSM5 | 75 | KL | 25 | Rb | Acetate | Na | Hydroxide | 1 |
| 26 | NaX | 25 | KL | 75 | Li | Hydroxide | Li | Acetate | 0.5 |
| 27 | NaY | 50 | KL | 50 | Sr | Acetate | Ca | Acetate | 0.5 |
| 28 | Naβ | 75 | NaY | 25 | Ba | Hydroxide | Ba | Nitrate | 1.5 |
| 29 | NaZSM5 | 25 | Naβ | 75 | Cs | Nitrate | K | Hydroxide | 0.5 |
| 30 | NaX | 50 | Naβ | 50 | Mg | Hydroxide | Mg | Acetate | 1 |
| 31 | NaY | 75 | Naβ | 25 | Ca | Acetate | Ca | Nitrate | 2 |
| 32 | Naβ | 25 | NaZSM5 | 75 | Sr | Hydroxide | Sr | Nitrate | 1 |
| Second generation | | | | | | | | | |
| 33 | KL | 100 | | | Sr | Acetate | | | |
| 34 | NaY | 100 | | | | | Ca | Nitrate | 1.5 |
| 35 | Naβ | 100 | | | | | Sr | Acetate | 1 |
| 36 | NaX | 100 | | | Li | Acetate | | | |
| 37 | NaZSM5 | 100 | | | K | Nitrate | | | |
| 38 | NaX | 100 | | | Rb | Nitrate | | | |
| 39 | KL | 100 | | | Cs | Hydroxide | | | |
| 40 | NaX | 100 | | | | | Mg | Acetate | 0.5 |
| 41 | Naβ | 100 | | | Mg | Nitrate | | | |
| 42 | NaZSM5 | 100 | | | Ca | Nitrate | | | |
| 43 | NaY | 100 | | | Ba | Nitrate | | | |
| 44 | NaX | 100 | | | Cs | Nitrate | Mg | Nitrate | 0.5 |
| 45 | KL | 100 | | | Mg | Acetate | Na | Acetate | 1.5 |
| 46 | NaY | 100 | | | Na | Acetate | | | |
| 47 | Naβ | 100 | | | | | Sr | Nitrate | 2 |
| 48 | NaX | 100 | | | | | Na | Hydroxide | 2 |
| 49 | NaZSM5 | 100 | | | | | K | Acetate | 0.5 |

Table 2 (*Continued*)

