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Oligomerization of isobutene over solid acid catalysts

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Abstract

Oligomerization of isobutene has been carried out in the liquid phase at mild conditions using *n*-butane as a diluent. The reaction was studied at low temperatures (30–70 °C) and at pressures high enough to ensure that the reaction takes place in the liquid phase. A number of different resins and zeolites were evaluated as catalysts for the dimerization. The best performance was obtained with Amberlyst 15 whereas the zeolites (H-ZSM5, H-Mordenite, β and Y) all showed very rapid deactivation.

Keywords: Oligomerization; Dimerization; Isobutene; Resin; Zeolite; Stability

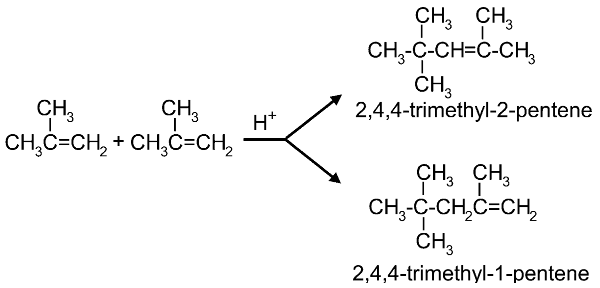
1. Introduction

In order to meet stricter environmental restrictions the trend for gasoline formulation will be towards lower evaporative emission, lower aromatics and more complete combustion [1]. The possible phase-out of MTBE will also demand a substitute. The solubility of MTBE in water is causing increasingly environmental concern and California has already decided to phase-out MTBE (from January 2004), and ethanol is now being used as the primary oxygenate in those areas requiring an oxygenate additive [2]. Today, MTBE represents approximately 3–4% of the total gasoline volume in U.S. [3].

An excellent substitute for MTBE could be isooctane. Isooctanes have a high octane number, in fact, 2,2,4-trimethylpentane is the reference component for rating the antiknock properties with RON and MON of 100 [4]. The isooctane components can be produced by alkylation or by dimerization if isobutene.

Alkylation is a well established process, but there are still problems related to this process. The commercial catalysts are either HF or H_2SO_4 based systems [5,6]. HF should not be used in new installations in populated areas due to its extreme toxicity [4], while H_2SO_4 is highly corrosive and produces great amounts of acid muds which are difficult to dispose. Alkylation processes based on solid acid catalysts are being developed, but so far the commercial applicability has to be proved [5,6].

Dimerization of isobutene can be carried out in the liquid phase at low temperatures as well as in the gas phase using acid catalysts [7,8]. One of the main problems associated with dimerization include product selectivity control (reactions (2)–(4)) due to high exotermicity of the process [4]. Dimerization of isobutene is shown in reaction (1).



(1)

Important side reactions:

$$iC_8^= + iC_4^= \rightarrow iC_{12}^= \quad (2)$$

$$iC_{12}^= + iC_4^= \rightarrow iC_{16}^= \quad (3)$$

$$iC_8^= + iC_8^= \rightarrow iC_{16}^= \quad (4)$$

Two isomers from dimerization of isobutene will be produced, namely 2,4,4-trimethyl-2-pentene (2,4,4TMP-2) and 2,4,4-trimethyl-1-pentene with heat of formation of 87.3 kJ/mol and 79.1 kJ/mol, respectively [8]. After

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dimerization, a hydrogenation step is needed to produce isooctane and both dimerization products shown in reaction (1) will be hydrogenated to 2,2,4-trimethylpentane.

An advantage of the oligomerization process is that it can be carried out in existing MTBE units [9,10]. This could be an interesting alternative for the MTBE producers if there comes a worldwide ban on MTBE.

Oligomerization of isobutene over resin catalysts is a well known reaction and was studied by Haag nearly forty years ago [11]. The reaction has also been studied as a side reaction to the MTBE reaction [8,12,13]. However, during the last years there has been a renewed interest in the process as indicated also by the large numbers of patents issued on the subject. A small selection of patents is included in the reference list [14–19].

The present work deals with a study of different catalysts for the liquid phase oligomerization of isobutene in the presence of *n*-butane. The main focus has been on Amberlyst 15, but other catalysts (resins and zeolites) have also been included.

