Acetone conversion to isobutene in high selectivity using zeolite β catalyst

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The catalytic activity of the proton forms of zeolite β and ZSM-5 are compared for the conversion of acetone. Zeolite β demonstrates markedly enhanced selectivity to isobutene and selectivities of >80% can be achieved for conversions up to 65%. In contrast high selectivities to isobutene with ZSM-5 can be attained only at very low conversions (≤5%).

Keywords: Acetone; isobutene; zeolite β

1. Introduction

Acidic forms of zeolites have been studied as catalysts for the conversion of a range of heterocompounds including alcohols, e.g. methanol [1,2], allyl alcohol [3], mercaptans, e.g. methane thiol [1], aldehydes, e.g. propanal [1] and ketones, e.g. acetone [4]. Chang and Silvestri [1] first described the flexibility of these catalysts and noted that at low conversions isobutene could be formed from acetone in high selectivity. Subsequently a number of studies have been made for acetone conversion over ZSM-5 and zeolite Y [4–8]. In particular the reaction is known to take place via aldolization and dehydration followed by cyclization, aromatization and cracking [5,6]. Recent ^{13}C NMR studies [6] have shown that diacetone alcohol, mesityloxide and isophorone are present on the zeolite surface during the acetone conversion reaction.

It is found that zeolite Y is not particularly active for this reaction [5], whereas ZSM-5 demonstrates high activity but low selectivity to any particular product. For H-ZSM-5 high selectivity to isobutene (~ 80%) can only be achieved at low conversion or when water is present as a co-reactant [5]. It is probable that the microporous structure of ZSM-5 facilitates secondary reactions which limit the selectivity to any particular product. In this paper the use of zeolite β as catalyst is

described and it is shown that this zeolite is considerably more selective to isobutene.

2. Experimental

2.1. PREPARATION OF ZEOLITE β

Zeolite β was prepared according to the method of Wadlinger et al. [9]. Sodium aluminate was prepared by dissolution of aluminium wire in aqueous sodium hydroxide and mixed well with aqueous tetraethylammonium (TEA) hydroxide to give solution **A**. Silica (Cabosil M-5, BDH) was thoroughly mixed with water to give a homogenised gel, denoted solution **B**. Solutions **A** and **B** were mixed to give a gel with composition

$$((TEA)_2O)_{2.5}(Na_2O)_{0.9}(Al_2O_3)_{1.0}(SiO_2)_{27.1}(H_2O)_{332},$$

which was aged at room temperature for 24 h prior to heating at 150°C in a 1 ℓ stainless steel autoclave with stirring (250 rpm). After crystallisation for 14 days, the zeolite was recovered, washed with distilled water, dried at 120°C for 16 h and calcined at 660°C for 16 h. The calcined zeolite was ion exchanged with 0.1 M NH_4NO_3 (1 h, 100°C) and converted to the proton form (H-β) by calcination (660°C, 3 h). X-ray diffraction and MAS NMR confirmed that the zeolite was H-β.

2.2. CATALYST STUDIES

Catalyst evaluation was carried out using a glass microreactor in which zeolite (0.5 g) was supported on silica wool. Acetone was fed to the reactor via a calibrated syringe pump and vaporised in a stream of dry nitrogen to give a controlled feed-rate of acetone/N_2. Products were analysed by gas chromatography using three GC columns: 2 m Poropak Q temperature programmed from 50–200°C; 2 m Poropak T temperature programmed from 50–200°C; 30 m DBI megabore column temperature programmed from 0–200°C. Product identification was supported by GCMS studies using VG7070 GCMS fitted with OV101 column.

3. Results and discussion

The conversion of acetone to hydrocarbons was investigated using zeolite β as catalyst for a range of conditions and the results are given in table 1 for data collected at 180 min time on stream. In addition, typical data giving the effect of time on stream are shown in fig. 1. There are two striking features observed for acetone conversion over zeolite β. The first is that at all reaction conditions, zeolite β exhib-

Table 1
Acetone conversion over zeolite β [a]

reaction temperature (°C)	370	370	400
acetone WHSV [b] (h^{-1})	0.8	1.6	1.6
acetone conversion (%)	64.6	37.1	48.8
product selectivity (%) by mass			
methane	0	0	0.1
ethane and ethene	0.2	0.1	0.3
propane and propene	7.1	2.5	4.7
isobutene	82.3	93.0	87.1
isobutane	0	0	0
2-butene	5.1	2.4	4.3
C_5	2.6	1.9	3.2
C_{6+}	2.7	0.1	0.3

[a] Data for time on line 180 min.
[b] N_2 diluent: 120 ml min^{-1}.

