Catalysis Letters 16 (1992) 389–398

The low-temperature oxidative coupling of methane over zirconium oxide

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Received 22 June 1992; accepted 18 September 1992

Zirconium oxide is shown to be capable of catalyzing the conversion of methane to ethane at temperatures as low as 530°C. The lowest temperature at which ethane is produced is found to be dependent upon the method employed for the preparation of the catalyst. The presence of surface hydroxyl groups appears to be necessary for the production of ethane at these low temperatures.

Keywords: Methane; oxidative dehydrogenation; zirconium oxide; hydroxyl; steaming

1. Introduction

Zirconium oxide has acidic, basic, oxidizing and reducing properties [1]. Utilizing these properties, zirconium oxide catalysts have been applied to reactions such as synthesis of methanol from synthesis gas [2], isomerization of 1-butene [3] and dehydration of alcohols [4]. The catalytic performance of zirconium oxide is strongly influenced by the preparation procedures and activation methods [5]. Zirconium oxide exhibits three polymorphic forms, the monoclinic, tetragonal and cubic phases [6]. Although the monoclinic phase is thermodynamically stable below 1170°C, the tetragonal phase may be stabilized at lower temperatures under certain conditions.

Methane is a main component of natural gas which is one of the most abundant raw materials throughout the world. Hence extensive studies have been made to convert methane to more valuable chemical feedstocks and liquid fuel, such as methanol, olefins, liquid paraffins and aromatics. Among various processes the oxidative coupling of methane is of considerable interest because it can produce C_2 compounds in one step. Since the pioneering work of Keller and Bhasin [7], many oxide catalysts have been proposed. These materials are

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reducible metals, alkali metals, alkaline earth metals and rare earth metals. Relatively few studies of zirconium oxide have been reported [8–12]. Evidence relating the oxidative coupling of methane to the basicity of the catalysts has appeared [13]. However, it is also clear that basicity, which may influence the formation of surface oxygen species, is not the only factor of importance for such catalysts [14]. Most of the methane conversion reaction studies are usually performed at a relatively high temperature of over 700°C. The selectivity to C_{2+} hydrocarbons was found to be relatively low over zirconium oxide unless alkali, alkaline earth metal and/or lanthanide were added. No work dealing with the catalytic activity of zirconium oxide at reaction temperatures less than 600°C has been reported.

In this work, it was found that even at the temperature of 530°C, C_2H_6 was formed over zirconium oxide in the oxidative coupling of methane and the C_2-lowest temperature (the lowest reaction temperature at which C_2H_6 formation was observed) strongly depends on the preparation procedure of zirconium oxide.

2. Experimental

Hydrous zirconium oxide samples were precipitated from a zirconium tetrachloride (Aldrich $99.9^{+}\%$) solution (0.3 mol/ℓ) by the addition of a calculated amount of ammonium hydroxide solution (4 M or concentrated) to produce a solution which possessed the final pH (usually 10.4), following the procedures proposed by Davis et al. [15]. Some samples are aged in the mother liquor at the final pH with stirring. The resultant precipitate was collected by filtration. The collected zirconium hydrous gel was washed with distilled water repeatedly. The white gel thus obtained was dried in air at 120°C overnight and calcined in static air at 500°C for 4 h unless otherwise stated. The preparation methods and physical properties are summarized in table 1.

Catalyst no. 320 was prepared by calcination of zirconyl nitrate (Aldrich $99.99^{+}\%$) at 500°C for 10 h in air. Catalysts nos. 316-600, 316-700 and 316-800 were obtained by calcination of catalyst no. 316 for 4 h at 600, 700 and 800°C, respectively. Their physical properties are shown in table 2.

The activities of the catalysts were determined using a continuous flow reactor mounted horizontally at atmospheric pressure. The reactor consisted of an 8 mm i.d. and 10 mm length quartz tube sealed to 4 mm i.d. quartz tubes on both ends. A measured amount of catalyst (usually 0.6 g) was placed in the 8 mm portion of the quartz tube with plugs of quartz wool at both ends. The temperature was measured by a thermocouple placed in contact with the outside wall of the reactor. The molar ratio of CH_4 to O_2 in the feed gas (15 ml/min; CH_4 215 Torr, O_2 12.6 Torr, He balance) was 17 unless otherwise stated. The reactant and products were analyzed on a HP5890A gas chromatograph with a

Table 1
Preparation and physical properties of zirconium oxide catalysts obtained from zirconium hydroxide

Catalyst no.	Final pH [a]	Aging at final pH (h)	%T [b]	BET area (m^2/g)
318	10.4 (8)	24	100	77.1
307	10.4 (8)	5	64	80.9
314	10.4 (11)	0	44	64.9
315	10.4 (9)	0	28	59.3
316	10.4 (5)	0	17	61.0
311	6 (0.1)	0	23	77.4

[a] Final pH of the solution at which zirconium hydroxide was formed. ( ) time (h) required to reach final pH.

