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Methane coupling catalysts based on zirconium combined with lanthanum

V.M. Niemi and A.O.I. Krause

Neste Oy, Technology Centre, PO Box 310, FIN-06101 Porvoo, Finland

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Two series of zirconium and lanthanum oxide based catalysts were synthesised, characterised (XRD, ESCA, BET) and tested for their effectiveness in the oxidative coupling of methane (OCM). Starting materials and the preparation method (ZrO_2 and wet impregnation, $ZrO(NO_3)_2 \cdot xH_2O + La(NO_3)_3 \cdot 6H_2O$ and coprecipitation) determined the bulk composition of the catalysts ($ZrO_2 + La_2O_3, La_2O_3 * 2ZrO_2$). Doping with alkali (Li, Na, K) or alkaline earth metal (Mg, Ca, Sr) increased the selectivity to hydrocarbons. The best C_2-hydrocarbon yields were obtained with the Sr-doped $ZrO_2 + La_2O_3$ catalyst (16.1%) and the Li-doped $La_2O_3 * 2ZrO_2$ catalyst (17.3%).

Keywords: oxidative coupling of methane (OCM); zirconium oxide; lanthanum oxide; lanthanum zirconium oxide

1. Introduction

For economic and environmental reasons natural gas conversion to more valuable products, methanol, liquid fuels or chemical feedstocks, has been a primary research area in catalysis in the past decade. One attractive route to convert methane, the main component of natural gas, is direct one-step oxidative coupling to ethane and ethylene (OCM). Since the work of Keller and Bhasin [1] hundreds of oxidative coupling catalysts have been developed, tested and reported. Most of these are reducible oxides, pure or doped oxides of rare-earth metals, or oxides of alkaline earth metals. Nearly all the elements of the periodic table, as such or combined, have at one time or other been incorporated in methane coupling catalysts. Zirconium-based methane coupling catalysts have not received much attention, however, perhaps because of the results which show that zirconium oxide has poor C_2-selectivity and oxidizes methane to CO and CO_2 [2–5]. The C_2-selectivity of zirconium oxide can, however, be enhanced by doping with alkali metals [6], alkaline earth metals [2,6], group IIIA metals [4], or NaCl [7] or by incorporating zirconium into the perovskite structure [8]. Moreover, although ZrO_2 oxidizes methane completely, it does possess a number of interesting features; acidic and basic properties, thermal and chemical stability and hardness [9–11]. Another oxide possessing acidic and basic properties [12], La_2O_3, has been shown to be an active catalyst in methane coupling either as such or doped [2,4,12–17]. The main objective in this work was to clarify the role of ZrO_2 in mixed Zr + La oxide OCM catalysts. One example of an alkali metal doped mixed Zr + La oxide catalyst has been specified in the patent application of Snamprogetti [18], but the effect of ZrO_2 has remained unclear.

2. Experimental

2.1. CATALYST PREPARATION

The reagents used, without further purification, in the preparation of the catalysts were as follows: ZrO_2 (99% Riedel–De Haën), $ZrO(NO_3)_2 \cdot xH_2O$ (Aldrich), $La(NO_3)_3 \cdot 6H_2O$ ($\geqslant$99% Merck), $Mg(NO_3)_2 \cdot 6H_2O$ (98.5% Merck), $Ca(NO_3)_2 \cdot 4H_2O$ (>98% Merck), $Sr(NO_3)_2$ ($\geqslant$99% Merck), LiOH (>98% Merck), $NaNO_3$ (>99.5% Merck), NaOH ($\geqslant$99% Riedel–de Haën) and KOH (87% J.T. Baker).

The catalysts were synthesised by wet impregnation or coprecipitation method. In the wet impregnation method, when ZrO_2 was one of the starting materials, the appropriate nitrates (La and alkali or alkaline earth metal) were dissolved in H_2O and poured over ZrO_2 and the mixture was stirred while heating until only a thick paste remained. In the coprecipitation method the nitrates of Zr and La ($ZrO(NO_3)_2 \cdot xH_2O$ and $La(NO_3)_3 \cdot 6H_2O$) were dissolved in H_2O and precipitated with a solution of NH_4OH (25%) or alkali hydroxide. In the case of alkali hydroxide precipitation the precipitate was filtered without washing, and when Mg, Ca or Sr dopant was added the mixture was evaporated after the NH_4OH precipitation. The catalysts were dried at 120°C overnight and calcined in a muffle oven in air according to the following heating program:

$$25°\mathrm{C} + 1°\mathrm{C/min} \rightarrow 800°\mathrm{C}\ (4\ \mathrm{h}) \rightarrow \text{slow cooling to room temperature}.$$

The calcined catalysts were crushed and sieved to 0.5–1.0 mm particles.

