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Nafion-H as catalyst for isobutane/2-butene alkylation compared with a cerium exchanged Y zeolite

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A solid superacidic Nafion-H polymer was examined as a catalyst for isobutane/2-butene alkylation and compared with a cerium-exchanged Y zeolite. Both catalysts demonstrate initial alkylation activity with rapid decrease in alkylation selectivity. The total product distributions were found to be significantly different after three hours of reaction. Nafion-H showed less selectivity towards iso-octanes, but formed relatively more 2,2,4-trimethylpentane. The differences between the two catalysts suggest dissimilar favoured reaction mechanisms.

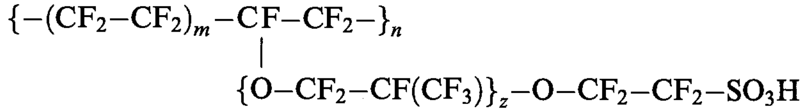
Keywords: isobutane/2-butene alkylation; Nafion-H; zeolite Y

1. Introduction

Alkylation of isobutane with light olefins gives branched paraffins favourable for the production of high octane gasoline. However, commercial alkylation processes involve use of the environmental hazardous sulphuric and hydrofluoric acids, and the catalyst costs are high [1,2]. Pentasil type of zeolites [3], different modified cubic faujasites [4–8], MCM-22 [9,10], MCM-36 [11], ZSM-4 [12] and zeolite β [9] are among the most studied alternatives. Over all these zeolites reaction resulted in rapid oligomerization instead of alkylation due to selectivity loss. The understanding of the catalytic properties of zeolites in alkylation is therefore important for further improvements.

Recently we have published data on H-EMT, H-FAU and CeY-98 (98% cerium exchanged zeolite) for isobutane/2-butene alkylation [13]. The results after three hours reaction showed a total preference for the 2,3,3- and 2,3,4-trimethylpentane (TMP) isomers compared with 2,2,4-TMP in the distribution of *i*-octanes. At thermodynamical equilibrium and in liquid acid alkylation, 2,2,4-TMP is the dominant iso-octane [4,5]. The difference in TMP distributions using zeolites or liquid acids suggests pore effects in the zeolite [14].

To investigate this effect further, we employed Nafion-H, a perfluorinated sulfonic acid resin with the general structure



$$\{-(\mathrm{CF_2}-\mathrm{CF_2})_m-\underset{\{\mathrm{O}-\mathrm{CF_2}-\mathrm{CF(CF_3)}\}_z-\mathrm{O}-\mathrm{CF_2}-\mathrm{CF_2}-\mathrm{SO_3H}}{\underset{|}{\mathrm{CF}}}-\mathrm{CF_2}-\}_n$$

(with $m = 5$–13.5, $n \approx 1000$ and $z = 1, 2, 3, \ldots$) as the catalyst. Nafion-H can be divided into hydrophobic ($\sim\mathrm{CF_2CF_2}\sim$) and hydrophilic ($\sim\mathrm{SO_3H}$) segments. The superacidity of the sulfonic acid group is attributed to the electron-withdrawing forces of the neighbouring perfluorocarbon groups [15]. Like 100% sulphuric acid, it has a Hammett acidity value of $\gtrsim -12$, and the thermal stability ranges up to 180–200°C [15,16]. Nafion-H has been tested as a catalyst in a wide variety of organic reactions, also in alkylation [16–20]. Different Nafion catalysed alkylation reactions are reviewed by Prakash and Olah [17] and include Friedel–Crafts alkylation, olefin/aromatic alkylation, alkylation with alcohols, alkyl esters, alkyl halides etc. The scope of this work is to investigate Nafion-H as a catalyst for isobutane/2-butene alkylation and to focus on possible differences in the products formed on a polymeric surface compared to porous zeolite materials like CeY-98.

2. Experimental

The superacidic Nafion-H (0.8 mmol $\mathrm{H^+}$/g) beads were obtained from Aldrich and predried at 100°C for 1 h. A commercial Y zeolite (Aldrich) was ion exchanged 98% with Ce (CeY-98), applying a procedure reported by Weitkamp [21]. The zeolite was calcined for 5 h in air at 540°C.

