



PARAFFIN ALKYLATION USING ZEOLITE CATALYSTS IN A SLURRY REACTOR: CHEMICAL ENGINEERING PRINCIPLES TO EXTEND CATALYST LIFETIME

K.P. de JONG, C.M.A.M. MESTERS, D.G.R. PEFEROEN, P.T.M. van BRUGGE and C. de GROOT

Shell Research B.V., P.O. Box 38000, 1030 BN Amsterdam, The Netherlands

Abstract — The alkylation of isobutane with 2-butene is carried out using a zeolitic catalyst in a well stirred slurry reactor. Whereas application of fixed bed technology using a solid acid alkylation catalyst has in the past led to catalyst lifetimes in the range of minutes, in this work we report catalyst lifetimes of 5–200 hours using a slurry reactor operated at high olefin conversion. From the experimental and modelling work we show that the key elements to extend catalyst lifetime appear to be (i) a zeolite (e.g. Beta) with high activity/stability, and high acid site density (low Si/Al ratio) and (ii) a low olefin concentration throughout the reactor, which is achieved by intensive reactor mixing, low to moderate olefin space velocity and a high paraffin to olefin feed ratio.

1. INTRODUCTION

Paraffin alkylation comprises the reaction between light paraffins (isobutane) and olefins (butenes) to form highly branched paraffins (C₈, notably trimethylpentanes). Its importance stems from gasoline manufacture for which it is essential to provide a high-octane, low density and volatility blending component virtually without sulfur and nitrogen. These favourable properties enhance the demand for alkylate. Per unit of product in the oil refinery, however, the production costs of alkylate are the highest of the gasoline pool components. In addition, the current processes make use of liquid acids (HF, H₂SO₄) which require extensive safety measures, thus further increasing costs. It is therefore not surprising that there is considerable activity towards developing an alternative alkylation process which is cheap(er) and intrinsically safe.

In Table 1 [1] the latest developments in alternative processes and their respective catalysts are summarised. Surprisingly, the alternatives explored by the industry all involve halogen-containing acids which may still bring about safety problems (corrosion, toxicity). From a technology-application point of view, it will be clear that a 'true solid acid' without halogens is preferred. Over the last 30 years zeolites have been studied as possible candidates for paraffin alkylation [2–8]. In general very short catalyst lifetimes (5–30 minutes) have been observed when applying fixed bed reactor technology while indications have been given that by using a slurry reactor significantly longer catalyst lifetimes can be obtained [3,4]. It is clear that extending the catalyst lifetime when working with zeolites will be a key item for the successful application of these catalysts. This forms the main theme of this paper — how can the zeolite catalyst survive under paraffin alkylation conditions? The nature of the catalyst as well as the reaction conditions appear to play a key role. We will show that by application of the principles discussed in this paper, the lifetime can be extended from minutes to hours. A feasible catalyst regeneration method remains mandatory for industrial application, fully comparable with the processes using liquid acids. As this paper is restricted to the subject of extending the catalyst lifetime, we refer to Mesters et al. [9] for an integrated view —including catalyst regeneration — of an alkylation process using zeolite catalysts.

2. CHEMISTRY OF PARAFFIN ALKYLATION

In this paper we consider the reaction of isobutane (P) and 2-butenes (O). The chemistry of alkylation is complex and has been discussed extensively in the past [10]. Subtle differences are apparent depending

Table 1
Solid acid alkylation developments [1]

Company	Catalyst	Status
Catalytica	BF ₃	7 bbl/d
Topsøe	CF ₃ SO ₃ H	0.5 bbl/d
Chevron/CRL	SbF ₅	10 bbl/d
Kerr McGee	AlCl ₃	Bench