| Sample | Zeolites | | | | Cations | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Type 1 | % | Type 2 | % | Exchange | Precursor | Impregnation | Precursor | % |
| 50 | NaZSM5 | 100 | | | | | Cs | Hydroxide | 2 |
| 51 | KL | 100 | | | | | Li | Hydroxide | 1 |
| 52 | NaY | 100 | | | | | Ca | Nitrate | 1.5 |
| 53 | KL | 100 | | | | | Ba | Acetate | 2 |
| 54 | Naβ | 100 | | | | | Rb | Hydroxide | 0.5 |
| 55 | NaY | 50 | KL | 50 | Ba | Acetate | Ca | Nitrate | 1.5 |
| 56 | NaZSM5 | 25 | NaY | 75 | Ca | Acetate | Sr | Acetate | 1 |
| 57 | KL | 75 | Naβ | 25 | Rb | Acetate | Li | Hydroxide | 2 |
| 58 | NaX | 50 | NaY | 50 | Na | Hydroxide | K | Nitrate | 0.5 |
| 59 | NaY | 50 | NaX | 50 | Sr | Nitrate | Ba | Acetate | 0.5 |
| 60 | Naβ | 75 | NaX | 25 | Cs | Hydroxide | Rb | Acetate | 1 |
| 61 | NaX | 25 | KL | 75 | Mg | Hydroxide | Cs | Hydroxide | 0.5 |
| 62 | NaZSM5 | 25 | Naβ | 75 | Li | Nitrate | Mg | Acetate | 1 |
| 63 | Naβ | 75 | NaZSM5 | 25 | K | Hydroxide | Na | Nitrate | 1.5 |
| 64 | KL | 75 | NaY | 25 | Ba | Acetate | Sr | Nitrate | 2 |
| Third generation | | | | | | | | | |
| 65 | NaX | 100 | | | | | Na | Acetate | 2.5 |
| 66 | NaZSM5 | 100 | | | | | Na | Acetate | 2.5 |
| 67 | NaX | 100 | | | | | Na | Hydroxide | 2.5 |
| 68 | NaX | 25 | NaZSM5 | 75 | | | Na | Hydroxide | 2.5 |
| 69 | NaX | 100 | | 0 | | | Mg | Acetate | 0.25 |
| 70 | NaX | 100 | | 0 | | | Mg | Nitrate | 0.25 |
| 71 | NaZSM5 | 25 | NaX | 75 | | | Mg | Acetate | 0.25 |
| 72 | NaZSM5 | 25 | NaX | 75 | | | Mg | Acetate | 2.5 |
| 73 | NaX | 25 | NaZSM5 | 75 | K | Acetate | Li | Acetate | 1 |
| 74 | NaX | 100 | | | | | Li | Hydroxide | 2 |
| 75 | NaZSM5 | 100 | | | K | Hydroxide | Mg | Acetate | 1 |
| 76 | NaZSM5 | 100 | | | | | Na | Acetate | 2 |
| 77 | NaY | 100 | NaX | | K | Nitrate | | | |
| 78 | NaY | 25 | NaX | 75 | | | Li | Hydroxide | 0.5 |
| 79 | NaY | 25 | NaX | 75 | K | Hydroxide | | | |
| 80 | KL | 100 | | | K | Nitrate | Li | Acetate | 0.5 |
| 81 | KL | 100 | | | | | Li | Hydroxide | 2 |
| 82 | KL | 100 | | | K | Nitrate | Mg | Acetate | 2.5 |
| 83 | NaZSM5 | 25 | NaY | 75 | | | Li | Hydroxide | 0.5 |
| 84 | NaZSM5 | 25 | NaX | 75 | K | Acetate | | | |
| 85 | NaZSM5 | 25 | NaX | 75 | | | Mg | Acetate | 2 |
| 86 | KL | 25 | NaZSM5 | 75 | | | Rb | Acetate | 2 |
| 87 | NaX | 25 | NaY | 75 | | | K | Acetate | 2 |
| 88 | NaX | 25 | NaY | 75 | | | Mg | Acetate | 0.25 |
| 89 | KL | 25 | NaX | 75 | | | Li | Acetate | 0.5 |
| 90 | KL | 25 | NaZSM5 | 75 | Li | Acetate | | | |
| 91 | NaZSM5 | 100 | | | | | Li | Hydroxide | 2 |
| 92 | NaX | 100 | | | | | Rb | Acetate | 0.5 |
| 93 | NaX | 100 | | | Rb | Acetate | | | |
| 94 | NaX | 100 | | | K | Nitrate | | | |
| 95 | NaZSM5 | 100 | | | K | Hydroxide | | | |
| 96 | NaZSM5 | 100 | | | | | Li | Acetate | 0.5 |

molar ratio = 5 and contact time = 0.5 h. Reaction was maintained during 18 h (time on stream), being possible to carry out seven analysis for each catalyst. Catalytic results are therefore calculated with the products analysis obtained after reaching catalyst stabilisation.

The amount of catalyst in each fixed bed microreactor is 0.4 g and particle size 0.4–0.6 mm, for which internal diffusion was checked not to be the controlling step when using a reference catalyst (CsOH-NaX). The complexity of the reaction products and the low amounts of some of them require a conventional GC Analysis (Varian 3380GC), using a Carbowax capillary column, reaching an analysis time of ca. 8 min.

With the purpose of validating the results obtained by the multi-sample reactor, catalytic tests were carried out by means of a conventional laboratory fixed bed reactor (10 mm of internal diameter, holding 5 g of catalyst, particle size 0.4–0.8 mm).

