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% C_2 selectivity is attained at 1073 K with 43% CH_4 conversion.

In this decade, much attention has been paid to the conversion of methane into more valuable products under oxidative[1] or non-oxidative[2] 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 La_2O_3 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 $ZrO(NO_3)_2$ solution with ammonia, followed by calcination for 3 h at 573 K. Then, the resulting zirconia (BET surface area = 266 m^2 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 m^2 g^{-1}) was impregnated with an aqueous solution of alkali- or alkaline earth-metal compounds such as Li_2CO_3 in which the alkali-metal 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 m^2 g^{-1}). The catalytic runs were carried out under atmospheric pressure and in a fixed-bed vertical-flow reactor constructed from a high-purity 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% CH_4, 5% O_2 and 80% N_2, 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 C_2H_6, C_2H_4, C_2H_2, C_3H_6 and C_3H_8, Porapack Q (2 m) and molecular sieve 5A (2 m) (TCD) columns for CH_4, CO_2, H_2O, H_2, O_2 and CO and another Porapack Q (1 m) (FID) column for small amounts of higher hydrocarbons such as C_4H_8 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 ZrO_2 catalysts at 1073 K are presented in Table 1, where data were taken after 30 min of reaction. In the ZrO_2 and sulfated ZrO_2 catalysts, some reaction took place, carbon oxides being, however, the dominant products and C_2 compounds were obtained in only 3% yield. For the Li-doped ZrO_2 catalyst without sulfate, the CH_4 conversion was almost unaltered, but C_2 selectivity (*ca.* 50%) improved slightly. It was found that 80.2% C_2 selectivity was achieved at 32.1% CH_4 conversion over the Li-doped sulfated ZrO_2 catalyst at a CH_4/O_2 ratio of 3. This is the first example of the use of solid super-acid-based catalysts for the oxidative coupling of CH_4. The C_2 yield (34.5%) was improved by the use of a CH_4/O_2 ratio of 2,† although the C_2 selectivity was slightly decreased. The C_2 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 CH_4/O_2 ratio of 9 without diluent, the C_2 selectivity was further increased; as high as 85.1% C_2 selectivity was attained at 30.7% CH_4 conversion,‡ which is desirable from the practical viewpoint. Fig. 1 shows the effects of reaction temperature on the CH_4 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_2 Yield[d] (%)
		C_2H_2	C_2H_4	C_2H_6	CO	CO_2	
ZrO_2	16.0	0.19	11.3	6.75	64.6	16.9	2.92
6%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%SO_4^{2-}/ZrO_2[g]	30.7[h]	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 [CH_4 (15%)–O_2 (5%)–N_2 (80%)]. Results are after 30 min of reaction. [b] The sulfated zirconia was prepared using $(NH_4)_2SO_4$. [c] Conversion and selectivity are based on the amount of methane reacted. [d] C_2 yield is obtained from the product of conversion and C_2 selectivity, where C_2 selectivity is the sum of C_2H_2, C_2H_4 and C_2H_6. [e] The sulfated zirconia was prepared using 0.5 m H_2SO_4. [f] Reactant gas [CH_4 (10%)–O_2 (5%)–N_2 (85%)]. [g] Reactant gas [CH_4 (90%)–O_2 (10%)]. [h] In this run, carbon and hydrogen mass balances were 94 and 92%, respectively: C mass balance = $(2 \times C_2H_6 + 2 \times C_2H_4 + 2 \times C_2H_2 + 3 \times C_3H_6 + 3 \times C_3H_8 + 4 \times C_4H_8 + 5 \times C_5H_{10} + 6 \times \text{benzene} + 7 \times \text{toluene} + CO + CO_2) \times 100/CH_4$ converted. H mass balance = $(3 \times C_2H_6 + 2 \times C_2H_4 + C_2H_2 + 3 \times C_3H_6 + 4 \times C_3H_8 + 4 \times C_4H_8 + 5 \times C_5H_{10} + 3 \times \text{benzene} + 4 \times \text{toluene} + H_2 + H_2O) \times 100/CH_4$ 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 reaction[9] 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 CH_4 conversion and C_2 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 C_2 and CO_x formation.[5]

The effect of catalyst components were examined using other acid sources and other alkali metals. In the Li-doped acid-promoted ZrO_2 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_4NO_3 (16.5) > none (8.7). (The values in parentheses represent the C_2 yield at 1073 K.) For the Na- and K-doped sulfated ZrO_2 catalysts, the CH_4 conversion was almost the same as for the Li-doped catalysts, but C_2 selectivity decreased to *ca.* 50%, nearly 30% lower than that for the Li-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%.