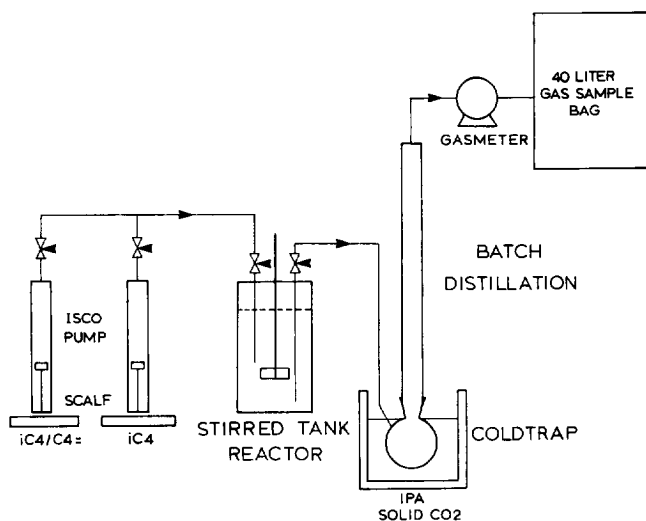


Fig. 1. Schematic representation of the semi-batch alkylation test facility.

on the catalyst used and effects of shape selectivity may be apparent when working with solid acids. The main and desired reaction is that between isobutane and 2-butenes to produce trimethylpentanes (e.g. 2,2,3-trimethylpentane). The main side reactions are those (i) to form heavy alkylate (Y) from secondary reactions of alkylate (A) with an additional olefin and (ii) oligomerisation reactions between olefins to produce higher olefins (D). Summarising:



As mentioned the chemistry is much more complex and involves reactions such as disproportionation, cracking, and self-alkylation, for which we refer to the literature [10]. For the theme of this paper, the usefulness of considering reactions (1)–(3) will be demonstrated.

The solid acid catalyst can be deactivated by blocking the acid sites (S) by D or Y. This assumption is essential for the remaining considerations. For both D and Y the high heat of desorption is considered to be an essential parameter. For the desorption of heavy alkylate (Y), which is paraffinic but highly branched material, the steric effects when using microporous materials such as zeolites is considered to be important. In order to promote reaction (1) as much as possible relative to the reactions (2) and (3), which cause catalyst deactivation, it is essential to lower the concentration of O and A as much as possible. Note that we arrive at this conclusion by assuming that reaction (1) is first order in olefin concentration while reaction (2) is second order in olefin concentration. Later we will indicate that under the conditions prevailing in this study reaction (2) is more detrimental to catalyst lifetime than is reaction (3).

Having established that a low olefin concentration is of paramount importance to extend catalyst lifetime, it is clear that we will have to operate the reactor at high conversion with sufficient extent of backmixing thus leading to the choice of a stirred slurry reactor [3,4].

3. EXPERIMENTAL

All alkylation reactions were carried out in the liquid phase, which mainly consisted of isobutane and alkylate product. The zeolite catalyst (60–140 mesh sieve fraction before use) was suspended in the hydrocarbon mixture by intense stirring. The reactor (250 ml autoclave, more details in Mesters *et al.* [9]) was filled with isobutane, heated to reaction temperature and, subsequently, the isobutane–butenes reaction mixture was added.

For catalyst-screening purposes we used a semi-batch operation (Fig. 1, SBR) in which the reaction mixture (isobutane/2-butenes = 5 v/v) was added to isobutane under reaction conditions. The molar amount of olefin added to the total amount of isobutane at the end of an experiment amounted to 0.1. In a typical experiment 18 g of (dried) catalyst was loaded to the reactor and 40 g of isobutane added. The reaction was then raised to the reaction temperature (75–100°C) and while stirring (1000 rpm) a mixture of isobutane/2-butenes (5/1 v/v) was then added at a given olefin addition rate (OAR) until 9 g of olefin had been added. Following the

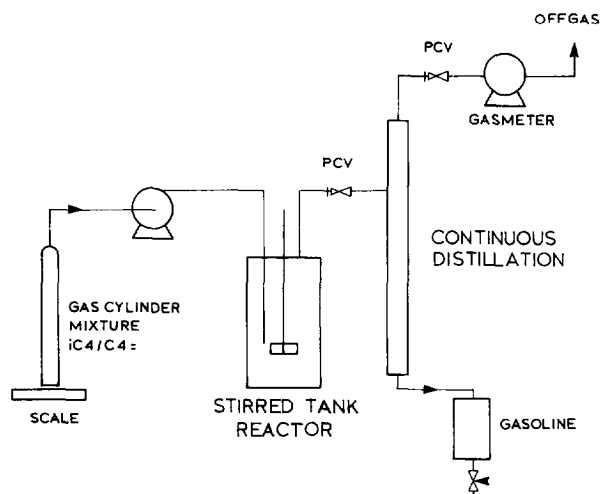


Fig. 2. Schematic representation of the continuously operated slurry alkylation test facility.