CeY-98 had a BET surface area of 592 $\mathrm{m^2/g}$ and a pore volume of 0.20 ml/g, while the surface area of Nafion-H was measured to 0.2 $\mathrm{m^2/g}$. The number of acid sites on CeY-98 was found to be 1.0 mmol/g by $\mathrm{NH_3}$ TPD measurements.

Liquid phase alkylation experiments were carried out in a 300 ml stirred semi-batch autoclave. The catalyst, 5 g of CeY-98 or 11 g Nafion-H, was placed in the reactor and dried before adding the isobutane (129 g). The mixture was heated to 80°C under nitrogen pressure. 2-butene was charged (0.106 g/min) until the molar ratio of 2-butene added to isobutane reached 1 : 10 (2 h). The stirring speed was set to 1200 rpm. One phase liquid samples were taken every 30 min and analysed by GC. Further details on experimental set-up and procedures are described elsewhere [13].

3. Results and discussion

The results after 3 h of reaction over Nafion-H and CeY-98 are summarised in table 1. Nafion-H gave the lowest total conversion of 2-butene per gram dry cat-

Table 1
Comparison of CeY-98 and Nafion-H activity and selectivity as alkylation catalysts after 3 h time of reaction

Catalyst	Nafion-H	CeY-98
conversion of 2-butene (g 2-butene converted / g dry catalyst)	0.4	1.0
yield (g C_{5-8} iso-paraffins / g 2-butene charged g dry catalyst)	0.02	0.04
selectivity (g C_{5-8} iso-paraffins / g 2-butene converted)	0.4	0.6
alkylate distribution (wt%)		
C_5 paraffins	6.4	4.4
C_6 paraffins	4.7	3.4
C_7 paraffins	4.7	4.3
C_8 paraffins	43.7	65.6
heavy prod. (C_{9+} paraffins and olefins)	41.6	22.4
i-octenes in C_8 product (wt%)	48.4	38.9
TMP/DMHx molar ratio	2.0	3.9

alyst. Fig. 1 shows the development of the butene conversion during the reaction. CeY-98 did show a higher initial activity compared with Nafion-H, but after 2 h the rate of conversion was about the same. The total turnover numbers (moles of 2-butene converted per mole active sites) were 18 and 10 for CeY-98 and Nafion-H, respectively. This estimate was based on ideal conditions, i.e. all acidic sites were accessible for reaction. Nafion-H beads have a low surface area (measured to 0.2 m^2/g), and it is questionable if all internal sulfonic acid groups are accessible for reaction. However, a microscopic investigation of cross sectioned deactivated beads, showed coking throughout the polymer.

CeY-98 exhibited the highest yield (defined as grams of C_5 to C_8 isoparaffins

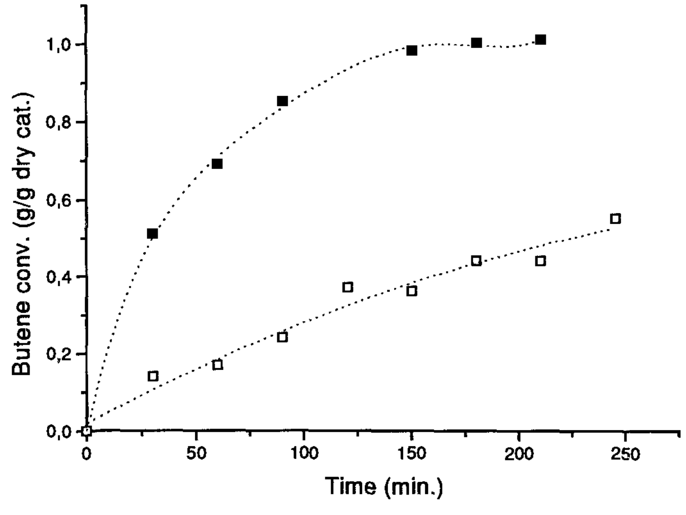


Fig. 1. Conversion of 2-butene (g/g dry catalyst) during reaction: (■) CeY-98 and (□) Nafion-H. Charging of 2-butene was stopped after 2 h.

per gram of 2-butene charged per gram of catalyst) and selectivity to alkylate (defined as grams of C_5 to C_8 iso-paraffins per gram of 2-butene converted) as shown in table 1. Nafion-H gave more heavy compounds than CeY-98, including isononanes, isononenes and larger molecules. Comparing the fraction of iso-octenes in the total C_8 product, Nafion-H also demonstrated a larger tendency of oligomerization instead of alkylation. After only 30 min of reaction, this fraction of octenes was for CeY-98 and Nafion-H 3.3% and 5.4% respectively, indicating a rapid loss of selectivity.