## 3. Results and discussion

### 3.1. Validation of the reaction assay

Firstly, the catalytic results of the reference catalyst CsOH-NaX reported in [28] were reproduced in the laboratory fixed bed reactor. The experimental conditions were as those described for run number 2 of [28]: 430 °C, toluene/methanol molar ratio of 1/7.5, toluene/$N_2$ molar ratio of 0.11/1, $N_2$ flow of 70 ml/min. The reproducibility of literature data was satisfactory (see Table 3). However, these experimental conditions were not applied in the screening, because the large amount of methanol in the feed gave rise to the formation of a large amount of water at high conversion. The presence of large amount of water is probably the reason for a quite rapid catalyst deactivation (basic sites poisoning). Coke formation on catalyst surface was also observed.

Table 3
Catalytic performance comparing the reference [28] and experimentally reproduced data

| Catalytic performances | Reference data (%) | Present results (%) |
|---|---|---|
| MET conversion | 69 | 70.8 |
| TOL conversion | 30 | 23.2 |
| EB selectivity | 74 | 80.2 |
| STY selectivity | 4 | 8.8 |
| (EB + STY) yield | 23.4 | 20.6 |

MET: methanol; TOL: toluene; EB: ethylbenzene; STY: styrene.

Secondarily, another experiment with the same catalyst (CsOH-NaX) was run with both multi-sample and conventional reactor, at the reaction conditions described in Section 2.3 (i.e. large toluene/methanol feed ratio, in order to limit both basic sites poisoning and coke formation). A good reproducibility between the multi-sample and the conventional fixed bed reactor was obtained: methanol conversion (%) of 98.6 and 100, and styrene yield (%) of 1.36 and 1.30, respectively. In addition, a good degree of reproducibility within the different microreactors of the multi-sample system was confirmed.

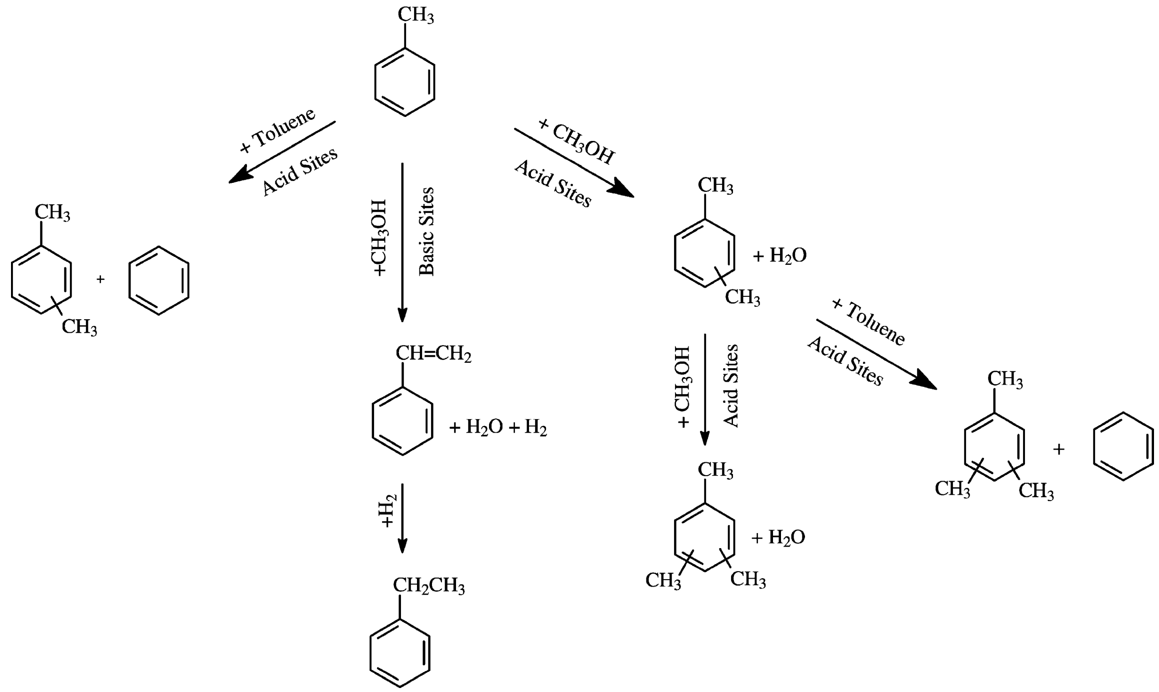
From the reaction products obtained, the following reactions are believed to occur in the catalytic test: toluene disproportionation, alkylation of toluene to xylenes, alkylation of toluene to ethylbenzene, alkylation of toluene to styrene, alkylation of xylenes to trimethylbenzenes, disproportion of xylenes and oligomerization of methanol. A reaction network based on product distribution is given in Scheme 1. The basic sites catalyse the side-chain alkylation, while the acidic sites catalyse the alkylation and transalkylation on the aromatic ring.