2.2. CATALYST CHARACTERIZATION

X-ray powder diffraction patterns were recorded with a Siemens Diffrac 500 (Cu Kα) diffractometer, and BET surface areas were determined with a Micromeritics Rapid Surface Area Analyzer 2200 (single point N_2 adsorption method). ESCA analyses were performed with a Surface Science Instruments X-probe model 101 using an Al Kα X-ray source. Alkali metal contents in the lanthanum zirconate oxide catalysts were determined with a Perkin Elmer atomic absorption spectrometer. Otherwise the chemical compositions (mole ratios of the metals) of the synthesised catalysts are based on the data of the starting materials.

2.3. CATALYST TESTING

The synthesised catalysts were tested in the continuous flow reactor apparatus shown in fig. 1. The reactor tube (fig. 2) was made of quartz. The usual amount of catalyst used in the tests was 1.0 g, and this was placed just above the narrowest part of the quartz tube with the help of quartz wool. The heating length of the oven was 550 mm. The actual reaction temperature (typically 700 and 750°C) was measured by thermocouples placed in the thermowell inside the reactor tube.

Gas flow (a total flow typically 100 ml/min and mole ratio $O_2 : CH_4 : N_2 = 1 : 4 : 20$ or $1 : 2 : 12$) into the reactor was regulated with precalibrated mass flow controllers (Brooks 5850 TR Series). Gases were CH_4 (99.95%, quality 3.5), N_2 (99.999%, quality 5.0) and synthetic air (20% O_2, quality 4.8 and 80% N_2, qual-

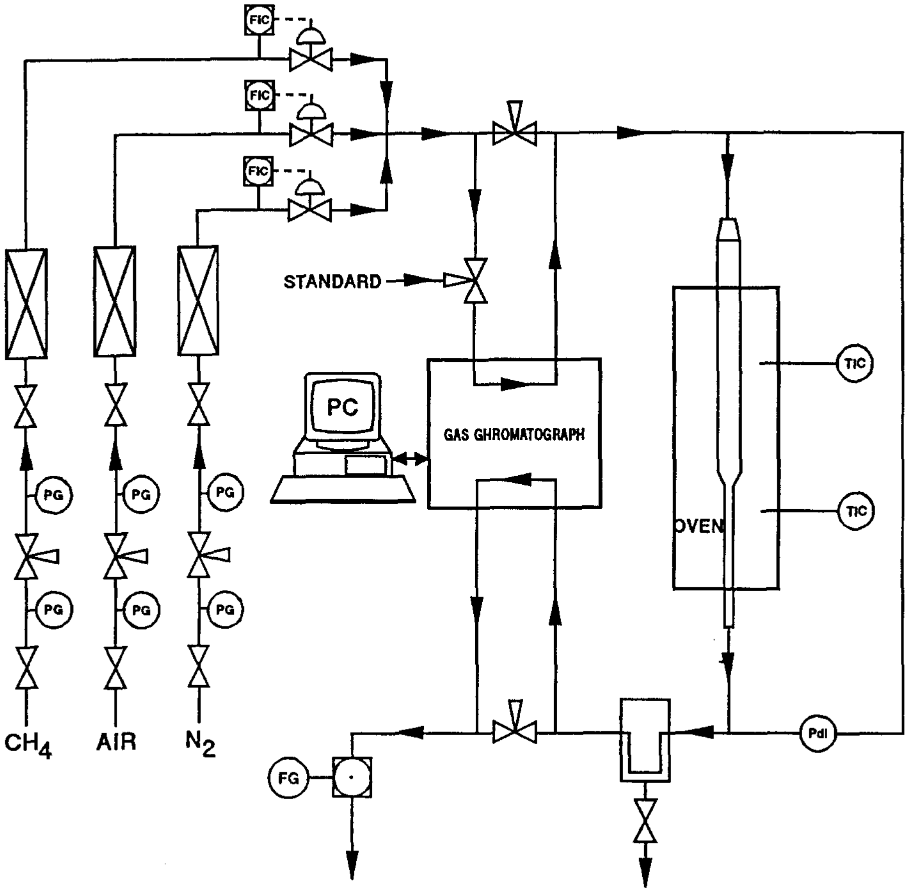

Fig. 1. Schematic drawing of the OCM microreactor apparatus.

