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Methane conversion over sulfated zirconia

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In a continuous-flow differential microreactor, sulfated zirconia (SZ), deliberately activated *in situ* by water, has converted methane at 673 K to a C_2–C_6 hydrocarbon mixture of which 65–70% was ethene and isobutane. Maximum conversion activity of $\sim$4.6%, corresponding to 4×10^{-4} mole methane reacted per mole sulfate per second, was attainable at S/(added H_2O) molar ratio of 3.0 and methane flow rate of 5.6×10^{-6} mol (g-SZ)$^{-1}$ s^{-1}. This methane conversion could be catalytic and may involve superacidic sites.

Keywords: methane, sulfated zirconia, ethene, isobutane, superacid

1. Introduction

The conversion of methane to useful products and/or raw materials has been a subject of intense study during the past few decades [1]. Much of the effort has been devoted to oxidative coupling and partial oxidation catalytic processes involving metallic active sites. There has been, however, much interest also in the possibility of direct conversion of methane to higher hydrocarbons. Conventional acid catalysts, such as zeolites, are not known to be efficient in such conversion, but liquid superacids, e.g., Magic Acid, were shown effective in low-temperature oligocondensation of methane to the t-butyl and t-hexyl cations [2]. Product mixtures of the reaction of methane with SbF_5-based superacids contained C_2–C_6 hydrocarbons [3]. The thermodynamically more favorable reaction of ethene with methane to form propane was investigated at ambient conditions under pressure over metal fluoride solid superacids and ^{13}C tagging proved that methane indeed had been ethylated [4]. Liquid superacids were also effective in this reaction [5].

Sulfated zirconia (SZ) has been claimed a strong solid superacid and shown to be active in the conversion of light alkanes, e.g., butane, under mild conditions [6]. It was even reported [7] to catalyze the methane–ethene reaction at 573 K although the results could not prove unequivocally that methane indeed participated in the process. Recently, SZ has been found inactive in direct methane conversion up to 723 K [8], but, in contrast, Fe/Mn-promoted SZ (FMSZ) did convert methane to some extent at that temperature, giving mostly ethane. It has been pointed out [8] that the mechanism of this conversion may not at all be acidic; rather, it could relate to the metal (Fe) oxide dispersed over the SZ.

Not long ago, a promotional effect of water on SZ has been reported for the case of n-butane isomerization; upon deliberate dosing of water before the catalytic run, the activity first increased then passed through a maximum as more water was added [9]. Prior to that observation, we reported a maximum "superacid" activity as a function of time, in the conversion of alcohols over SZ [10]. The effect was associated with the *in situ* formation of water in the reactor during the dehydration of the alcohols, which precedes their skeletal transformation, and the subsequent accumulation of that water on the SZ. In the case of methanol conversion between about 550 and 600 K, the product mixture consisted mainly of ethene and isobutane. In this communication, we report on a similar product mixture, albeit at higher temperature and much smaller conversion, in the reaction of methane with the same SZ sample, when water is added deliberately to the reactant feed.

2. Experimental

The SZ sample of this study was prepared as follows. To a solution of 210 g zirconyl nitrate hydrate (Aldrich, tech.) in 2800 g deionized water, 200 ml of 28% NH_4OH were slowly added under stirring. The zirconium hydroxide precipitate thus obtained (at pH 9.5) was filtered under vacuum suction, washed thoroughly with deionized water, and dried at 383 K to yield 115 g hydrous zirconium oxide. Two grams of this oxide were washed with 30 ml 1 N H_2SO_4 over a Büchner funnel, dried overnight at 383 K and calcined at 813 K for 3 h to give a SZ powder with 6.1 wt% SO_4 and 153 m^2/g BET surface area. Pressing the powder to tablets, then grinding and screening, provided eventually a 0.15–0.25 mm particle size fraction, of which 0.4 g was used for the reaction.

Methane conversion was performed in a differential fixed-bed flow microreactor with an on-line GC (Shimadzu GC-9A) and a sampling arrangement. Samples withdrawn from the reactor downstream at various times were analyzed consecutively using a Supelco Petrocol DH capillary column. The methane gas reactant (Matheson, "Ultra High

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Purity", used without further purification) was shown to contain 99.96% methane and 0.04% ethane. Prior to the reaction, the catalyst was activated *in situ* at 773 K under $\sim 2:1$ air : helium gas stream for 1 h. Cooling to the reaction temperature was done under pure helium. The reaction was started ("time zero") by simultaneously adding to the helium stream methane (9.0 kPa partial pressure, flow rate of 5.6×10^{-6} mol (g-SZ)$^{-1}$ s^{-1}) from a side gas line and liquid water (1.9 kPa, as gas) from a Sage syringe pump. Methane conversion was calculated from the expression

$$\frac{\sum_{n=2}^{6+} N_n n/\mathrm{MW}_n}{\sum_{n=1}^{6+} N_n n/\mathrm{MW}_n} \times 100,$$

where MW_n is the molecular weight and N_n, the GC counts of C_n, a hydrocarbon (alkane, alkene) with a carbon number n.