### 3.2. Search progress

#### 3.2.1. Results, learning and library design

Composition and preparation procedure for the 96 catalysts is displayed in Table 2. Fig. 2 shows the catalytic performances for the three generations. When considering the catalytic performances of all the catalysts tested, a positive evolution can be recognized. Specifically, an improvement can be observed in the formation of side-chain alkylation products (styrene and ethylbenzene) and a decrease in ring-alkylation products (xylenes). Inspite of these improvements of the catalytic performances, the best results are in the same range of those obtained by the reference catalyst [28]: 1.15% of styrene obtained with sample 64 with respect to 1.36% with the reference catalyst.

*3.2.1.1. First generation.* Seven catalysts (i.e. nos. 16, 17, 18, 22, 23, 26 and 31) showed a fitness (result of the objective function) above 36 (Fig. 2) and were



Scheme 1. Toluene–$CH_3OH$ alkylation reaction network over acid–base catalysts.

therefore selected to form the class of good catalyst on which the learning proceeded.

It was of course impossible to get clear rules from only 32 samples, yet tendencies could be enlightened. For example, the effect of cations was difficult to evaluate since the hits were quite dispersed and there was not enough data to remove ambiguities. Nevertheless, with variable coding of the cations charge (+1 or +2), it was clear that alkali cations were three times better than alkali-earth cations. Among the preparation variables, the nature of the zeolite showed a great influence: 44% of catalysts containing NaX were good against 10% for NaBeta. All catalysts containing Ba and Mg were bad, whereas for other cations there was at least one with good performances. High loading of cations for the impregnation (2 wt.%) was favourable, since 50% of the catalysts with a loading of 2 wt.% showed good results. It appeared also that there was not a privileged preparation method and that there was likely no synergy when mixing zeolites.

These results can be easily explained taking into account the basicity of the catalyst. Indeed, NaX is more “basic” than NaBeta because of its larger amount of Na located as counter-ion of Al in the structure (Table 1, see $SiO_2/Al_2O_3$ molar ratio). Zeolites containing Ba and Mg may present some extra Brönsted acidity due to the hydrolysis of water by the divalent cations. Finally, an excess of alkali cations over the exchange capacity will probably generate clusters of alkali oxide within the pores of the zeolite that present strong basicity [29].

In order to get a better tendency view, the algorithm parameters were tuned in such a way that a diverse generation of catalysts was designed, thus promoting the browsing of the parameter space. As a consequence, a lower probability was given by the algorithm to generate mixture of zeolites, because in the first generation any synergetic effects were not obtained.

*3.2.1.2. Second generation.* Although the yields are still far below the chemist requirements, the results showed clearly an overall improvement of the performances. The learning process was re-trained on both the first and second libraries (64 samples) by selecting those catalysts (i.e. nos. 26, 37, 40, 48 and 57) with fitness above 153.