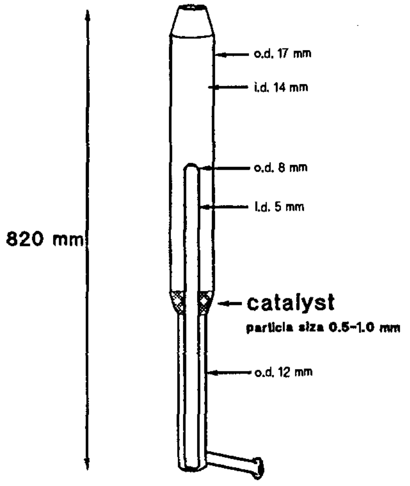

Fig. 2. Quartz reactor tube.

ity 5.0), all delivered by AGA. The gases were premixed before entering the reactor tube. The feed and product gases were analysed on-line with a gas chromatograph (HP 5890 Series II) equipped with a Porapak N column (3 m) for CO_2 and C_2–C_4 hydrocarbons and a molecular sieve 5Å column (1 m) for H_2, O_2, N_2, CH_4 and CO. Both FID and TCD detectors were used to analyse the gases. The valve system used in the gas chromatograph allowed a direct analysis of all gases from the same on-line sample.

The catalysts were heated to the reaction temperature under a slow flow of synthetic air, and before sampling the catalyst was stabilized with the relevant feed for 40 min. The main results are shown at the higher reaction temperature ($\sim$ 750°C) where the total time of the feed was 4 h.

The conversion of methane (X_{CH_4}) was calculated from the product sample assuming that no carbon is deposited on the catalysts. The selectivities of products (S_i) were calculated from the conversion of methane to each product on a carbon basis. The C_2-yield (Y_{C_2}) is defined as the product of the methane conversion and the selectivity to C_2-hydrocarbons.

3. Results and discussion

3.1. IMPREGNATED CATALYSTS

The catalysts based on ZrO_2 were synthesised by the wet impregnation method (except pure ZrO_2 which was simply pressed, crushed and sieved). The test results for the catalysts at 750°C are set out in table 1. Surface areas of all the catalysts were very low (under 10 m^2/g). X-ray powder diffraction patterns indicated that the bulk materials of the ZrO_2-based catalysts consisted mainly of metallic oxide

Table 1
Results of catalysts based on ZrO_2 (X = conversion, S = selectivity, Y = yield)

Catalyst	T (°C)	$O_2 : CH_4 : N_2$ (mol)	X_{CH_4} (%)	X_{O_2} (%)	S_{C_2} (%)	S_{CO_x} (%)	Y_{C_2} (%)
ZrO_2	755	1 : 2 : 12	21.9	75	4.5	95.4	1.0
	751	1 : 4 : 20	12.1	87	7.1	92.9	0.9
ZrO_2/La	756	1 : 2 : 12	37.4	100	33.3	64.6	12.4
(1 : 1)	751	1 : 4 : 20	23.2	100	50.3	46.3	11.6
ZrO_2/La/K	761	1 : 2 : 12	35.5	94	39.1	58.6	13.9
(1 : 1 : 1)	755	1 : 4 : 20	22.5	99	58.5	38.3	13.2
ZrO_2/La/K	761	1 : 2 : 12	36.4	98	37.4	60.3	13.6
(4 : 1 : 1)	755	1 : 4 : 20	21.7	99	56.1	41.7	12.2
ZrO_2/La/Na	758	1 : 2 : 12	25.2	63	53.1	43.4	13.4
(1 : 1 : 1)	756	1 : 4 : 20	18.2	80	64.3	30.8	11.7
ZrO_2/La/Na	755	1 : 2 : 12	24.3	53	48.7	48.5	11.8
(4 : 1 : 1)	752	1 : 4 : 20	17.7	70	63.8	32.0	11.3
ZrO_2/La/Li	755	1 : 2 : 12	14.2	34	48.0	50.5	6.8
(1 : 1 : 1)	748	1 : 4 : 20	10.6	47	54.8	43.5	5.8
ZrO_2/La/Li	761	1 : 2 : 12	34.7	97	29.8	68.5	10.3
(4 : 1 : 1)	754	1 : 4 : 20	19.3	99	40.8	57.1	7.9
ZrO_2/La/Sr	752	1 : 2 : 12	40.0	100	40.4	55.8	16.1
(1 : 1 : 1)	749	1 : 4 : 20	24.7	97	58.6	35.8	14.5
ZrO_2/La/Sr	762	1 : 2 : 12	40.0	99	39.8	56.7	15.9
(4 : 1 : 1)	752	1 : 4 : 20	25.2	99	57.4	37.2	14.5
ZrO_2/La/Ca	748	1 : 2 : 12	39.3	100	39.7	56.5	15.6
(1 : 1 : 1)	744	1 : 4 : 20	23.9	100	57.1	36.9	13.7
ZrO_2/La/Ca	751	1 : 2 : 12	39.1	100	34.8	62.3	13.6
(4 : 1 : 1)	749	1 : 4 : 20	24.1	100	51.8	43.6	12.5
ZrO_2/La/Mg	751	1 : 2 : 12	38.9	100	35.3	62.0	13.7
(1 : 1 : 1)	750	1 : 4 : 20	24.1	99	52.8	43.1	12.8
ZrO_2/La/Mg	751	1 : 2 : 12	38.4	99	30.9	67.1	11.9
(4 : 1 : 1)	751	1 : 4 : 20	23.1	99	46.9	50.1	10.8

