

# Ethane conversion in the presence of iron- and manganese-promoted sulfated zirconium dioxide: evidence of autocatalysis and oligocondensation chemistry

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**Ethane reacts in the presence of Fe- and Mn-promoted sulfated ZrO<sub>2</sub> to form butane, ethene, methane and H<sub>2</sub> at temperatures  $\geq 473$  K; the data indicate autocatalysis with carbocation intermediates as in superacid solution chemistry.**

Light alkanes in liquid superacids react at temperatures  $< 273$  K, giving heavier hydrocarbons *via* carbenium and carbonium ion intermediates.<sup>1</sup> In the presence of Fe- and Mn-promoted sulfated ZrO<sub>2</sub> (FMSZ), propane reacts similarly, being converted largely into butane at 473 K,<sup>2</sup> and butane is catalytically isomerised and disproportionated even at 298 K.<sup>3,4</sup> The propane product distribution and the high catalytic activity for butane conversion suggest superacid chemistry.<sup>1</sup> Although FMSZ was called a superacid,<sup>5</sup> the acid strength is still debated.<sup>6,7</sup> Our goal was to probe the acidic character of FMSZ (and, for comparison, acidic USY zeolite) by investigating its reactivity and catalytic activity with a relatively unreactive alkane (ethane).

FMSZ,<sup>4</sup> containing approximately 1 mass% Fe, 0.5 mass% Mn and 1.8 mass% S, was made by stepwise incipient wetness impregnation of sulfated Zr(OH)<sub>4</sub> with aqueous Fe(NO<sub>3</sub>)<sub>3</sub> then aqueous Mn(NO<sub>3</sub>)<sub>2</sub> and calcined in static air at 923 K. The BET surface area and pore volume were about 90 m<sup>2</sup> g<sup>-1</sup> and 0.2 ml(NTP) g<sup>-1</sup>, respectively.

Ethane conversion was carried out in a once-through packed-bed flow reactor under the following conditions: temperature, 473–723 K; pressure, 101 kPa; ethane partial pressure, 5–20 kPa; mass of FMSZ, 0.5–1.5 g; feed (ethane + N<sub>2</sub>) flow rate, 10–80 ml(NTP) min<sup>-1</sup>. The products were H<sub>2</sub>, methane, ethene, butane and traces of aromatics; at 473 K they were predominantly butane and ethene. Butane selectivity decreased from 30% (at 0.01% conversion) at 473 K to 10% (at 0.1% conversion) at 673 K. In the temperature range 473–623 K, the conversion to butane, ethene and methane decreased with increasing time on stream (TOS). At temperatures  $> 623$  K, the conversion into butane decreased monotonically with increasing TOS, but the conversion to ethene and to methane decreased and then increased with TOS (suggesting autocatalysis), followed by another declining period (Fig. 1). The length of the first declining period for ethane conversion decreased with increasing temperature and ethane partial pressure. H<sub>2</sub> was observed only at temperatures  $> 673$  K; at 723 K, production of H<sub>2</sub> was characterised by a period of increasing conversion followed by a slow decline with TOS.

At 723 K, 20 kPa ethane partial pressure, and  $5.5 \times 10^{-6}$  mol s<sup>-1</sup> g<sup>-1</sup> space velocity, the number of ethane molecules converted/sulfate group was  $> 1$  after 18 h TOS; ethane conversion was then catalytic. Catalysis was not demonstrated at lower temperatures.