3. Results and discussion

Without water addition, methane conversion over SZ under the conditions of this work, was negligible, as expected, and so was it with water but at a temperature of 623 K. Practically, the reaction of methane over SZ occurred only at 673 K and in the presence of added water. The change in total methane conversion as a function of time on stream (TOS) is shown in figure 1, and product distribution and selectivity at the various TOS values at which reaction mixtures were analyzed, are presented in table 1. As seen, the conversion first increases and reaches a maximum, then declines towards 900 s at which time it approaches a constant value of 2.3%. The main single product of this methane conversion is ethene; its percent in the product mixture increases from 38 to 48 mol% during the run. In contrast, the sum of concentrations of propane and isobutane decreases with TOS, starting from 51.5 mol%; the decline of isobutane is moderate but that of propane is dramatic. The selectivity to the olefin in C_2 and to the branched product in C_4 is very high and about constant. However, propene selectivity in C_3 changes from 0 at the beginning of the run, to 0.8 at 900 s on stream.

The increased conversion during the first 2 min on stream is associated with the activation of SZ by water. If all the water reacts with the sulfate to provide S–OH Brønsted acid sites (one site per one H_2O molecule added), then the transient turnover frequency (TOF), defined as molecules of methane converted per S–OH site per second, would show the behavior as depicted in figure 1. An exponential decay is obtained with TOF of 2.4×10^{-3} s^{-1} at 30 s on stream. From a TOF graph generated by exponential regression ($R^2 = 0.99$), the conversion behavior could be interpolated to give a maximum of 4.6% (at 200 s on stream) corresponding to 2.6×10^{-7} mol(CH_4) (g-SZ)$^{-1}$ s^{-1}, or 4.0×10^{-4} mol(CH_4) (mol-S)$^{-1}$ s^{-1}. This maximum occurred when the molar amount of H_2O delivered was 0.33 of the molar amount of sulfate. Assum-

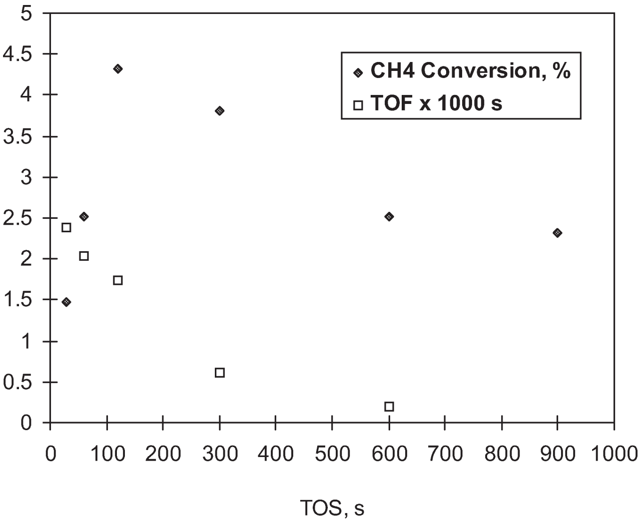


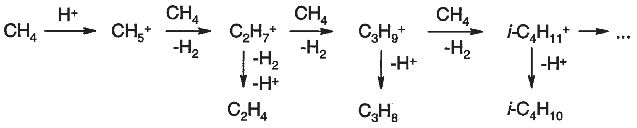
Figure 1. Methane conversion and turnover frequency (see text for definition) as function of time on stream.

Table 1
Product distribution and selectivity in methane conversion over SZ.