Table 2
Properties of zeolites

Catalyst	Comment	Si/Al (mol/mol)	T-area (m ² /g)	MPV (ml/g)	UCS (nm)
USY	Deal. Y	3	77	0.26	2.455
VUSY	Deal. Y	6	76	0.24	2.435
XVUSY	Deal. Y	13	110	0.27	2.425
XXVUSY	Deal. Y	25	93	0.26	2.420
Beta		15	220		

Source of the materials: Zeolyst International.

reaction, the reactor content was transferred to a cold trap and a batch distillation performed. Gas and liquid products were analysed by gas chromatography (GC). We noted that the stirring speed may have been too low to obtain optimal suspension of the catalyst particles.

In Fig. 2 the continuously operated slurry reactor (CSTR) is shown. Again the reactor was filled with isobutane followed by addition of the reaction mixture (isobutane/butenes) at reaction temperature while stirring. The stirring speed has been varied between 1000 and 5000 rpm under this reaction set up. Furthermore, distillation was carried out continuously together with analysis of the vapour phase. The total reactor effluent was analysed using a GC technique which included a high-pressure injection method that was developed in-house. The most important process parameters varied with this set up have been temperature, isobutane/butenes ratio of reactants (P/O ratio, v/v), and the olefin space velocity (OSV, kg/(kg·h)). We measured detailed product composition, product yield and (related) butenes conversion. The latter quantity was measured accurately by establishing the very low olefin concentration in the outlet gas. The catalyst lifetime was defined as the time between the start of an experiment and when the butenes conversion dropped below 0.90. As will be shown below for the greater part of the catalyst lifetime the olefin conversions observed are well above 0.99. Although we will not report detailed data on yield and product composition, we note that in the alkylation process the amount of alkylate based on reaction (1) was 204%w as determined from the amount of olefin fed. In all experiments reported here the actual alkylate yield ranged from 180 to 210 %w, which unequivocally shows that alkylation and not oligomerisation is the dominant reaction in this work.

The catalysts discussed in this paper are all zeolites, the properties of which have been summarised in Table 2. In order to establish the effects of acid site density, zeolites Y have been studied with varying Si/Al ratios that were obtained by different extents of stabilisation. Zeolite Beta has also been studied and details are shown. The zeolites were used without binder material.

4. RESULTS AND DISCUSSION

4.1. Effects of the nature of the zeolite. Using the CSTR we compared the performance of a zeolite Y and a zeolite Beta catalyst under the reaction conditions indicated in Table 3. From the results it is clear that, compared to zeolite Y, Beta displays favourable properties with respect to catalyst lifetime. This is the more

Table 3

Comparison of the performance of Beta and USY. Conditions: OSV = 0.2 kg/kg-h, P/O = 30 v/v, temperature 90°C, continuous operation

Catalyst	Time at butene breakthrough, hours
USY	13
Beta	25

surprising when one takes into account that the number of acid sites per unit weight of catalyst is much higher for USY than for Beta (*vide infra*).

4.2. Effects of the acid site density. As discussed in section 2, blocking of acid sites by oligomers or heavy alkylate is an important cause of catalyst deactivation in paraffin alkylation. From this it follows that a higher concentration of acid sites in the catalyst (the so-called acid site density) may enhance catalyst lifetime. To study this effect we compared a series of zeolite Y catalyst with varying Si/Al ratios in our SBR. Although this type of equipment only provides indicative values for the catalyst lifetimes the results are instructive. Experiments were performed at 75°C with OAR = 0.15 kg/(kg-h). From taking samples at regular intervals the catalyst age at breakthrough (CAB, kg olefins fed/kg catalyst) has been determined. In addition to the CAB, the content of trimethyl-pentanes in the C₈ fraction was used a measure of alkylate quality. The results are summarised in Fig. 3. Clearly, a lower Si/Al ratio (= higher acid site density) favours a longer catalyst lifetime in line with comments made above. It is noteworthy that the quality of the alkylate is also enhanced by the zeolites containing more acid sites. Note that this quality is derived from the content of trimethylpentanes in the C₈ fraction of the liquid product.