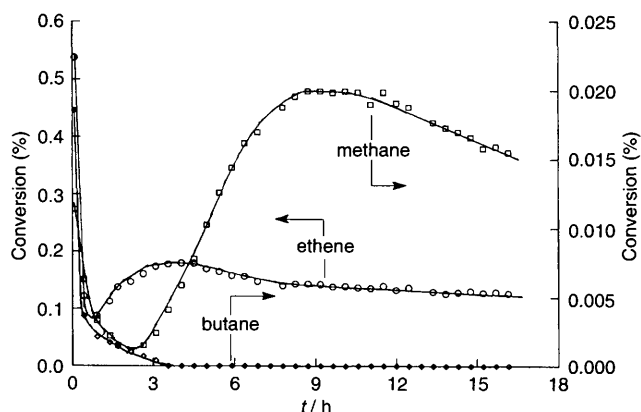
Initial ethane conversion rates were estimated by extrapolating conversions in the first declining period to zero TOS. At 723 K and 20 kPa alkane partial pressure, the rate of ethane conversion in the presence of FMSZ ( $4 \times 10^{-8}$  mol s<sup>-1</sup> g<sup>-1</sup>) is lower than that of propane conversion (determined by extrapolating published data,<sup>8</sup>  $4 \times 10^{-6}$  mol s<sup>-1</sup> g<sup>-1</sup>). The products formed from ethane (or propane<sup>2</sup>) at 473 K are nearly the same as those reported<sup>1</sup> for reaction in superacid solution.

Adopting the analogy to superacid chemistry for the reactions

in the presence of FMSZ, we suggest reaction cycles whereby ethane is first protonated to form C<sub>2</sub>H<sub>7</sub><sup>+</sup>, which collapses to either H<sub>2</sub> and C<sub>2</sub>H<sub>5</sub><sup>+</sup> or methane and CH<sub>3</sub><sup>+</sup> [Fig. 2(a)]. Then C<sub>2</sub>H<sub>5</sub><sup>+</sup> is deprotonated to give ethene (CH<sub>3</sub><sup>+</sup> deprotonation is energetically unfavourable). The initial decrease in conversion with TOS is attributed to deactivation of acidic sites. Oligocondensation to give butane is suggested to proceed [Fig. 2(b)] as ethane combines with adsorbed C<sub>2</sub>H<sub>5</sub><sup>+</sup> to form C<sub>4</sub>H<sub>11</sub><sup>+</sup>, which is deprotonated to give butane. Autocatalysis is postulated to set in as C<sub>2</sub>H<sub>5</sub><sup>+</sup> and CH<sub>3</sub><sup>+</sup> [Fig. 2(b)] function as chain carriers [Fig. 2(c)]. Thus, ethane is converted into ethene, along with methane. The conversions to ethene and to methane ultimately decrease with TOS as the number of these chain carriers declines, *e.g.* because carbonaceous deposits form on FMSZ.

This carbocation chemistry accounts for the ethane reactivity with FMSZ, being consistent with Olah's results,<sup>1</sup> except that Olah did not observe autocatalysis, presumably because products were analysed only following the batch reactor experiment. The behaviour suggestive of autocatalysis in ethane conversion was not observed for propane<sup>2</sup> or butane.<sup>4</sup> The difference may be associated with the higher reactivities of propane and butane and the correspondingly shorter initial declining periods.

Presuming that the carbocation chemistry inferred here for ethane conversion in the presence of FMSZ also pertains to butane isomerisation catalysed by FMSZ, we suggest that the initial increase in conversion of butane in a flow reactor can be attributed to build-up of C<sub>4</sub>H<sub>9</sub><sup>+</sup>, which reacts with butane to form C<sub>8</sub>H<sub>19</sub><sup>+</sup>, which rearranges and splits into 2-methylpropane + C<sub>4</sub>H<sub>9</sub><sup>+</sup>. In contrast, Adeeva *et al.*<sup>9</sup> proposed a classical bifunctional (metal-acid) carbenium ion mechanism for butane isomerisation catalysed by FMSZ, whereby C<sub>4</sub>H<sub>9</sub><sup>+</sup> reacts with butene (formed by butane dehydrogenation) to give C<sub>8</sub>H<sub>17</sub><sup>+</sup>, which undergoes  $\beta$ -scission to form C<sub>4</sub>H<sub>9</sub><sup>+</sup> and 2-methylpropene, with subsequent hydrogen transfer giving 2-methyl-



**Fig. 1** Conversion of ethane to gas-phase hydrocarbons at 723 K in the presence of Fe- and Mn-promoted sulfated zirconia. Feed ethane partial pressure, 10 kPa; total feed flow rate, 40 ml(NTP) min<sup>-1</sup>; mass of FMSZ, 1.0 g.