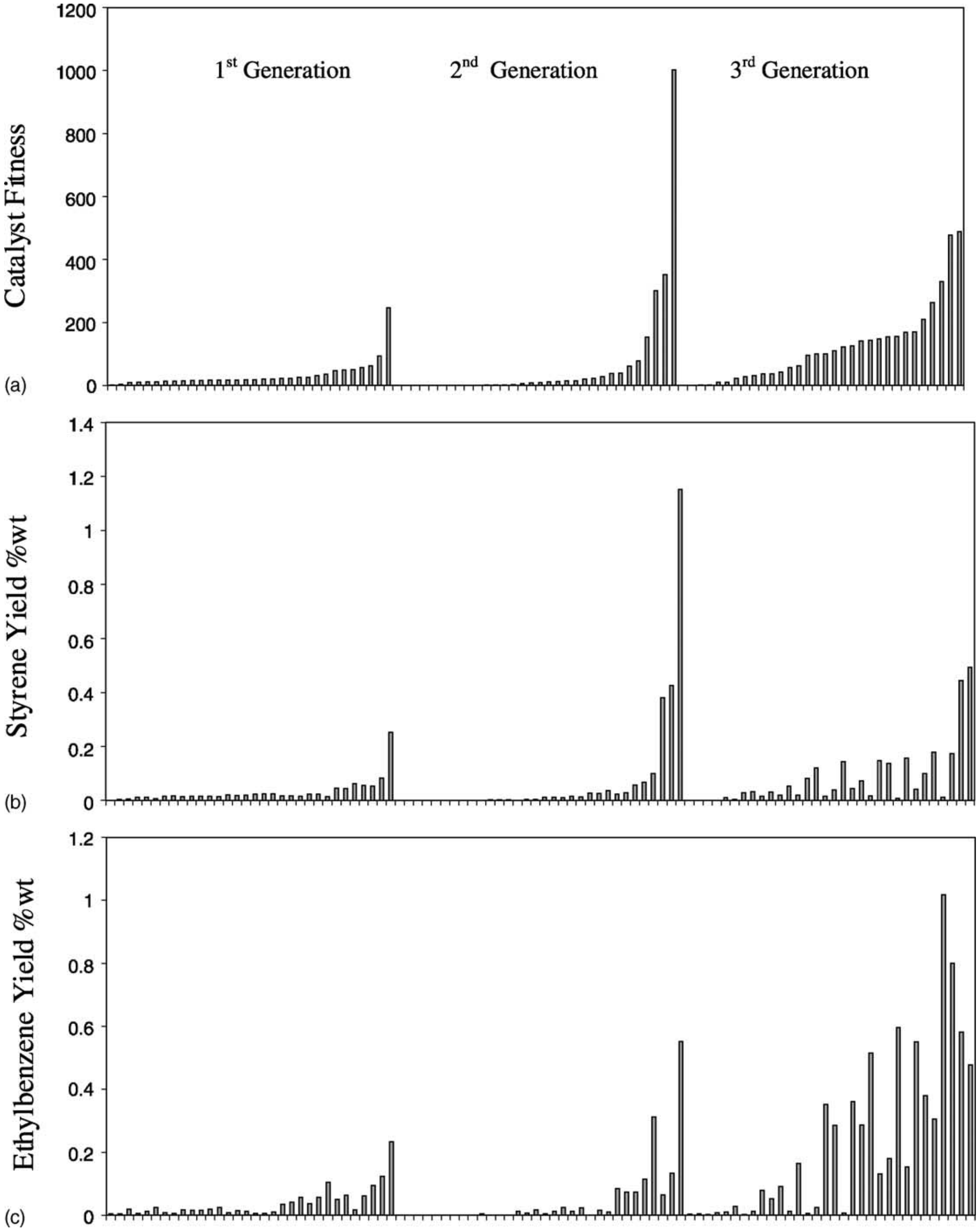


Fig. 2. Experimental results from the assay in the multi-sample reactor: (a) objective function, (b) styrene yield, (c) ethylbenzene yield and (d) xylenes yield for all the catalysts tested. The samples displayed are fitness-ordered for each generation.

