Excellent effect of lithium-doped sulfated zirconia catalysts for oxidative coupling of methane to give ethene and ethane

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Li-doped sulfated zirconia catalysts are found to be effective for oxidative coupling of methane; *ca.* 80% C₂ selectivity is attained at 1073 K with 43% CH₄ conversion.

In this decade, much attention has been paid to the conversion of methane into more valuable products under oxidative¹ or non-oxidative² conditions. Of many routes, oxidative coupling of methane (OCM) to give C_2 hydrocarbons is still one of the most promising choices for direct methane conversion. Generally, research efforts have been directed towards a search for new efficient catalysts and basic metal oxides such as MgO, CaO and La₂O₃ are mostly used as catalysts or supports. However, it seems likely that the strong basicities of the catalysts used are not always required.³

Here, fairly super-acidic metal oxides were examined as catalyst supports for the OCM reaction and lithium-doped sulfated zirconia systems were found to be excellent candidates for C_2 formation.

The catalysts were prepared as follows. Sulfated zirconia was prepared by the conventional two-step method,4 in which amorphous zirconia was first synthesized by hydrolysing an aqueous ZrO(NO₃)₂ solution with ammonia, followed by calcination for 3 h at 573 K. Then, the resulting zirconia (BET surface area = $266 \text{ m}^2 \text{ g}^{-1}$) was added to $(NH_4)_2SO_4$ solution and evaporated to dryness, accompanied by calcination in air for 3 h at 973 K. The resultant sulfated zirconia (72.8 m² g⁻¹) was impregnated with an aqueous solution of alkali- or alkaline earth-metal compounds such as Li₂CO₃ in which the alkalimetal content was 5 mass% (the mass percentage is defined as the ratio of Li to ZrO_2). This was then evaporated to dryness, drying overnight at 373 K with calcination in air at 873 K for 3 h (the surface area of the resulting catalyst = $7.3 \text{ m}^2 \text{ g}^{-1}$). The catalytic runs were carried out under atmospheric pressure and in a fixed-bed vertical-flow reactor constructed from a highpurity alumina tube (id = 6 mm) packed with 0.5 g of catalyst and mounted inside a tube furnace. The catalyst was pretreated in nitrogen at 1073 K for 1 h. Then, the reactant gas mixture (15% CH₄, 5% O₂ and 80% N₂, 50 ml min⁻¹) was introduced at W/F = 4.1 g cat h mol⁻¹. The products were analysed on-line by gas chromatography (GC) equipped with a Syncarbon-S (FID) column for C₂H₆, C₂H₄, C₂H₂, C₃H₆ and C₃H₈, Porapack Q (2 m) and molecular sieve 5A (2 m) (TCD) columns for CH₄, CO₂, H₂O, H₂, O₂ and CO and another Porapack Q (1 m) (FID) column for small amounts of higher hydrocarbons such as C₄H₈ and benzene.

The major products of the oxidative coupling of methane are ethene, ethane, carbon monoxide and carbon dioxide with only trace amounts of acetylene, but-1-ene and benzene. The results obtained in the various ZrO₂ catalysts at 1073 K are presented in Table 1, where data were taken after 30 min of reaction. In the ZrO₂ and sulfated ZrO₂ catalysts, some reaction took place, carbon oxides being, however, the dominant products and C₂ compounds were obtained in only 3% yield. For the Li-doped ZrO₂ catalyst without sulfate, the CH₄ conversion was almost unaltered, but C₂ selectivity (ca. 50%) improved slightly. It was found that 80.2% C2 selectivity was achieved at 32.1% CH4 conversion over the Li-doped sulfated ZrO2 catalyst at a CH4/ O₂ ratio of 3. This is the first example of the use of solid superacid-based catalysts for the oxidative coupling of CH₄. The C₂ yield (34.5%) was improved by the use of a CH_4/O_2 ratio of 2,[†] although the C₂ selectivity was slightly decreased. The C₂ yield obtained here is found to be considerably better than results reported in the catalysts systems based on basic metal oxides such as MgO.¹ Moreover, at a CH₄/O₂ ratio of 9 without diluent, the C₂ selectivity was further increased; as high as 85.1% C₂ selectivity was attained at 30.7% CH₄ conversion,[‡] which is desirable from the practical viewpoint. Fig. 1 shows the effects of reaction temperature on the CH₄ conversion and the