[b] Molar% of tetragonal phase (remainder; monoclinic phase).

TC detector. Porapak T (18 ft × 1/8 in, programmed 50–160°C) was used to analyze CO_2, C_2H_4, C_2H_6, C_2H_2, C_3, HCHO, H_2O and CH_3OH. Molecular sieve 5A (1 m × 1/8 in, 50°C) was employed in the analysis of O_2, CO and CH_4. The conversion of methane was calculated from the products and the methane introduced in the feed. The selectivities were calculated from the conversion of methane to each product on a carbon base. The details of the apparatus and the procedures have been described elsewhere [16]. The reaction temperatures were changed in 10°C intervals to explore the C_2-lowest temperature.

Powder X-ray diffraction patterns were recorded on a Siemens Model D500 diffractometer using nickel-filtered Cu Kα radiation. Patterns were recorded over the range $2\theta = 5–70°$. The catalyst was a mixture of monoclinic and tetragonal phases. The molar% of tetragonal phase (%T) was calculated from the ratio of the peak intensities [17],

$$\frac{(1,\ 1,\ 1)_T}{1.6(1,\ 1,\ -1)_M + (1,\ 1,\ 1)_T},$$

where T and M denote tetragonal and monoclinic phases, respectively.

Table 2
Preparation and physical properties of zirconium oxide catalysts obtained by calcination

Catalyst [a] no.	Raw material	Calcination	Crystal size (nm) [b]	BET area (m^2/g)
320	$ZrO(NO_3)_2$	500°C, 10 h	–	60.9
316-600	no. 316	600°C, 4 h	18	35.7
316-700	no. 316	700°C, 4 h	22	24.9
316-800	no. 316	800°C, 4 h	27	13.1

[a] All catalysts are pure monoclinic phase.

[b] Crystal size was determined from X-ray diffraction data using Scherrer's equation.

The average particle size of the zirconium oxide was determined from Scherrer's equation [18].

3. Results and discussion

The effect of time-on-stream on the conversion and selectivity over the catalyst no. 316 at 530°C (the C_2-lowest temperature) is shown in fig. 1. The main products of the reaction were CO, CO_2, H_2O, H_2 and C_2H_6. A considerable amount of water was produced over all catalysts but is not reported. Excellent carbon mass balances ($100 \pm 2\%$) were obtained for the reaction. When successive experiments were done on the same catalyst, a reproducibility of $\pm 20\%$ for C_2H_6 was observed. Conversion of oxygen was around 97% and was virtually constant during 6 h on-stream. It is observed that the conversion of methane and product distribution were also virtually constant. Hence the results collected at $\approx 1/2$ h on-stream are reported hereafter. In the absence of the catalyst, the conversion of methane at 600°C was less than 0.005% and the products were only carbon dioxide and water. This shows that contribution of the homogeneous oxidation of methane with oxygen in gas phase is negligibly small compared with the catalytic conversion over zirconium oxide under the reaction conditions adopted in this work. The participation of the water gas shift reaction in the present studies cannot be excluded.

The C_2-lowest temperatures and product distribution over various zirconium oxides are summarized in table 3. It can be seen that the C_2-lowest temperature