phases (ZrO_2 and La_2O_3). Where alkaline earth metal dopants were added, minor MgO, CaO and $Sr_xZr_yO_z$ phases were detected as well (fig. 3, only main peaks indicated). Alkali metals did not form crystalline phases.

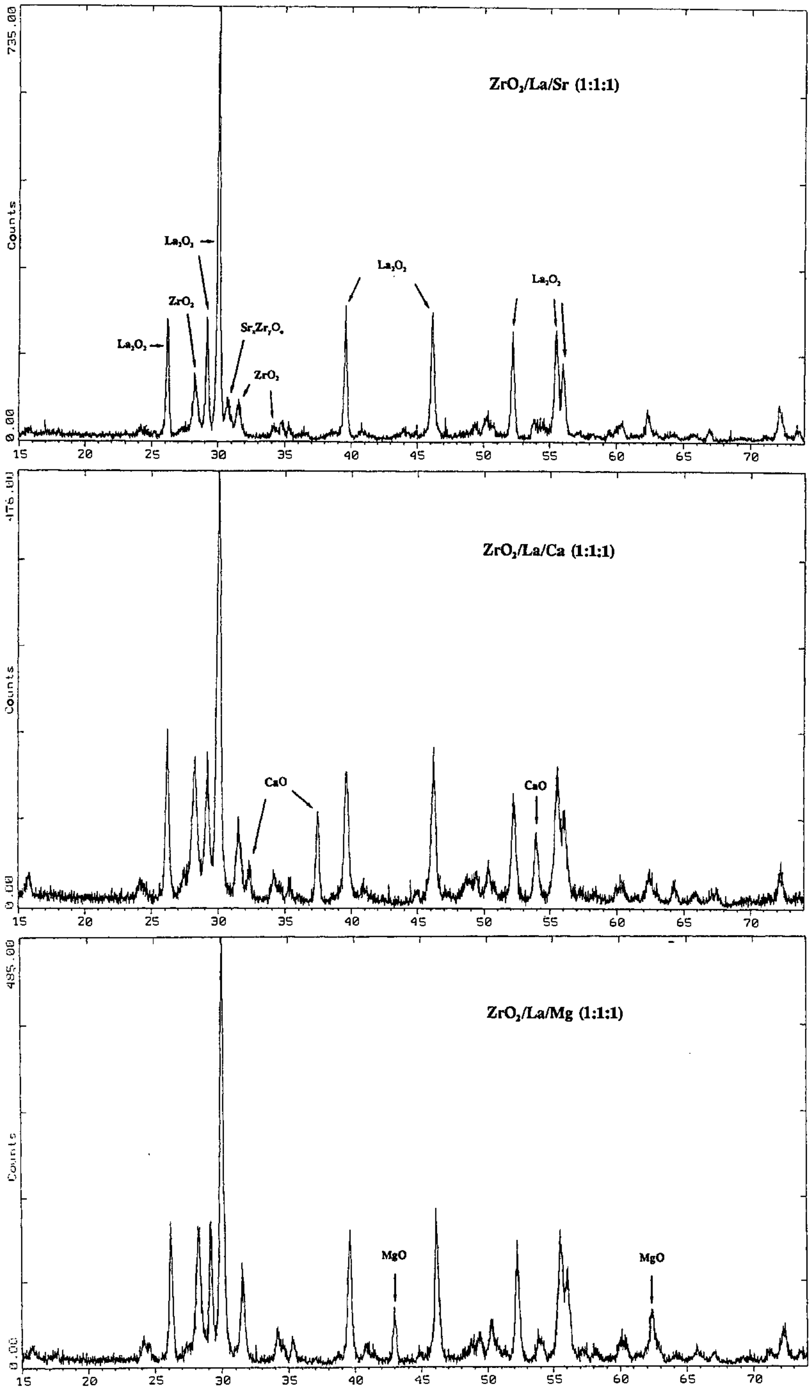

Fig. 3. XRD spectra of Sr-, Ca- and Mg-doped ZrO$_2$/La catalysts.