From these results it is obvious that the high acid site density is crucial in prolonging catalyst life. In combination with the above result that zeolite Beta is a very attractive catalyst, exploring the synthesis or modification of Beta to arrive at a lower Si/Al ratio should be straightforward. It should be kept in mind, however, that the favourable properties of Beta, as used in this work should be maintained when increasing the acid site density. Amongst others, the rapid transport of the product molecules out of the pores is considered to be important, requiring e.g. small crystals of Beta. Furthermore, an important way of enhancing the acid site density in the reactor is by using more concentrated slurries.

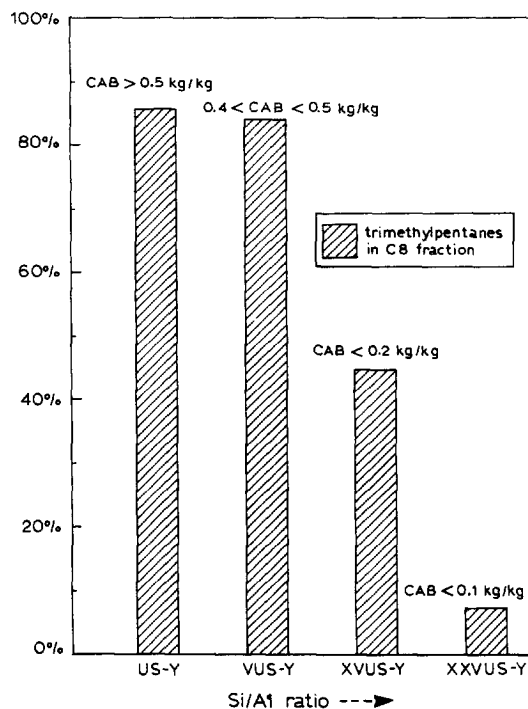


Fig. 3. The effect of Si/Al ratio of zeolite Y catalysts on product composition at catalyst age of 0.5 kgbutenes fed/kgcatalyst. CAB is the catalyst age at breakthrough of butenes.

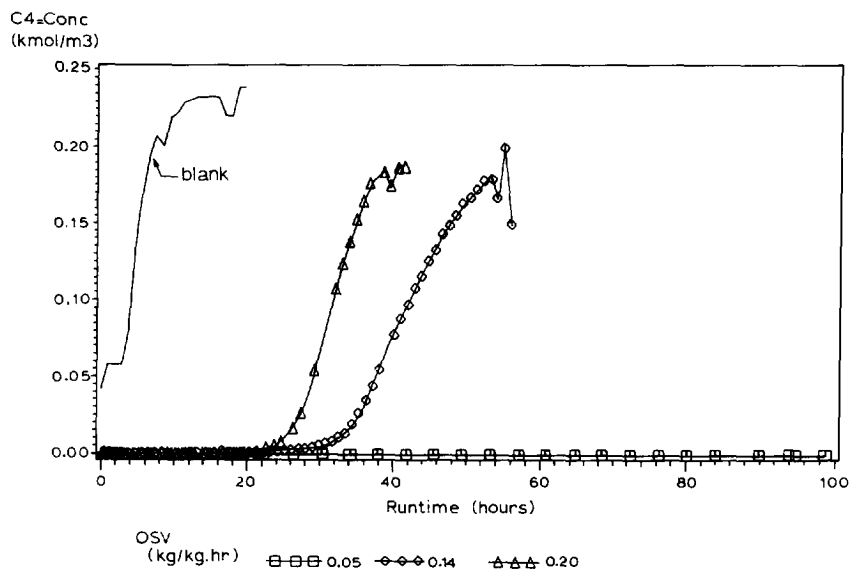


Fig. 4. Butenes concentration in the liquid phase as a function of time for different space velocities. Conditions: P/O ratio 30 v/v, temperature 90°C, catalyst zeolite Beta, continuous operation.