	TOS (s)					
	30	60	120	300	600	900
	Product distribution, wt% (mol%)					
$C_2^=$	24.4 (38.2)	28.6 (42.4)	28.9 (42.6)	27.8 (42.4)	33.5 (48.0)	34.4 (48.0)
C_2	2.1 (3.0)	4.4 (6.0)	6.9 (9.5)	3.9 (5.6)	7.6 (10.1)	7.0 (9.1)
$C_3^=$	–	0.75 (0.7)	1.5 (1.4)	5.9 (6.0)	6.9 (6.5)	13.6 (12.7)
C_3	21.8 (21.7)	15.8 (14.9)	13.6 (12.7)	10.1 (9.8)	6.8 (6.2)	4.1 (3.7)
iC_4	39.2 (29.6)	41.5 (29.7)	36.9 (26.3)	36.5 (26.9)	31.5 (21.8)	32.3 (21.8)
nC_4	2.4 (1.8)	2.4 (1.7)	2.4 (1.7)	1.7 (1.2)	1.1 (0.77)	–
iC_5	5.6 (3.4)	6.8 (3.9)	7.8 (4.4)	10.3 (6.1)	8.3 (4.6)	8.5 (4.6)
nC_5	–	–	0.27 (0.15)	–	–	–
C_{6+}	4.5 (2.2)	–	1.8 (0.9)	3.8 (1.9)	4.4 (1.9)	–
	Selectivity					
$C_2^= / \sum C_2$	0.93	0.88	0.82	0.88	0.83	0.84
$iC_4 / \sum C_4$	0.94	0.95	0.94	0.96	0.97	1.00
$C_3^= / \sum C_3$	0	0.047	0.103	0.378	0.513	0.775

ing an average TOF value of 1.3×10^{-3} s^{-1} in the TOS range 0–600 s, 0.8 molecules of CH_4 were converted per S–OH. Since apparently not all the added water reacted with the sulfate, especially at higher TOS, the real number of methane molecules converted per site could be over unity. In that case, the process was catalytic.

Even though the reaction of methane described here was influenced by water, it could not be due to steam reforming which is known to occur only with heavier transition metal catalysts and at much higher temperature. Therefore, in the absence of synthesis gas ($CO + H_2$) as intermediate reactant, Fischer–Tropsch synthesis could not be responsible for the hydrocarbon product mixture obtained. Even though other mechanisms are still possible, one major reaction route seems most suitable here, agreeing with liquid superacid chemistry [2,3] and based on the same principles as used in the recently proposed mechanism of ethane conversion on FMSZ [11]; interestingly, the latter reaction also yielded (besides methane) ethene and "butane". Thus, it is believed that methane molecules add consecutively to a methonium ion first produced by methane protonation, thereby self-condensing to higher alkonium ions. This results eventually in isoalkanes, predominantly isobutane, but owing to the severity of the reaction, much of the C_2 surface intermediate species tends to desorb, through dehydrogenation, as ethene, rather than to continue the condensation. Likewise, a portion of the C_3^+ species deprotonates to propane. While isobutane disproportionation, giving propane and isopentane, cannot be ruled out based on the current results, it seems more likely that in this methane conversion reaction, isopentane is formed directly, i.e., simply by continuing the chain propagation process beyond isobutane. A simplified sequence of single pathways leading to most of the reaction products, could be as follows:



$$CH_4 \xrightarrow{H^+} CH_5^+ \xrightarrow[-H_2]{CH_4} \underset{\substack{\downarrow -H_2,\ -H^+ \\ C_2H_4}}{C_2H_7^+} \xrightarrow[-H_2]{CH_4} \underset{\substack{\downarrow -H^+ \\ C_3H_8}}{C_3H_9^+} \xrightarrow[-H_2]{CH_4} \underset{\substack{\downarrow -H^+ \\ i\text{-}C_4H_{10}}}{i\text{-}C_4H_{11}^+} \longrightarrow \ldots$$

It may, of course, be argued that since ethene is formed as major product, the C_{3+} mixture could result from its condensation-cracking [7] and/or from its reaction with methane [3,4]. However, a direct propagation of carbonium ions without involving the energetically unfavorable primary carbenium ions (e.g., $C_2H_5^+$) is more likely under our conditions; thus, there is no reason to regard ethene essentially as an intermediate in the above methane conversion.

If the mechanistic picture proposed here is correct, then methane conversion over SZ may be considered as evidence that SZ is capable of becoming a strong superacid when treated with adequate amounts of water. Earlier literature claiming superacidity in this catalytic system [6] did not distinguish between SZ and H_2O/SZ (or "H_2O-promoted" SZ). The decline in TOF can thus be explained at least in part by the diminishing strength of surface acid sites as more sulfate hydroxylation takes place and the concentration of Brønsted acid sites is increased. In spite of the rather low conversion level of methane, as judged by the amount of gaseous product, the deactivation of SZ may perhaps be also due to carbonaceous deposits formed as unaccounted for side products. Further, it cannot be ruled out at this stage that, as in the case of liquid superacids [3], SZ may have acted in the above conversion not only as strong acid but also as oxidant scavenger for the dihydrogen. While removing the thermodynamic constraint of hydrogen generation from methane, this scavenging function may have partially destroyed active (sulfate) sites, by reducing them.

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