The results in table 1 confirm the earlier observations [2–5] that zirconium oxide oxidized methane mainly to CO_x products. At 700°C the major product was carbon monoxide, whereas at 750°C it was carbon dioxide. Combining ZrO_2 with lanthanum improved the methane and oxygen conversions and C_2-selectivity considerably, as observed earlier with calcium-doped ZrO_2 [2].

From the results in table 1 we can see that the alkali metals suppressed the activity of the catalysts more than did the alkaline earth metals. This is clearly seen in the lower conversions of oxygen. The most deactivating dopant was lithium, followed by sodium and potassium. Liu et al. [4] earlier observed the same kind of behaviour with alkali sulphate and alkaline earth metal doped lanthanum oxides, where the alkali-doped catalysts required a gas hourly space velocity (GHSV) half that of the alkaline earth metal doped catalysts to reach the same conversion level. Liu et al. [4] also pointed out that the promoter effect of alkali metals increases with cationic size (i.e. $Li^+ < Na^+ < K^+$). Because in our experiments the conversion of oxygen is not on the same level, however, direct comparison of the alkali metal doped catalysts is not possible. With the alkaline earth metal doped catalysts, methane conversion and C_2-selectivity increased and CO_x-selectivity decreased when moving downwards in the alkaline earth metal group (i.e. $Mg^{2+} \rightarrow Ca^{2+} \rightarrow Sr^{2+}$). Liu et al. [4] and Yamashita et al. [14] report similar observations for alkaline earth metal doped lanthanum oxides.

In all the catalysts, reducing the amount of lanthanum and dopant in relation to zirconium ($1:1:1 \rightarrow 4:1:1$) decreased the C_2-yield (exception Li) because, although the activity remained on the same level, the C_2-selectivity decreased. With all the catalysts, methane conversion was lower, C_2-selectivity higher and C_2-yield slightly lower with the feed composition $1:4:20$ than the feed composition $1:2:12$.

ESCA study of the ZrO_2/La/Ca (1 : 1 : 1) catalyst (surface composition detailed in table 2) revealed that there is no Zr present on the surface of the catalyst, implying that ZrO_2 is only a support material. To verify this observation two similar catalysts were synthesised, one with no zirconium oxide and the other with magnesium oxide replacing zirconium oxide. The test results of these catalysts are shown in table 3. There were no differences between the catalysts with zirconium and magnesium, while the best C_2-yield was achieved with the catalyst without any

Table 2
ESCA surface composition of ZrO_2/La/Ca (1 : 1 : 1) and (4 : 1 : 1) catalysts

Element	ZrO_2/La/Ca (1 : 1 : 1) (at%)	ZrO_2/La/Ca (4 : 1 : 1) (at%)
Zr	–	2.9
La	10.1	10.4
Ca	6.0	7.9
O	59.4	56.3
C	24.5	22.5
total	100.0	100.0

Table 3
Test results for catalysts without zirconium compared to ZrO_2/La/Sr catalyst (feed $O_2 : CH_4 : N_2 = 1 : 2 : 12$)

Catalyst	T (°C)	X_{CH_4} (%)	X_{O_2} (%)	S_{C_2} (%)	S_{CO_x} (%)	Y_{C_2} (%)
ZrO_2/La/Sr (4 : 1 : 1)	762	40.0	99	39.8	56.7	15.9
MgO/La/Sr (4 : 1 : 1)	753	40.9	100	39.1	57.4	16.0
La/Sr (1 : 1)	752	41.1	100	42.6	52.9	17.5

support. Clearly, for this kind of catalyst the presence of zirconium does not have an important effect on the results.