2. Experimental

The following catalysts were included in the study: Amberlyst 15 (Fluka AG), Dowex 50 WX8 (Fluka AG), Zeolite-β (Zeolyst), H-Mordenite (PQ Zeolites), Y-Zeolite (PQ Zeolites) and H-ZSM5 (PQ Zeolites) with two different silica/alumina ratios (15 and 25).

The reaction was carried out in a plug flow reactor (i.d. ~ 4.6 mm), where the catalyst was kept in place with quartz wool. The reactants were introduced using liquid flow controllers (Bronkhorst HI-TEC) and the feed was then mixed and preheated to the reaction temperature. The reactor system was placed in a water bath to control the reaction temperature. A backpressure regulator kept the system pressure at 10 bar to ensure liquid phase in the reactor.

Different pretreatments were used for the resin catalysts and for the zeolites. The resin catalysts (20–35 mesh) were weighted, diluted with SiC (~30 mesh) and transferred to the reactor. The catalysts were then dried in situ for 75 min at approximately 107 °C with a nitrogen flow of 230 ml/min for removal of water from the catalyst before the reaction [20]. In order to avoid loss of sulfonic groups, temperatures above 115 °C were carefully avoided. The zeolite catalysts (20–35 mesh) were calcinated in dry air (1 bar) to convert to the H-form before use. The temperature was raised to 500 °C at 5 °C/min and kept for 8 h before the temperature was lowered to 200 °C. The temperature was kept at 200 °C until use. After cooling the catalyst was quickly transferred, weighed, diluted with SiC (~ 30 mesh) and transferred to the reactor. In the reactor, samples were dried in situ at 115 °C for 2 h with nitrogen flow of 230 ml/min.

After catalyst pre-treatment, the system was pressurized with nitrogen. The pressure was set high enough to ensure that the reaction was performed in liquid phase (10 bar). *n*-Butane was introduced and when the reactor system was filled with *n*-butane, the flow was switched to bypass the reactor and isobutene was then added to the feed bypassing the reactor. The feed composition was analysed with an online GC until feed composition was constant, indicated by a constant ratio between the integrated peak areas. The flow (with known composition) was then switched to the reactor system and the product composition was analyzed using the online GC.

The reaction product was analysed with a Hewlett-Packard GC Model 5890A equipped with a flame ionization detector (FID) and a liquid injector valve for samples injection. The products were separated on a PONA (Crosslinked Methyl Silicone Gum) capillary column (50 m × 0.2 mm × 0.5 μm).

The number of acid sites of the resins Amberlyst 15 and Dowex WX8 were determined by titration. Ion exchange resins samples (1.0 g, 20–50 mesh Amberlyst 15 and 20–50 mesh Dowex 50 WX8) were weighed and subsequently stirred for 20 min in a 100 ml 0.1 M KCl solution, before the solution was titrated with a 0.1987 M KOH solution. The acidic properties of the zeolites were studied by ammonia TPD (not shown).

3. Results and discussion

The number of acid sites on Amberlyst 15 and Dowex 50 found by titration were 4.68 and 5.02 mmoleqv [H^+]/g, respectively. The numbers obtained are per gram catalyst as obtained from Fluka. Various ways of drying the samples are described elsewhere [20]. These results fit well with values given by the supplier (4.6 mmoleqv/g) for Amberlyst 15.

The conversion as a function of time on stream (TOS) at 40 °C and 10 bar for all the catalysts is shown in Fig. 1, where only Amberlyst 15 exhibits a relatively good stability. The zeolites have a high initial conversion, but deactivates rapidly. This is probably due to the production of high molecular weight oligomers inside the zeolite pores. This agrees well with the fact that the zeolites with the smallest pores deactivate fastest (H-ZSM5). Amberlyst 15 has lower initial activity than Zeolite-β and Y-Zeolite, but the deactivation is much less pronounced for Amberlyst 15. Dowex 50 showed hardly any activation at all, even though it has a higher number of acid sites per gram catalyst (5.02 mmoleqv/g versus 4.62 mmoleqv/g). This can be explained by the fact that the experiments have been performed over dried catalysts. Dowex 50 is a gel type resin, and in the dried form (in the absence of a polar solvent) the pores "collapse" [21]. In this state, no internal catalytic surface is available. O'Connor et al. [7] obtained a similar result on a similar catalyst (Duolite C20). Pore distribution and surface area for dried Dowex have been checked by Kjetså [20] and showed no pores even if crushed, and the surface area was very low (0.057 m^2/g) representing only the external area. It has been showed, however, that dried