Table 4

Predicted and observed catalyst lifetimes with zeolite Beta in continuous operation-effects of process variables. Temperature 90°C, continuous operation

OSV (kg/kg-h)	P/O (v/v)	ASV (kg/kg-h)	Catalyst lifetime	
			exp.-h	model-h
0.045	30	0	185	166
0.1	30	0	60	65
0.2	30	0	24	27
0.4	30	0	9-10	10
0.2	20	0	19	21
0.4	15	0	5	6.6
0.2	30	0.1	21	23
0.2	30	0.2	16	20
0.4	30	0.1	9.5	9.5

4.3. Effects of process conditions. In paraffin alkylation the process economics are heavily affected by the distillation section (separation of alkylate, isobutane and normal butane). The size of the distillation section is affected by the feed P/O ratio since the excess isobutane has to be separated and recycled to the reactor, thus favouring a low P/O ratio. The size of the reactor is inversely proportional to the OSV, thus favouring high values of this parameter. Here we report on how these two important process parameters affect catalyst lifetime.

Experiments were carried out in the CSTR at 90°C with P/O = 30 v/v for the feedstock, and variation of the OSV. Zeolite Beta was the catalyst. In Fig. 4 the olefin concentration in the liquid phase as a function of time on stream is shown. The curve for the blank experiment (no catalyst) indicates the characteristic time for refreshing the content of the autoclave. At OSV = 0.05 a catalyst lifetime of 180 h has been observed whereas higher values of OSV led to a substantial shortening of the catalyst life. Careful determination of the olefin concentrations early in the experiments showed that at higher OSV the conversion levels dropped (albeit they were still well above 99.9%). These tiny but increasing olefin concentrations at higher OSV cause more rapid deactivation via dimerisation/oligomerisation according to reaction (2).

Experiments with variation of the feed mixture composition (P/O ratio) were carried out (Table 4). In line with results from the literature [3,4] a lowering of the P/O ratio led to a shortening of the catalyst lifetime. For example, with zeolite Beta operated at 90°C with an OSV = 0.4 kg/(kg-h), the catalyst lifetime dropped from 9.5 to 5 h when lowering the P/O feed mixture from 30 to 15. In this case the olefin concentration during the initial phase of the experiment was affected but the alkylate concentration in the reactor was also higher. More rapid catalyst deactivation is caused by a combination of dimerisation and heavy alkylate formation, i.e. reactions (2) and (3).

The impact of alkylate concentration was studied more directly by co-feeding alkylate produced in previous experiments. The so-called alkylate space velocity (ASV, $\text{kg}_{\text{alkylate}}/\text{kg}_{\text{cat}} \cdot \text{h}$) was varied between 0.05 and 0.25. The results (Table 4) show that at OSV = 0.4 $\text{kg}/\text{kg} \cdot \text{h}$ and ASV = 0.1 $\text{kg}/\text{kg} \cdot \text{h}$ the impact of alkylate is small if any. At lower OSV, however, the impact is pronounced.

5. MODELLING

In this section we attempt to explain most of the experimental findings reported thus far by developing a reactor model that includes catalyst deactivation. The chemistry used is that described in section 2 but now we explicitly include the active site (S) to take part in the reactions leading to equations (4)–(7):



in which X is a complex of an olefinic dimer and an acid site and Y comprises heavy alkylate blocking an active site. Reactions (6) and (7) thus cause catalyst deactivation. Assuming that the reactions as described can be treated as elementary steps, we can write the corresponding rate equations and the time-dependent molar balances for the CSTR as:

$$V_r * \delta P / \delta t = \phi_v * (P^0 - P) - k_1 * P * O * S * V_r \quad (8)$$

$$V_r * \delta O / \delta t = \phi_v * (O^0 - O) - (k_1 * P + k_2 * O + k_4 * A) * O * S * V_r \quad (9)$$