The poorer results for wet impregnated ZrO_2/La/X (4 : 1 : 1) catalysts than (1 : 1 : 1) catalysts can be explained by the effect of pure zirconium oxide. Raising the zirconium content leaves some zirconium on the surface of the catalyst (ESCA surface composition shown in table 2), allowing oxidation to CO_x, with the result that the C_2-selectivity decreases. Fig. 4 shows the effect of the feed composition ($CH_4 : O_2$ ratio) on the C_2-yield at 700°C for the ZrO_2/La/Ca (1 : 1 : 1) catalyst. When the $CH_4 : O_2$ ratio was decreased from 6 to 1, the C_2-yield remained roughly at the same level, because, when the CH_4 conversion increased, the C_2-selectivity decreased. In tests of the stability of the ZrO_2/La/Ca (1 : 1 : 1) and ZrO_2/La/Sr (1 : 1 : 1) catalysts they were found to be stable during 6 and 14 runs.

3.2. PRECIPITATED CATALYSTS

When $ZrO(NO_3)_2 \cdot xH_2O$ and $La(NO_3)_3 \cdot 6H_2O$ were used as starting materials and coprecipitation was the preparation method (NH_4OH (25%) or alkali hydrox-

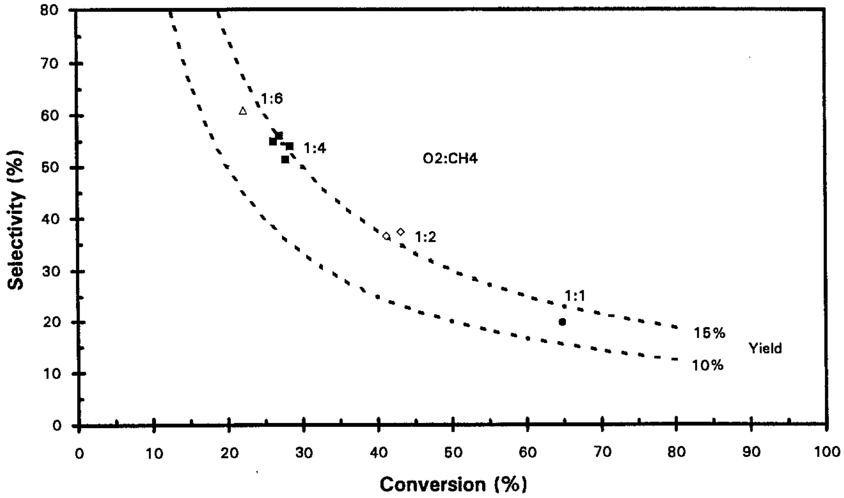

Fig. 4. The effect of feed composition ($CH_4 : O_2$ ratio) on the C_2-yield at 700°C with ZrO_2/La/Ca (1 : 1 : 1) catalyst.

ide solution as precipitant), the bulk material of the catalysts after calcination was mainly lanthanum zirconate oxide phase, $La_2O_3 * 2ZrO_2$. Deviation from this rule was the fresh LiOH-precipitated catalyst which yielded very complex XRD patterns that remained unsolved. However, the lanthanum zirconate oxide phase was the main crystalline phase of that catalyst after use in OCM reaction. The elemental X-ray distribution map of the Li-doped $La_2O_3 * 2ZrO_2$ catalyst, made by scanning electron microscopy in combination with EDS technique, showed a uniform distribution of lanthanum and zirconium throughout the catalyst. Nevertheless, small agglomerations of zirconium or lanthanum cannot be completely ruled out. The XRD spectra of Na-doped and fresh and used Li-doped $La_2O_3 * 2ZrO_2$ catalysts are shown in fig. 5. Earlier, Khan and Ruckenstein [7] recorded nearly the same type of unknown, complex XRD patterns for an $Na^+–ZrO_2–Cl^-$ catalyst prepared by the sol–gel process as we recorded for fresh Li-doped $La_2O_3 * 2ZrO_2$ catalyst. Likewise in their XRD experiments on Li-doped lanthanum titanate oxide ($La_2O_3 * 2TiO_2$) catalysts, Kalenik and Wolf [19] found several different phases depending on the lithium loading (not shown). When calcium was used as dopant and NH_4OH as precipitant, also minor amounts of CaO and $CaZrO_3$ phases were present. Doping with magnesium led to minor MgO phase and strontium to minor $Sr_xZr_yO_z$ and La_2O_3 phases.

The methane coupling results and the specific surface areas of the coprecipitated catalysts are summarized in table 4. As can be seen lanthanum zirconate oxide without dopant had very poor C_2-selectivity and the main product was carbon dioxide. This is contrary to the findings of Lane et al. [20] which indicated that lanthanum titanate oxide $La_2O_3 * 2TiO_2$ without dopant possessed fairly good C_2-selectivity (at 750°C above 50% at the conversion level of 20%, feed $CH_4/O_2 = 4$). In our tests the only lanthanum zirconate oxide catalyst with C_2-selectivity over 50% was that precipitated with LiOH. Like us, Kalenik and Wolf [19] also observed lithium dopant clearly to enhance C_2-selectivity of the lanthanum titanate oxide catalyst (at 750°C nearly 80% at the conversion level of 20%, feed $CH_4/O_2 = 4$).