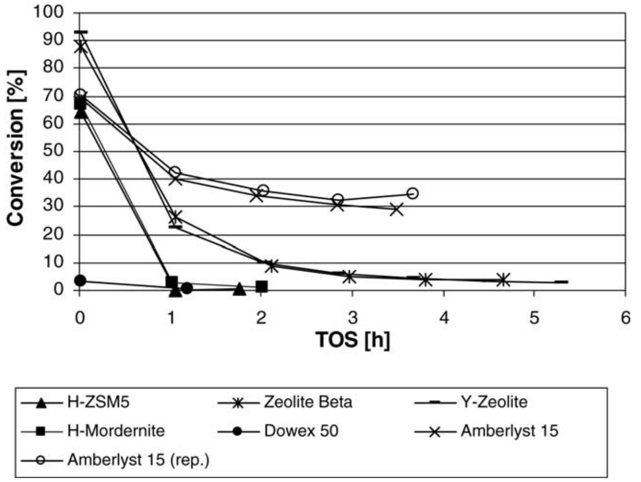

Fig. 1. Stability tests of different zeolites and resins. Temperature = 40 °C; pressure = 10 bar; WHSV = 60 $g_{isobutene}\ g_{cat}^{-1}\ h^{-1}$.

Amberlyst 15 has a surface are in the range 44–46 m^2/g, and most of the pores are in the range of what may be called mesopores (50–300 Å).

Amberlyst 15 clearly shows the best performance for the conditions in this study and this catalyst has, therefore, been studied in greater detail. A stability test at 60 °C and 10 bar is given in Fig. 2A. After about 8 h of time on stream (TOS), the reaction temperature is varied between 70 °C, 60 °C, 50 °C and 40 °C (after catalyst stabilisation). In order to follow the deactivation, 60 °C is chosen as a reference point and experiments at 60 °C were repeated immediately after each temperature. The deactivation rate at 40 °C, 50 °C and 60 °C is given in Fig. 2B. The figure shows the conversion over the initial conversion, which gives a relative deactivation rate at the different temperatures. The figure shows clearly that the deactivation rate decreases with increasing temperature. It is well known that deactivation in acidic microporous materials is normally caused by coke formation. Low temperature gives higher formation rates of the large oligomers which blocks the intrinsic pores and acid sites. The literature values clearly showed an optimium temperature for a minimum coke formation in zeolites [22].

On the basis of the experiments performed at different temperatures on a stabilized catalyst which is shown in Fig. 2A, an apparent activation energy is calculated. It is assumed that the reaction is 1st order and the reactor is modelled as a plug flow reactor. As shown in Fig. 3A, an apparent activation energy of 48 kJ/mol is obtained. Experiments have also been performed at low conversion ($X < 10\%$) giving a similar activation energy (Fig. 3B) by