Table 1 Catalytic performances for oxidative coupling of methane over Li-promoted sulfated zirconia catalysts^a

	Catalyst ^b	Conversion (%)	Selectivity ^c (%)					C
			C_2H_2	C_2H_4	C_2H_6	СО	CO_2	Yield ^{d} (%)
	ZrO ₂	16.0	0.19	11.3	6.75	64.6	16.9	2.92
	$6\% \overline{SO_4^2}$ /ZrO ₂	16.8	0.27	11.7	6.29	66.2	15.3	3.06
	5%Li/ZiO ₂	17.2	0.62	27.2	22.9	16.4	31.9	8.74
	5%Li/6%SO ₄ ²⁻ /ZrO ₂	32.1	1.21	58.3	20.7	9.69	5.70	25.8
	5%Li/6%SO ₂ ²⁻ /ZrO ₂ ^e	35.5	1.72	58.9	9.99	21.2	4.79	25.1
	$5\% Li/6\% SO_4^2 - /ZrO_2^f$	43.3	0.67	58.3	20.7	11.7	6.10	34.5
	5%Li/6%SO42-/ZrO2g	30.7 <i>h</i>	0.62	56.8	27.7	5.36	4.27	25.7

^{*a*} *Reaction conditions*: T = 1073 K, P = 0.1 MPa, total flow = 50 ml min⁻¹, reactant gas [CH₄ (15%)–O₂ (5%)–N₂ (80%)]. Results are after 30 min of reaction. ^{*b*} The sulfated zirconia was prepared using (NH₄)₂SO₄. ^{*c*} Conversion and selectivity are based on the amount of methane reacted. ^{*d*} C₂ yield is obtained from the product of conversion and C₂ selectivity, where C₂ selectivity is the sum of C₂H₂, C₂H₄ and C₂H₆. ^{*c*} The sulfated zirconia was prepared using $(NH_{4})_2$ SO₄. ^{*c*} Conversion and selectivity are based on the amount of methane reacted. ^{*d*} C₂ yield is obtained from the product of conversion and C₂ selectivity, where C₂ selectivity is the sum of C₂H₂, C₂H₄ and C₂H₆. ^{*e*} The sulfated zirconia was prepared using $(0.5 \text{ m} H_2$ SO₄. ^{*f*} Reactant gas [CH₄ (10%)–O₂ (5%)–N₂ (85%)]. ^{*s*} Reactant gas [CH₄ (90%)–O₂ (10%)]. ^{*h*} In this run, carbon and hydrogen mass balances were 94 and 92%, respectively: C mass balance = $(2 \times C_2$ H₆ + $2 \times C_2$ H₄ + $2 \times C_2$ H₂ + $3 \times C_3$ H₆ + $3 \times C_3$ H₈ + $4 \times C_4$ H₈ + $5 \times C_5$ H₁₀ + $6 \times$ benzene + $7 \times$ toluene + CO + CO₂) × 100/CH₄ converted. H mass balance = $(3 \times C_2$ H₆ + $2 \times C_2$ H₄ + C_2 H₂ + $3 \times C_3$ H₆ + $4 \times C_3$ H₈ + $4 \times C_4$ H₈ + $5 \times C_5$ H₁₀ + $3 \times$ benzene + $4 \times$ toluene + H₂ + H₂O) × 100/CH₄ converted. In other runs the C and H mass balances were also between 90 and 95%. In any run, the remainder of gaseous products must be a very small amount of oxygenates such as methanol. Also, the formation of bulk lithium carbonate during the reaction⁹ was not detected by powder X-ray diffraction, the patterns of which remained unchanged before and after reaction. Further study is under way to improve the C and H mass balances.

selectivities under no-diluent conditions. The CH₄ conversion and C₂ selectivity increased with increasing reaction temperature up to 1073 K, whereas CO_x selectivity decreased. These findings could be explained, at least partly, by a difference in the activation energy between C₂ and CO_x formation.⁵