Table 4

Results of $La_2O_3 * 2ZrO_2$ catalysts (feed $O_2 : CH_4 : N_2 = 1 : 2 : 12$, * calculated)

Doping metal	Content (wt%)	SA (m^2/g)	T (°C)	X_{CH_4} (%)	X_{O_2} (%)	S_{C_2} (%)	S_{CO_x} (%)	Y_{C_2} (%)
–	–	1.1	756	29.1	100	1.8	96.0	0.5
Li	6.2	0.9	751	34.1	75	50.7	45.3	17.3
Na	5.0	7.7	759	31.3	100	22.8	76.5	7.1
Na + K	3.7 + 3.8	7.1	759	29.8	100	32.6	66.1	9.7
K	20.8	2.3	757	34.0	100	28.4	70.6	9.7
Mg	6.2*	–	756	29.0	88	13.8	85.8	4.0
Ca	4.4*	1.2	751	32.2	100	9.4	90.2	3.0
	11.7*	1.5	750	32.2	100	10.0	89.7	3.2
	26.5*	3.9	758	29.8	100	5.5	94.2	1.6
Sr	22.5*	3.6	758	32.9	83	35.5	62.3	11.7

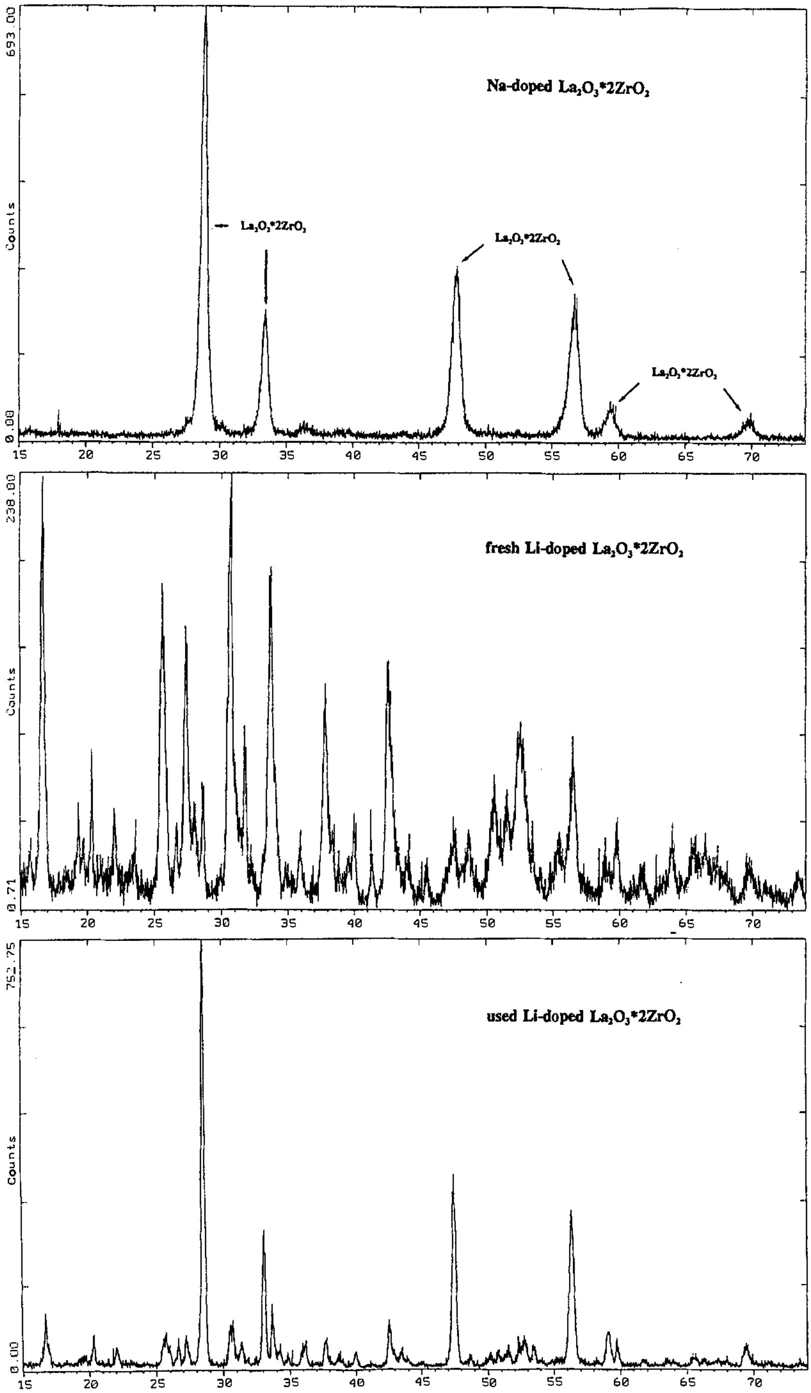

Fig. 5. XRD spectra of Na-doped and fresh and used Li-doped lanthanum zirconate oxides.

One negative feature of alkali metal dopants is that they are slowly lost during the run (e.g. 50% lithium loss for the Li/$La_2O_3 * 2TiO_2$ catalyst over a 50 h run [19]. Doping with magnesium and calcium improved the C_2-selectivity only slightly relative to the lanthanum zirconate oxide without dopant. Strontium enhanced the C_2-selectivity somewhat more than potassium and sodium.

The pure and Na/K-doped lanthanum zirconate oxide catalysts were stable over 6 h runs. However, with the Li-doped $La_2O_3 * 2ZrO_2$ catalyst the C_2-selectivity increased and CO_x-selectivity decreased slowly for 4 h (fig. 6), after which time the catalyst was more stable. These changes were probably caused by modifications in the crystalline structure, from the unsolved complex phases to purer $La_2O_3 * 2ZrO_2$ phase.