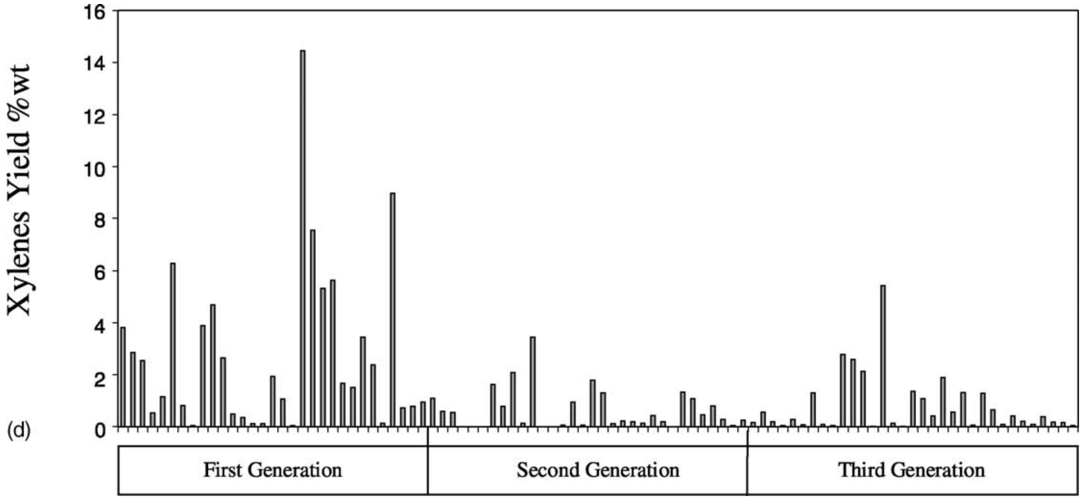


Fig. 2. (*Continued*).

It is important to note that the model was trained here with a very different set of catalysts that were useful to validate or invalidate the rules discovered at the first library. The zeolite NaX was confirmed as the best zeolite (18% of hit), whereas NaBeta and NaY led to bad catalysts. The cation effects were still difficult to evaluate since good performances were quite well distributed among the different preparations. Nevertheless, Li showed the highest probability to find good performances rate (22% of hit), whereas Ca, Sr and Ba showed only bad fitness. These results confirmed the relevance of the cation charge. Furthermore, we observed that K, Li and Rb all led to 20% of hits after ionic exchange, while Li, Mg and Na gave rise to 40, 20 and 20% of hits, respectively, in the case of impregnation. Interestingly, the cation loading in the case of the impregnation was revealed as a major feature. Indeed, we observed that the highest hit rates (16%) were obtained with the highest and lowest loading (2 and 0.5 wt.%, respectively), whereas medium loading results in only bad catalysts.

We have to keep in mind that the rules generated were only statistical tendencies and had no “direct” physical meaning. However, this unexpected behaviour would call for further investigations and characterisation.

As said before, besides the basic sites, weak acid sites are also required for this reaction in order to adsorb and “activate” the toluene molecules. The acid sites are in this case associated with the Lewis acidity of the cations and this follows the order Li $>$ Na $>$ K $>$ Rb $>$ Cs and Mg $>$ Ca $>$ Ba. If one considers that the basicity of the exchanged or the impregnated zeolite will follow the reverse order, it appears that a trade off between the two functions is required and this is shown above by the influence of the cation.

*3.2.1.3. Third generation.* The third generation was designed in such a way that the discovered rules were exploited. Thus, algorithm parameters were tuned to focus on: (i) NaX zeolites, (ii) ionic exchange with Li and K, (iii) impregnation with Li, Mg and Na, (iv) higher and lower weight loadings for impregnation (2.5 and 0.25 wt.%) and (v) acetate and hydroxide precursors for impregnation.

### *3.2.2. Validation of the rules performed on the 96 samples*

Results of the three libraries validated most of the rules determined after the screening of the second library (new set of good zeolites, i.e. nos. 26, 37, 40, 48, 67, 72, 73, 80 and 94). Among the zeolites, NaX was clearly the best material (36% of hits). K (31% of hits) and Li, Mg and Na were confirmed as the best cations for the ionic exchange and the impregnation, respectively. The high hit rates (33%) obtained for impregnated zeolites at 2 wt.% were very meaningful, allowing a clear validation of a rule that could be