The effect of catalyst components were examined using other acid sources and other alkali metals. In the Li-doped acidpromoted ZrO₂ catalysts, the effect of acid precursors other than $(NH_4)_2SO_4$ was in the order: $(NH_4)_2SO_4$ (25.8) > 0.5 m H_2SO_4 (25.1) > NH_4Cl (22.9) > trimethyleneborate (22.3) > $(NH_4)_3PO_4$ (19.3) > NH_4NO₃ (16.5) > none (8.7). (The values in parentheses represent the C₂ yield at 1073 K.) For the Na- and K-doped sulfated ZrO₂ catalysts, the CH₄ conversion was almost the same as for the Li-doped catalysts, but C₂ selectivity decreased to *ca.* 50%, nearly 30% lower than that for the Li-



Fig. 1 Effect of the reaction temperature on the oxidative coupling of methane over 5% Li-doped 6 mass% SO_4^{2-}/ZrO_2 catalysts without diluent. *Conditions*: CH₄ (90%)–O₂ (10%), feed 50 ml min⁻¹, catalyst 0.5 g. CH₄ conversion (\bigcirc); selectivities: C₂ (\bullet), CO_x (\Box).



Fig 2 Effect of sulfate content on the product yields. *Conditions*: CH₄ (15%)–O₂ (5%)–N₂ (80%), feed 50 ml min⁻¹, 1073 K. The mass% of sulfate content is defined as the ratio of SO₄^{2–} to ZrO₂. Selectivities: C₂ (\bigcirc), CO_x (\bigcirc).

doped catalyst. Over catalysts promoted with 10 mass% of Li, both CH_4 conversion and C_2 selectivity were slightly reduced and, as a result, the C_2 yield decreased to *ca*. 19%.

The effectiveness of the Li-doped sulfated ZrO₂ catalysts on the oxidative coupling of CH₄ is still not clear. Since the effect of Li doping on MgO support has been already reported,6 it seems likely that the preparation of sulfated ZrO₂ surface is a key step in our catalyst system. In fact, the catalyst performances depend on the sulfate content (Fig. 2) and calcination temperature: a maximum C₂ yield is attained over the catalysts which contain 6 mass% sulfate and are calcined at 923-973 K, being closely related to the preparation conditions of sulfated ZrO_2 as solid superacids.⁷ If so, sulfated metal oxides other than ZrO_2^8 might be also effective as supports. We found that, for an Li-doped sulfated SnO₂ catalyst, § 82.4% C₂ selectivity at 1073 K is achieved at 30.5% CH₄ conversion. Also, a ZrO₂ catalyst, impregnated with an aqueous solution containing both (NH₄)₂SO₄ and Li₂CO₃, followed by calcination in air at 873 K for 3 h, showed much lower reactivity than that prepared by the two-step method. By investigating all these findings, it is concluded that Li doping over a super-acid surface is required for the generation of high catalytic performances for the ZrO₂based OCM reaction reported here.

Further work is in progress not only to carry out reaction on larger experimental scales, but also to elucidate the nature of the Li-doped solid super-acid catalysts.

Footnotes

 \dagger In this run, after reaction for 5 h at 1073 K, methane conversion was decreased (43.3 to 39%), whereas C₂ selectivity was slightly increased (79.7 to 82.1%).

‡ In this run, the amount of oxygen required to reach 30.7% CH₄ conversion could approximately correspond to that contained in the feedstock, if we assume the following reaction steps including thermal cracking of ethane or ethene to form ethene or acetylene, although further investigation will be required for the reaction scheme. (1) 2CH₄ + 1/2O₂ \rightarrow C₂H₆ + H₂O, (2) C₂H₆ \rightarrow C₂H₄ + H₂, (3) C₂H₄ \rightarrow C₂H₂ + H₂, (4) CH₄ + 3/2O₂ \rightarrow CO + 2H₂O, (5) CO + 1/2O₂ \rightarrow CO₂, (6) CH₄ + H₂O \rightarrow CO + 3H₂. In fact, in this run, the expected amount of hydrogen was observed by GC analysis. Also, in a separate experiment using the same catalyst, we confirmed that efficient C₂H₄ formation from C₂H₆ was observed even at 1023 K in the absence of O₂, consistent with a thermodynamical calculation.

 $\$ SnO2 impregnated with 6 mass% $(NH_4)_2SO_4$ was calcined at 873 K for 3 h.

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