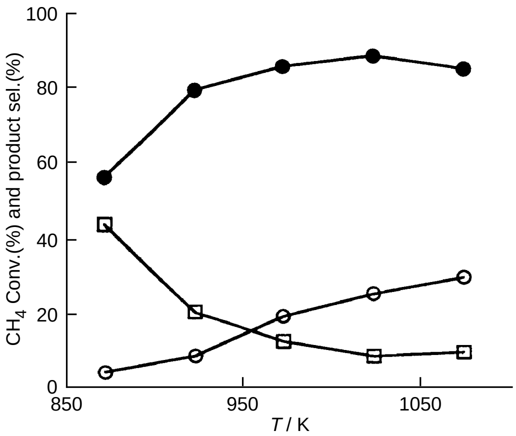

Fig. 1 Effect of the reaction temperature on the oxidative coupling of methane over 5% Li-doped 6 mass% SO_4^{2-}/ZrO_2 catalysts without diluent. *Conditions*: CH_4 (90%)–O_2 (10%), feed 50 ml min^{-1}, catalyst 0.5 g. CH_4 conversion (○); selectivities: C_2 (●), CO_x (□).

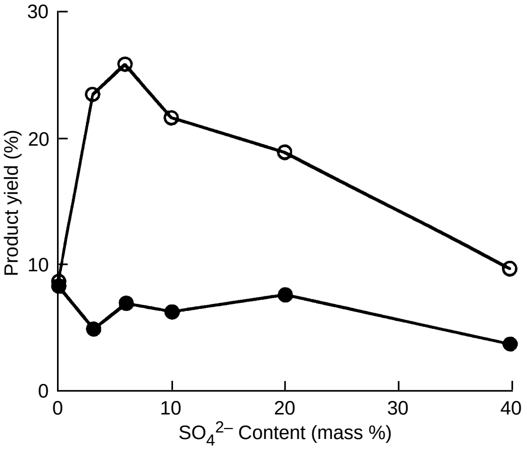

Fig 2 Effect of sulfate content on the product yields. *Conditions*: CH_4 (15%)–O_2 (5%)–N_2 (80%), feed 50 ml min^{-1}, 1073 K. The mass% of sulfate content is defined as the ratio of SO_4^{2-} to ZrO_2. Selectivities: C_2 (○), CO_x (●).

The effectiveness of the Li-doped sulfated ZrO_2 catalysts on the oxidative coupling of CH_4 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 ZrO_2 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 C_2 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 SnO_2 catalyst,§ 82.4% C_2 selectivity at 1073 K is achieved at 30.5% CH_4 conversion. Also, a ZrO_2 catalyst, impregnated with an aqueous solution containing both $(NH_4)_2SO_4$ and Li_2CO_3, 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 ZrO_2-based 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

† In this run, after reaction for 5 h at 1073 K, methane conversion was decreased (43.3 to 39%), whereas C_2 selectivity was slightly increased (79.7 to 82.1%).

‡ In this run, the amount of oxygen required to reach 30.7% CH_4 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) $2CH_4 + 1/2O_2 \rightarrow C_2H_6 + H_2O$, (2) $C_2H_6 \rightarrow C_2H_4 + H_2$, (3) $C_2H_4 \rightarrow C_2H_2 + H_2$, (4) $CH_4 + 3/2O_2 \rightarrow CO + 2H_2O$, (5) $CO + 1/2O_2 \rightarrow CO_2$, (6) $CH_4 + H_2O \rightarrow CO + 3H_2$. 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 C_2H_4 formation from C_2H_6 was observed even at 1023 K in the absence of O_2, consistent with a thermodynamical calculation.

§ SnO_2 impregnated with 6 mass% $(NH_4)_2SO_4$ was calcined at 873 K for 3 h.

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