$$V_r * \delta A / \delta t = \phi_v * (A^0 - A) + (k_1 * P - k_4 * A) * O * S * V_r \quad (10)$$

$$V_r * \delta D / \delta t = \phi_v * (D^0 - D) + (k_2 * O * O - k_3 * D) * S * V_r \quad (11)$$

$$\delta S / \delta t = -(k_3 * D + k_4 * O * A) * S \quad (12)$$

The parameters C^0 and ϕ_v are directly related to OSV, ASV and P/O according to:

$$O^0 = \text{OSV} / (\text{ASV} + \text{OSV} * (1 + \text{P/O})) * \Phi / M_{w,O}$$

$$P^0 = (\text{P/O}) * \text{OSV} / (\text{ASV} + \text{OSV} * (1 + \text{P/O})) * \Phi / M_{w,P}$$

$$A^0 = \text{ASV} / (\text{ASV} + \text{OSV} * (1 + \text{P/O})) * V_r * \Phi_c * \Theta_c / (3600 * \Phi)$$

$$D^0 = 0.$$

Equations (8)–(12) are numerically integrated starting at $t=0$ with the reactor completely filled with P and $S_{t=0}$ is the concentration of acid sites. $S_{t=0}$ is calculated from the Si/Al ratio of the zeolite:

$$S_{t=0} = \Phi_c * \Theta_c / (M_{w,\text{SiO}_2} * (1 + \text{Si/Al})) \quad [\text{kmol}/\text{m}^3_{\text{reactor}}]$$

The conversion is calculated as:

$$\alpha = 1 - O/O^0$$

In Fig. 5 the experimental results for the butenes conversion as a function of time are compared with those of the model. An excellent fit is observed. The kinetic rate constants together with the physical constants (densities, catalyst hold-ups, Si/Al ratio and molecular weights) used in the model, are shown Table 5. In Table 4 for a set of experiments the observed and calculated catalyst lifetimes (defined as time when butenes conversion drops below 0.90) are given. A fair agreement between measured and calculated catalyst lifetimes is noted. The values for the rate constants seem reasonable in the relative sense: the rapid dimerisation reaction (k_2) gives rise to a higher rate constant than do the alkylation reactions (k_1 and k_4). We note that k_1 basically determines the level of olefin conversion, the ratio of k_1 versus k_4 sheds light on the relative importance of olefin and alkylate concentration on catalyst lifetime. The value of k_3 is not very sensitive for levels above 0.1. Although the absolute values of the rate constants are difficult to interpret, it seems reasonable that $k_2 \gg k_1, k_4$.

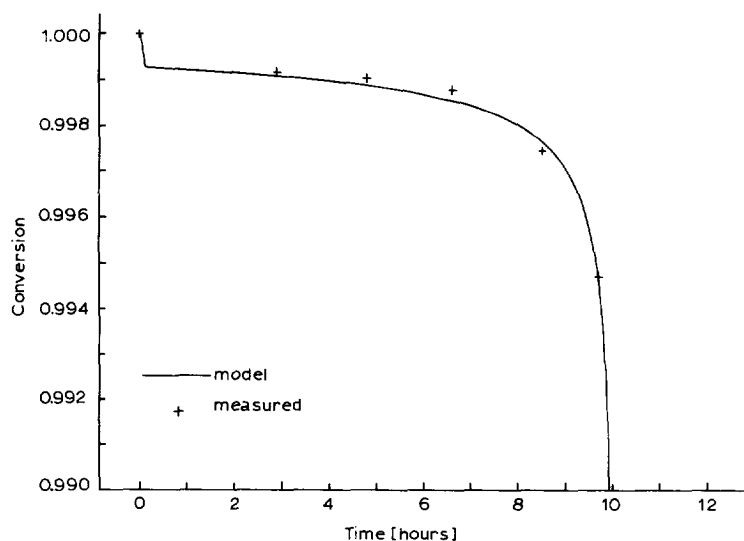


Fig. 5. Conversion of butenes versus time-on-stream: experiment versus model. Conditions: catalyst zeolite Beta, P/O ratio 30 v/v, temperature 90°C, OSV = 0.4 kg/kg.h.