CeY-98 gave the highest molar ratio of trimethylpentanes to dimethylhexanes (TMP/DMHx) (table 1). Fig. 2a illustrates the formation of the TMP and DMHx

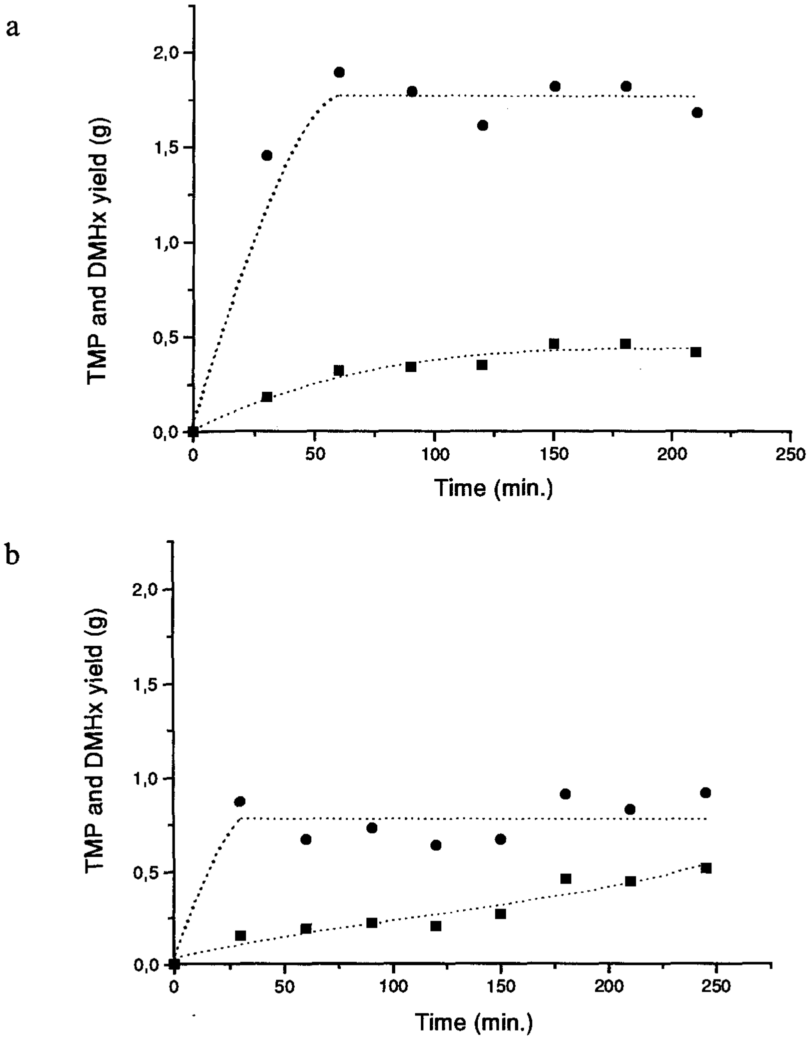


Fig. 2. The development of the trimethylpentane (●) and the dimethylhexane (■) yields (g) with catalyst deactivation for (a) CeY-98 and (b) Nafion-H.

during the reaction for CeY-98. After 60 min the production of TMP stopped, while the yield of DMHx increased for 150 min. Nafion-H was still generating DMHx after 150 min, but no TMP was formed after 30 min of reaction as seen by fig. 2b. Figs. 3a and 3b show the normalised iso-octane distribution after 30 min and 180 min, respectively. Nafion-H produced generally more dimethylhexanes than CeY-98 during the experiment, except for the key isomer 3,4-DMHx. The carbocation of 3,4-DMHx is believed to result from addition of a secondary butyl cation to 2-butene [5,22]. In an active catalyst the ion is expected to isomerise to 2,3- and 2,4-DMHx. However, due to catalyst deactivation, further isomerisation is limited, resulting in an increasing amount of the 3,4 isomer in the liquid product [5]. The molar ratios (2,3-DMHx + 2,4-DMHx)/3,4-DMHx for Nafion-H were 14 and 7 after 30 and 180 min, respectively. For CeY the corresponding ratios were 3.3 and 1. The comparison between the DMHx distributions of the catalysts suggests that Nafion-H has an overall greater ability to isomerise the 3,4-DMHx carbocation than the zeolite even after ageing.