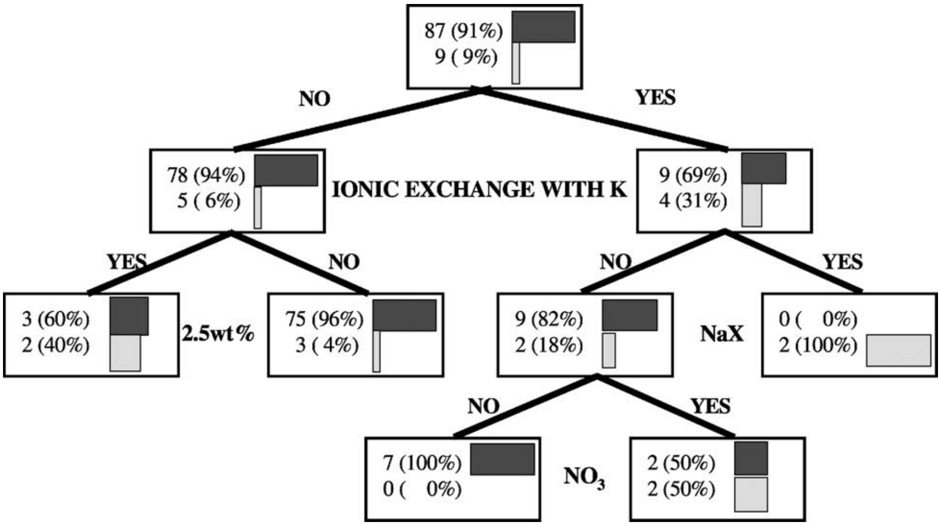


Fig. 3. Data modelling performed with the C4.5 algorithm on 96 catalysts. The dark and light charts represent the "bad" and "good" catalysts, respectively. Each node represents a disjunctive variable.

applied for further optimisation. Nevertheless, one minor rule was invalidated, nitrates, which appeared as bad precursors for ionic exchange in the first library, seemed clearly the best precursors type after the third screening. Because of the stochastic features of the screening, invalid tendencies can appear at the very beginning of the study, when not enough samples are tested. Therefore, it is utmost important to validate the learning process as the screening proceeds.

Learning on the additional aggregated variables (Table 1) has also confirmed the empirical rules. Clearly zeolites with low silica–alumina ratio ($SiO_2/Al_2O_3 < 5$), and therefore with lower average Sanderson's electronegativity after alkali introduction, and with pore diameter of 7.4 Å show better yields. On the other hand, cations, which combine high ionization energy and low crystal ionic radius, give better results. These trends confirm partially the good performances obtained for the NaX zeolite and the Li, K, Mg cations. The results given by these additional variables may appear redundant with the variables of the preparation, yet they could have been useful if a reduction of the space dimension would have been required for the data treatment.

For validation purposes, the same data set associated with the same objective function was analysed by the inductive graph technique C4.5 [30]. This decision tree method (Fig. 3) is a top–bottom classification where the nodes represent the modality of the variables (here the modality is two because we have only disjunctive variables) and the dark and light bars represent the percentage of the population which belong to the bad and good catalyst class, respectively. The classification shows clearly the relevance of performing ionic exchange with K since it increases the hit rate from 9 to 31%. In this case, when NaX is used as zeolite a rate of 100% is obtained. When NaX is not used, the choice of nitrate as precursor increases the probability from 18 to 50% to get a hit. On the other hand, when the ionic exchange with K is not chosen, the choice of 2.5 wt.% of impregnation allows increasing drastically the probability from 6 to 40%.

## 4. Conclusions

From the application of the combinatorial methodology to the study of basic zeolite catalyst, some interesting conclusions can be extracted. (i) High-throughput screening is possible also in the presence of a complex reaction as the side-chain alkylation of toluene to styrene and ethylbenzene. (ii) Solid basic zeolites can be prepared in parallel by one robotic apparatus. (iii) Application of screening strategy allows dealing with a reduced number of materials, taking into account all the preparation variables of one complex catalytic system.

The catalytic results obtained through this combinatorial work support the bifunctional acid–base nature of the catalysts for this reaction. The fact that NaX zeolite gives the best results among the different zeolites (KL, NaZSM5, NaBeta, NaY), confirms that the low $SiO_2/Al_2O_3$ molar ratio and the corresponding high basicity of the alkali exchanged samples (i.e. Li, K and Mg) are adequate to catalyse the first reaction step, i.e. the dehydrogenation of methanol to formaldehyde. It is interesting to notice that, differently from the literature data, the best results are not obtained with the most basic Rb and Cs exchanged samples, probably due to the low charge/radius ratio of the cations and to their consequent low acidity. The acidity in these catalysts seems to be fundamental to favour the adsorption–activation of toluene.

Nevertheless, based on the large number of variables and samples studied, it can be concluded that zeolite-based catalyst probably become limited to carry out the transformation of toluene into styrene with yields high enough to represent an industrial alternative to the existing processes.

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