its extremely high selectivity for total C_4 hydrocarbons (typically >90%). This is significant, since the conversion of a C_3 compound to a C_4 hydrocarbon in high selectivity and at high conversion is unusual. The second is that during the initial period of the reaction (fig. 1) the initial C_4 product is almost exclusively isobutane. However, as catalyst deactivation occurs due to coke deposition, the selectivity to isobutane is decreased and there is a concomitant increase in isobutene. Detailed

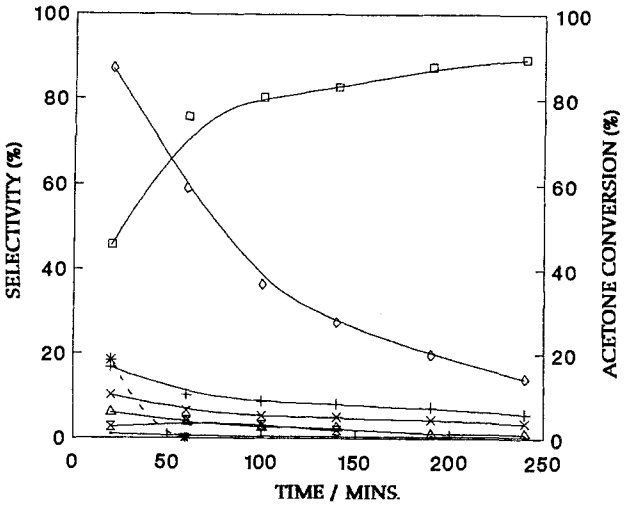

Fig. 1. Effect of time on stream on product selectivity for acetone conversion over zeolite β at 370°C. Acetone WHSV= 1.6 h^{-1}, N_2 diluent 120 ml min^{-1}. (×) Ethene; (+) propene/propane; (*) isobutane; (□) isobutene; (△) C_5; (⧖) C_6; (◇) acetone conversion.

GC and GCMS analysis was used to confirm the product assignments. In the initial stages of the reaction it is considered that isobutane formation is most probably formed via hydride donation to a tertiary butyl cation, since this is known to be an exceptionally rapid process [10]. Subsequently proton loss from the tertiary butyl cation becomes dominant as the catalyst deactivates and the product then becomes mainly isobutene (typically >80% selectivity).

A comparison of the catalytic performance of zeolite β and ZSM-5 ($SiO_2/Al_2O_3 = 30$, i.e. comparable to zeolite β) was also undertaken (table 2). Although ZSM-5 demonstrated high selectivity to isobutane within the C_4 fraction, it demonstrated much lower overall selectivity to C_4 hydrocarbons and gave higher selectivities to C_{6+} products, and in addition CH_4 selectivity was significantly enhanced. It was apparent that zeolite ZSM-5 was considerably more active than zeolite β for acetone conversion and so some experiments were carried out at a decreased temperature (table 2). However, it was always observed that zeolite β was more selective to C_4 hydrocarbons, particularly isobutene; although at very low acetone conversions ZSM-5 can give high selectivities to isobutene, as noted previously by Chang and Silvestri [1].

For zeolite β, during a 7 h catalytic test at 370°C and acetone WHSV 1.6 h^{-1}, it was found that carbon laydown amounted to 10% of the catalyst mass (0.05 g C, 1.6% C fed to reactor). For the acetone converted, the principal product was isobutene (selectivity ca. 90%), and in addition $CO + CO_2$ was formed at ca. 10% of total selectivity to hydrocarbons. Similar levels of $CO + CO_2$ have been found to be present in previous studies [1].

The observation of such high selectivities to isobutene from acetone are intriguing. However, the high selectivity is consistent with a mechanistic proposal by Dolejsek et al. [8] in which isobutene and carbon dioxide are formed from the decomposition of surface species considered to be similar in composition to mesi-

Table 2
Acetone conversion over zeolite ZSM-5 [a]

reaction temperature (°C)	378	328	328
time on stream (min)	120	100	360
acetone conversion (%)	58.9	31.1	3.8
product selectivity (%) by mass			
$C_1 + C_2$	1.9	1.8	0.6
propane and propene	11.7	6.4	1.1
isobutene	25.7	51.2	78.8
isobutane	0.6	0.3	0.1
n-butene	0.1	0	0
2-butene	7.9	4.9	1.3
C_5	5.7	3.2	0.3
C_{6+}	46.4	32.2	17.9

[a] WHSV = 1.6 h^{-1}.

tyloxide. ^{13}C labelling studies by this research group have indicated that the isobutene contained three carbon atoms from one acetone molecule and one carbon atom from the methyl group of another acetone molecule. However, the present study demonstrates for the first time that sustained high isobutene selectivities can be achieved at high acetone conversions using zeolite β as a catalyst. These high selectivities result from the decreased activity of zeolite β for the secondary reactions of hydrocarbons, i.e. oligomerisation and cracking, that are dominant for zeolite ZSM-5.

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