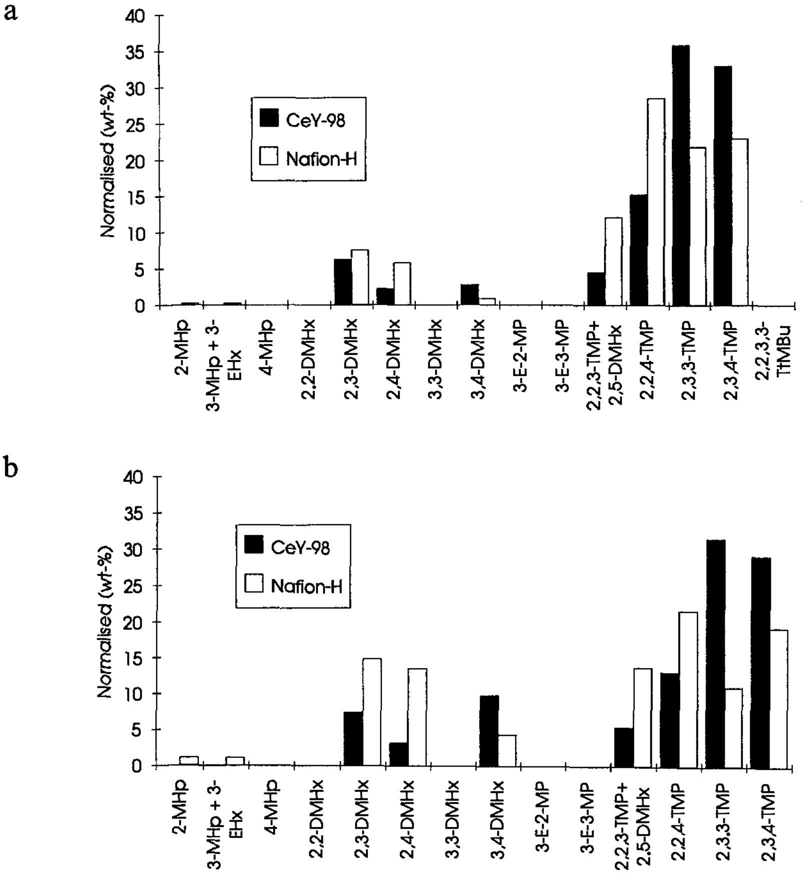


Fig. 3. Normalised distributions of iso-octanes formed by isobutane/2-butene alkylation over CeY-98 and Nafion-H after (a) 30 min and (b) 3 h.

The normalised distribution of iso-octanes (figs. 3a and 3b) shows that Nafion-H predominantly gives 2,2,4-TMP, while 2,3,3- and 2,3,4-TMP are the main components for CeY-98. Furthermore, CeY-98 produced a low amount of 2,2,3-TMP compared with Nafion-H. In fig. 4 the TMP distributions after 3 h are normalised and plotted together with the thermodynamical equilibrium values calculated for the gas phase at 80°C using data from Stull [23]. 2,2,4-TMP is the most favoured isomer at thermodynamical equilibrium while 2,2,3-TMP is the least favoured one. Nafion-H gave a TMP distribution closer to the equilibrium values, especially high in 2,2,4-TMP and low in 2,3,3-TMP in contrast to CeY-98. It seems that the TMP distribution formed over a zeolite is controlled by kinetics and not by thermodynamics.

The low contributions of 2,2,4-TMP from the overall TMP concentration in zeolite catalysed isobutane/butene alkylation are in the literature explained by steric effects and diffusion control caused by the narrow zeolite pores [5,14]. Chu and Chester [5] showed in their experiments, using a batch reactor, a decrease of the (2,2,3-TMP + 2,2,4-TMP)/(2,3,3-TMP + 2,3,4-TMP) ratio when the butene feed rate was increased. 2,3,4-TMP and 2,3,3-TMP have least sterical hindrance in their transition state and the highest rates of diffusion of the four isomers. This was claimed to be a possible reason for the observed selectivity change [5].