4. Conclusions

Although under the conditions of the OCM reaction zirconium oxide completely oxidizes the converted methane, its C_2-selectivity could be enhanced by combining it with lanthanum. The choice of the starting materials and preparation method (ZrO_2 and wet impregnation or $ZrO(NO_3)_2 \cdot xH_2O + La(NO_3)_3 \cdot 6H_2O$ and coprecipitation) has a pronounced effect on the bulk composition of the final catalyst ($ZrO_2 + La_2O_3$ or $La_2O_3 * 2ZrO_2$, respectively). With low zirconium contents the doped $ZrO_2 + La_2O_3$ catalysts behaved like doped La_2O_3 catalysts. Both alkali and alkaline earth metal dopants (the most efficient being strontium) increased the C_2-selectivity, and hence the C_2-yield. With high zirconium contents the C_2-selectivity of the doped $ZrO_2 + La_2O_3$ decreased due to the strong oxidizing nature

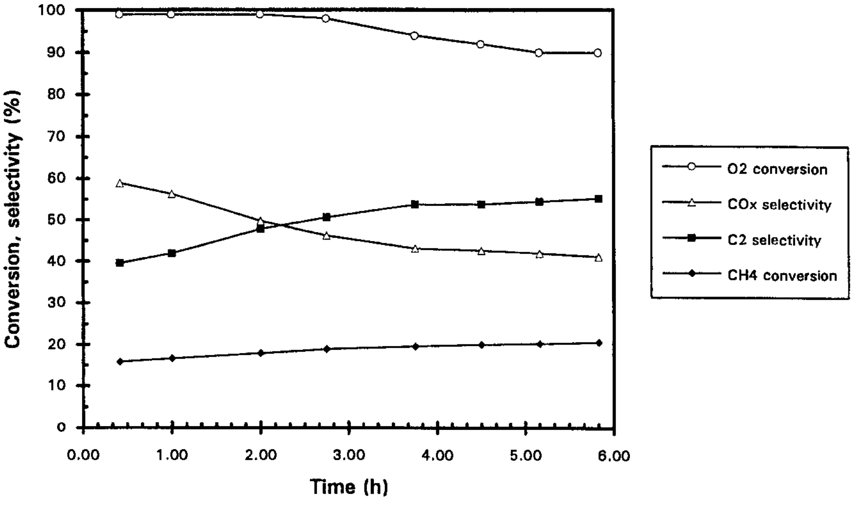

Fig. 6. Stability of the Li-doped $La_2O_3 * 2ZrO_2$-catalyst at 750°C with the feed $O_2 : CH_4 : N_2 = 1 : 4 : 20$.

of pure ZrO_2. The undoped lanthanum zirconate oxide ($La_2O_3 * 2ZrO_2$) catalyst also was intensely oxidizing. Unlike the $ZrO_2 + La_2O_3$ catalysts, the only effective dopant for the $La_2O_3 * 2ZrO_2$ catalyst was lithium.

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