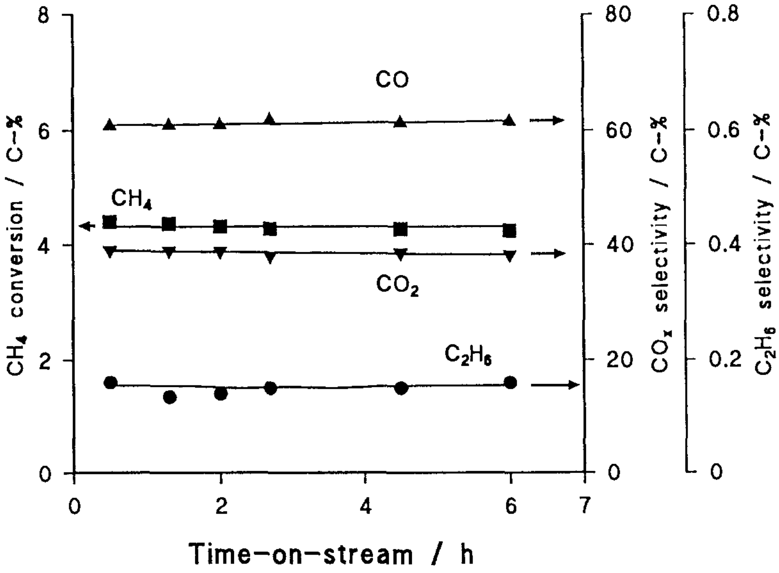

Fig. 1. Effect of time-on-stream on catalytic activity and selectivity of catalyst no. 316. Reaction temperature 530°C, feed 15 ml/min (CH_4 215 Torr, O_2 12.6 Torr, He balance).

Table 3
The C_2-lowest temperature and product distribution over various ZrO_2 catalysts [a]

Catalyst no.	%T [b]	C_2-lowest temperature (°C)	CH_4-conv. (%)	Selectivity (%)			O_2-conv. (%)
				CO	CO_2	C_2H_6	
318	89	570	2.74	58.62	41.19	0.19	73
307	36	540	2.25	75.46	24.24	0.30	63
314	15	530	4.27	62.08	37.76	0.17	95
315	8	530	4.23	61.83	38.05	0.12	95
316	4	530	4.40	60.80	39.04	0.16	97
311	5	590	4.59	76.56	23.35	0.10	100
320	0	570	2.17	76.50	23.35	0.16	47

[a] Feed 15 ml/min (CH_4 215 Torr, O_2 12.6 Torr, He balance).
[b] After 6 h of reaction at the C_2-lowest temperature.

strongly depended on the preparation method of the catalysts. The %T of all catalysts decreased after the reaction at the C_2-lowest temperature for 6 h. It should be noted that the conversion of oxygen is relatively high over the catalysts nos. 311, 314, 315 and 316 but oxygen consumption of nearly 100% is not necessary to observe the formation of C_2H_6 in the effluent gas as can be seen over the catalyst no. 307. The C_2-lowest temperatures over catalysts nos. 314, 315 and 316 were the same value of 530°C though the %T varied from 17 to 44%. Moreover, over these three catalysts the conversion of methane and the product distribution were almost the same. On the contrary the C_2-lowest temperature of the catalyst no. 311 was as high as 590°C although its %T was between those of the catalysts nos. 315 and 316. The pure tetragonal zirconium oxide (catalyst no. 318) gave a relatively high C_2-lowest temperature of 570°C. After the reaction at 570°C for 6 h the %T of the catalyst no. 318 decreased to 89%. These results suggested that crystal phase (%T) did not play a main role in determining the C_2-lowest temperature.

As can be seen in tables 1 and 2, the BET surface area increases in the order of catalysts nos. $315 < 320 < 316 < 314 < 318 < 311 < 307$. On the other hand the C_2-lowest temperature rises in the order of the catalysts nos. 314, 315, $316 < 307 < 318$, $320 < 311$. This indicated that there is no clear correlation between BET surface area and the C_2-lowest temperature.

From the above results, it is suggested that neither %T nor BET surface area is a decisive factor in determining the C_2-lowest temperature. Since the final pH of the precipitation and the aging time at that pH strongly affected the C_2-lowest temperature (tables 1 and 3), the surface properties of zirconium oxide are assumed to be the key factors in determining the catalytic performance of zirconium oxide.

In further experiments, the effect of the molar ratio of CH_4 to O_2 in the feed gas was investigated at a reaction temperature of 530°C. In these experiments

Table 4
Effect of CH_4/O_2 molar ratio of feed on product distribution over catalyst no. 316 [a]

Partial pressure of O_2 (Torr)	CH_4-conv. (%)	Selectivity (%)			O_2-conv. (%)
		CO	CO_2	C_2H_6	
102	17.59	42.62	57.38	0.00	49
24.2	7.91	54.83	45.07	0.10	79
12.6	4.40	60.80	39.04	0.16	97

[a] Feed: 15 ml/min (CH_4 215 Torr, O_2 variable, He balance: total 760 Torr). Reaction temperature 530°C.

the partial pressure of CH_4 was not changed while that of O_2 was varied. The results are shown in table 4. The selectivity to C_2H_6 was the highest at the lowest O_2 partial pressure. The conversion of methane and molar ratio of CO_2 to CO increased with the O_2 partial pressure, while the conversion of O_2 and selectivity to C_2H_6 decreased. At an O_2 pressure of 102 Torr, C_2H_6 formation was not detected, that is, with excess oxygen methane is converted into only CO and CO_2 probably due to the successive oxidation of C_2H_6.