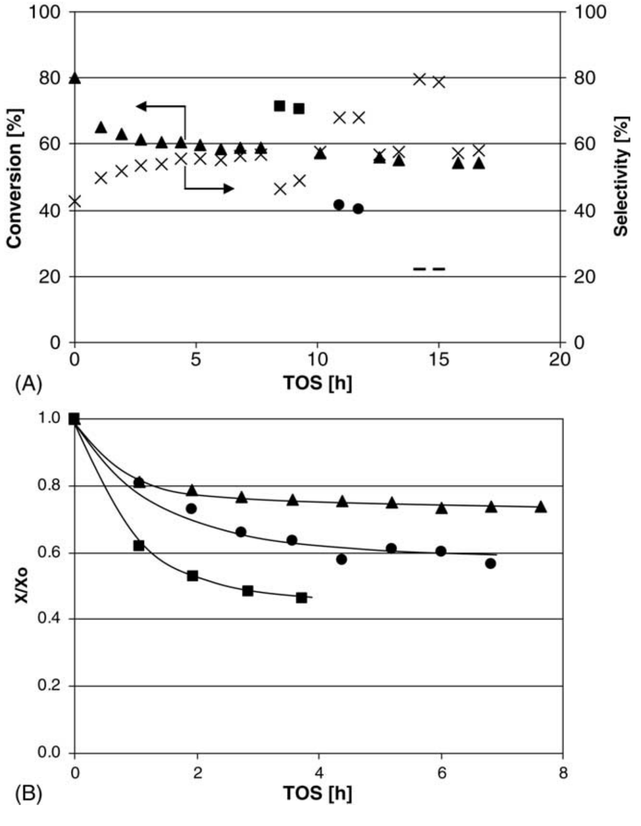

Fig. 2. (A) Conversion of isobutene over Amberlyst 15 at different temperatures: (▲) 60 °C; (■) 70 °C; (●) 50 °C; (–) 40 °C; (×) ~ selectivity to isooctane. (B) Deactivation rates for 40 °C (■); 50 °C (●); and 60 °C (▲); $T = 60$ is calculated from figure A.

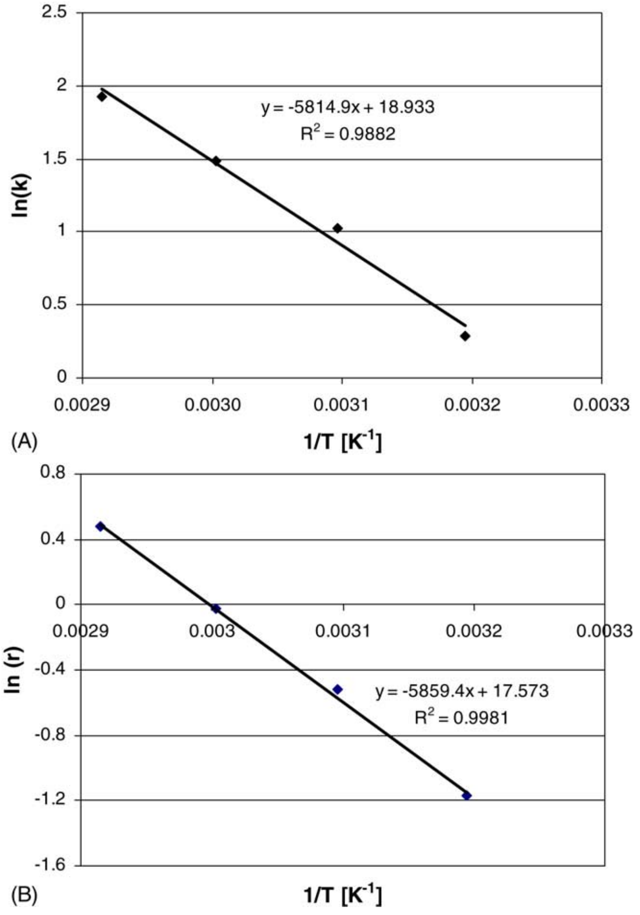

Fig. 3. Arrhenius plot for the oligomerization reaction. Conversion: ~20–70% (A) and ~6–9% (B).

assuming differential conditions. This indicates that the isobutene oligomerization is an apparent first order reaction.

The activation energy measured is lower than given in literature (66.6 kJ/mol given by Haag [11]). Rehrfinger and Hoffmann [8] also obtained an apparent activation energy in the order of 40 kJ/mol, and they concluded that the low activation energy could be explained by the influence of diffusion in the gel phase of the microparticle. This could possibly also be the case in this study. Since the activation energy was obtained on a stabilized catalyst, where a lot of coke is expected to be formed inside the pores, the coke formation has partially blocked pores and induced diffusion resistance. This could also explain why we did not observed diffusion limitations in the initial tests which were done on fresh catalysts.

4. Conclusions

Dimerization of isobutene in liquid phase at low temperature (∼30–70 °C) showed fast deactivation of all zeolites tested. Dowex 50 (gel resin) showed hardly any activity at all, while Amberlyst 15 exhibited a relative good activity and stability. Deactivation experiments over Amberlyst 15 showed higher deactivation rate at lower temperature in the temperature range 40–60 °C. An apparent activation energy was calculated to 48 kJ/mol. The relatively low value could have been caused by internal diffusion limitations induced by coke formation. The results indicated a first order kinetic with respect to isobutene.

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