As described, the fraction of 2,2,4-TMP employing Nafion-H was high compared with the results using CeY-98. This could support the diffusion limitation theory in zeolite pores suggested by Chu and Chester [5]. However, the TMP molecules have similar kinetical diameter, and therefore large differences in the diffusivity due to their sizes are not expected. Plug flow reactor experiments have shown that the formation of 2,2,4-TMP was high after 1 min time on stream over zeolite beta and zeolite Y, decreasing rapidly after only a few minutes time [4,6]. Very active catalysts tested in a semi-batch slurry reactor produced, compared with

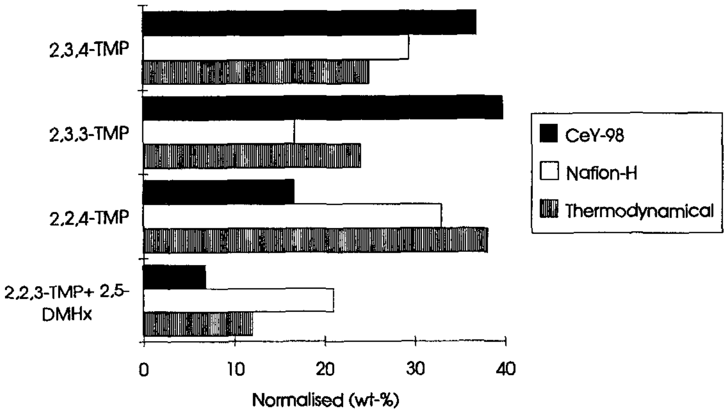


Fig. 4. Normalised distribution of trimethylpentanes (TMP) from isobutane/2-butene alkylation after 3 h reaction over CeY-98 and Nafion-H, together with the calculated equilibrium distribution at 80°C.

CeY, high amounts of 2,2,4-TMP isomers even after a long period of time and showed little loss of the alkylate selectivity [24].

The observed differences in the formation of 2,2,4-TMP over Nafion-H and CeY-98 can possibly be explained by acidity distribution. It is likely that the strongest acid sites in a zeolite deactivate first. Because 2,2,4-TMP is formed mainly in the first minutes for most zeolites tested, the formation is probably more dependent on the strongest acidic sites than the other isomers. The relatively higher production of 2,2,4-TMP over Nafion-H than CeY, may be due to a more homogeneous distribution of acid sites strength, making formation of 2,2,4-TMP possible even after a certain degree of coking.

Another possible explanation of the TMP selectivity for the two catalysts may be a different degree of self-alkylation. Kirsch et al. [25] proved by an isotope study with a faujasite type of zeolite that self-alkylation of isobutane produced as much 2,2,4-TMP as butene alkylation. Self-alkylation is more likely to occur at low butene concentrations, because, as stated above, the zeolites produced the highest amount of 2,2,4-TMP when the catalysts were most active [4,6,24]. A higher degree of self-alkylation on Nafion-H should be expected to cause an increased *n*-butane level in the product. This was confirmed by the results after 3 h time of reaction giving *n*-butane/2,2,4-TMP ratios of 0.5 and 1.1 for CeY-98 and Nafion-H, respectively. Zeolites with low Si/Al ratios have an affinity for polar molecules resulting in a preferred adsorption of olefins versus paraffins [14,26]. Therefore, the zeolite probably has higher concentrations of butenes accessible compared with Nafion-H, which might result in less self-alkylation.

Chu and Chester [5] increased the charging rate of butene in their experiments and therefore enhanced the butene concentration in the reactor. This lead to a larger 2,2,4-TMP selectivity loss. The observed change in TMP ratio with WHSV may therefore be due to catalyst deactivation or less self-alkylation and not to diffusion limitations.

4. Conclusion

Nafion-H was active for isobutane/butene alkylation but lost the alkylate selectivity rapidly. The polymeric catalyst was less selective towards iso-octanes compared to porous materials like zeolites. Also, Nafion-H had a preference for the 2,2,4-TMP isomer among iso-octanes compared to CeY-98 caused by different promotion of the reaction pathways.

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