The catalysts with different calcination temperature were prepared from the catalyst no. 316. Increasing the calcination temperature caused an increase in the particle size of zirconium oxide and a decrease of the BET surface area (table 2), which suggests that sintering of zirconium oxide crystals occurred with calcination. The effect of calcination temperature on the catalytic performance is summarized in table 5. The catalytic activity of the original catalyst no. 316 is shown in table 3. The C_2-lowest temperature rose from 530 to 580°C with increase in the calcination temperature from 500 to 800°C while the molar ratio of CO_2 to CO decreased. The product distributions over the catalysts nos. 316-700 and 316-800 were almost the same.

Preliminary experiments showed a hysteresis in catalytic performance during the reaction, that is, the C_2-lowest temperature decreased after the reaction at over 600°C. Therefore, the effect of the reaction and the steaming on the catalytic performance was investigated. The catalytic reaction was performed at

Table 5
Effect of calcination temperature on the C_2-lowest temperature [a]

Catalyst no.	C_2-lowest temperature (°C)	CH_4-conv. (%)	Selectivity (%)			O_2-conv. (%)
			CO	CO_2	C_2H_6	
316-600	540	4.18	68.68	31.21	0.11	90
316-700	580	4.13	70.51	29.39	0.11	98
316-800	580	4.23	70.38	29.50	0.12	97

[a] Feed: 15 ml/min (CH_4 215 Torr, O_2 12.6 Torr, He balance).

Table 6
Effect of pretreatment on the C_2-lowest temperature [a]

Catalyst no.	Pretreatment (R or S) [b]	SA [c] (m^2/g)	Reaction temperature (°C)	CH_4-conv. (%)	Selectivity (%)			O_2-conv. (%)
					CO	CO_2	C_2H_6	
311	no	77.4	550	3.32	87.36	12.64	0.00	74
311	no		560	3.54	85.93	14.07	0.00	79
311	R	46.9	560 [d]	4.04	72.88	27.03	0.09	93
311	S	49.4	550 [d]	3.97	64.28	35.60	0.13	100
316-800	no	–	540	3.17	78.26	21.74	0.00	66
316-800	R	–	540 [d]	3.30	72.57	27.27	0.16	76
316-800	S	–	540 [d]	3.19	71.51	28.35	0.14	78

[a] Feed: 15 ml/min (CH_4 215 Torr, O_2 12.6 Torr, He balance).

[b] R: reaction at 600°C for 4 h; S: steaming at 600°C for 4 h in 20 ml/min He flow containing 20 Torr H_2O.

[c] BET surface area after pretreatment.

[d] The C_2-lowest temperature after the pretreatment.

600°C for 4 h just before the C_2-lowest temperature was determined. Steaming was carried out at 600°C for 4 h with 20 ml/min He flow containing 20 Torr of H_2O. The C_2-lowest temperature and product distribution after the pretreatment (the reaction or the steaming) are summarized in table 6. Catalytic performance at the same reaction temperature but before the pretreatment is also shown in table 6 for comparison. The formation of C_2H_6 was not observed at these temperatures when the reaction was carried out before the pretreatment. After the reaction at 600°C for 4 h, the C_2-lowest temperature of the catalysts nos. 311 and 316-800 dropped from 590 to 560°C and from 580 to 540°C, respectively (tables 3, 5 and 6). It is interesting to note that over both catalysts the conversion of methane and the molar ratio of CO_2 to CO at the same reaction temperature increased after the reaction. After the steaming at 600°C for 4 h the C_2-lowest temperature of the catalysts nos. 311 and 316-800 also decreased from 590 to 550°C and from 580 to 540°C, respectively. At the same reaction temperature both the conversion of methane and selectivity to carbon dioxide increased after the steaming as well as after the reaction. The surface area of catalyst no. 311 decreased after the reaction and after the steaming from 77.4 to 46.9 and 49.4 m^2/g, respectively. These observations provide further support for the supposition that the BET surface area does not affect the C_2-lowest temperature directly.