Table 5
Kinetic constants and physical properties in the alkylation lifetime model

Kinetic constants		Physical properties
k_1	1.3	Si/Al = 15 mol/mol
k_2	175	Liquid density = 450 kg/m ³
k_3	100	Catalyst density = 937 kg/m ³
k_4	0.25	Slurry hold up = 0.2 m ³ /m ³

Note that the above model applies simple chemistry and is not able to describe, e.g., how the product quality changes with time on-stream.

The model has thus substantiated quantitatively the argument obtained from the experiments that maintaining a low olefin and alkylate concentration (with emphasis on the former) is crucial in alkylation. This is no different from the processes using liquid acids in which well mixed reactors operated at high olefin conversion are applied. For the slurry reactor this leads to challenges in a number of areas, notably (1) effective introduction of olefins without invoking locally high olefin concentrations, (2) effective mixing at different scales of length, and (3) scale-up of the slurry reactor while taking these aspects into account.

6. CONCLUSIONS AND NEEDS FOR FUTURE WORK

Paraffin alkylation to produce high-octane gasoline components (alkylate) can be carried out successfully in a slurry reactor using a zeolitic catalyst. Application of fixed bed technology using this catalyst has led to catalyst lifetimes in the range of minutes whilst in this work we report lifetimes of 5–200 h using a well mixed slurry reactor operated at high olefin conversion. Maintaining the olefin concentration at low values for as long as possible is important both to produce (paraffinic) alkylate and to extend the catalyst lifetime.

From the experimental work the following key items to extend catalyst lifetime appear to be:

- A zeolite with high activity/stability, possibly related to intrinsic acid strength and favourable transport characteristics such as desorption of the alkylate from the micropores. At present, zeolite Beta appears to be the most attractive zeolite.
- The acid site density of the zeolite was shown to be important both to enhance the alkylate quality and to extend the catalyst lifetime. Using zeolite Y a low Si/Al ratio (high acid site density) appeared to be attractive.
- The catalyst lifetime dropped when the reaction was carried out at high OSV or low feed P/O ratio. This was attributed to a higher olefin and — for the latter case — also to a higher alkylate concentration, leading to enhanced formation of dimers and heavy alkylate.

A simple kinetic model was effective in describing catalyst deactivation via both dimerisation and heavy alkylate formation.

From experiment and modelling the following items are advocated for further investigation:

- The effects of the details of the zeolite structure and morphology (e.g. crystal size) in relation to performance in alkylation.
- Enhancement of the acid site density with promising solid acids such as zeolite Beta (lower Si/Al ratio).
- Reactor engineering aspects related to scale-up, mixing, high slurry concentration and separation of product and catalyst.

Further work on the items indicated above should bring this process concept within the bounds of economic reality.

NOTATION

- ASV alkylate space velocity [$\text{kg}_{\text{alkylate}}/\text{kg}_{\text{cat}}\cdot\text{h}$]
 C^0 inlet concentrations of O, P and A [$\text{kmol}/\text{m}^3_{\text{liquid}}$]
 k_i rate constant
 $M_{w,i}$ molecular weight of compound i [kg/kmol]
 OSV olefin space velocity [$\text{kg}_{\text{olefin}}/\text{kg}_{\text{cat}}\cdot\text{h}$]
 P/O paraffin/olefin ratio of feed [kg/kg]
 V_r reactor volume [$\text{m}^3_{\text{reactor}}$]

Greek letters

- ϕ_v volume flow [$\text{m}^3_{\text{liquid}}/\text{s}$], which is constant, assuming constant density of feed and products — this seems appropriate in view of the large excess of isobutane in the reactor
 Φ density of the liquid [$\text{kg}/\text{m}^3_{\text{liquid}}$]
 Φ_c catalyst particle density [$\text{kg}/\text{m}^3_{\text{cat}}$]
 Θ_c catalyst hold up [$\text{m}^3_{\text{cat}}/\text{m}^3_{\text{reactor}}$]

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