The enhancement effect of the reaction at 600°C on the production of C_2H_6 and the conversion of methane suggested that the active sites for both C_2H_6 production and methane conversion increased during the reaction. Two explanations for such a conclusion may be advanced. Although the reaction temperatures are relatively low it may be anticipated that carbon-containing species are deposited on the surface during the reaction. These may contain sites which are active for one or more steps of the coupling process. Further, it is possible that the water produced during the reaction may generate hydroxyl groups on the surface of the catalyst. However, since no colour change was observed after the reaction at 600°C significant quantities of carbonaceous species may not be formed during the reaction at 600°C. The steaming at 600°C had the same effect as the reaction on the C_2-lowest temperature of zirconium oxide catalysts, which also supports the latter possibility.

As can be seen in table 5, raising the calcination temperature of the catalyst no. 316 caused an increase in the C_2-lowest temperature. However, either the steaming or the reaction at 600°C for 4 h lowered the C_2-lowest temperature of the catalyst no. 316-800. These results strongly suggest that the hydroxyl groups on the surface created in the presence of water play an essential role in the production of C_2H_6.

Positive effect of steaming on oxidative coupling of methane on lanthanide catalysts was reported by Lunsford et al. [19]. Increase in the selectivity to C_{2+} hydrocarbons was also achieved over the catalyst system Ni–Ca–K by the addition of water vapour to the feedstream [20]. Although some tentative explanations of the role of water vapour have been proposed, the actual function of water in the oxidative coupling of methane is not understood.

It has been proposed that oxidative coupling of methane is initiated by the catalytic activation of methane to form methyl radicals and that an acid–base pair ($M^{n+}_{LC}O^{2-}_{LC}$; subscript LC denotes low coordination) on the metal oxide surface is involved in the abstraction of a hydrogen atom from the methane molecule as is shown in fig. 2 [21]. The anion sites are regenerated by dehydroxylation of the catalyst surface to give water and anion vacancies (eq. (2)). An anion vacancy reacts with O_2^- leading to the formation of O^- (eq. (3)).

On the basis of this mechanism the number of active sites for methyl radical formation (acid–base pair; $M^{n+}_{LC}O^{2-}_{LC}$) is expected to be proportional to the

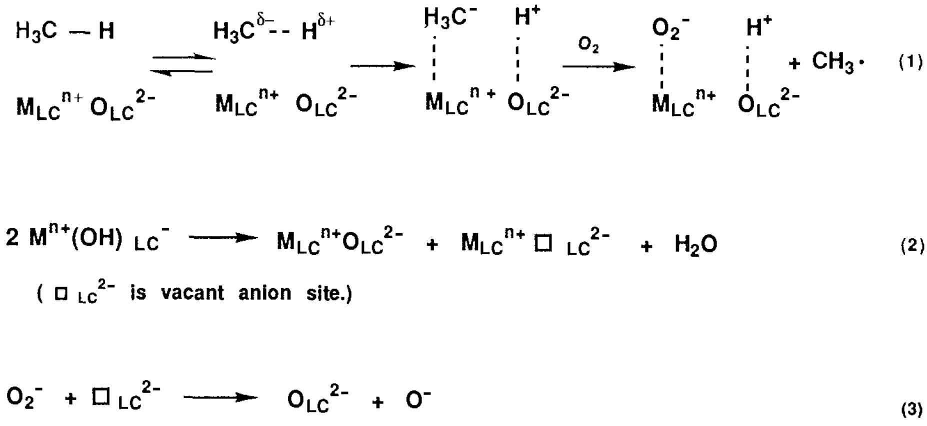

Fig. 2. Mechanism of oxidative coupling of methane involving an acid–base pair (ref. [21]).

concentration of surface hydroxyl groups through eq. (2) (fig. 2) under the reaction conditions. Thus the enhancement produced by the steaming and reaction at 600°C may be attributed to an increase in the number of surface hydroxyl groups by the above pretreatment. Calcination of zirconium oxide in an oxygen atmosphere is considered to lead to the formation of the stoichiometric oxide ($Zr^{4+}O^{2-}$) and to the decrease in the number of the low-coordination acid–base pairs ($Zr^{4+}_{LC}O^{2-}_{LC}$). It is considered that this decrease in the number of active sites after calcination of zirconium oxide may lead to the increase in the C_2-lowest temperature (table 5).

In conclusion, the C_2-lowest temperature found with zirconium oxide strongly depends on the procedure employed for the preparation of the catalyst. The main factor which determines the C_2-lowest temperature is considered to be the surface hydroxyl groups of the catalysts which is closely related to the catalytic active site (acid–base pair) for the oxidative coupling of methane.

Acknowledgement

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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