

Oxidative Dimerization of Methane over BaCO₃, SrCO₃ and these Catalysts promoted with Alkali

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The yield and selectivity for formation of C₂ hydrocarbons from CH₄ and O₂ were 18.2 and 48.4% respectively over 2 g of BaCO₃ at 1073 K at a CH₄:O₂ ratio of 2.0:1, whereas the yield and selectivity were 2.5 and 99.5% over SrCO₃ at 973 K at a CH₄:O₂ ratio of 37.9:1.

Various materials (PbO–Al₂O₃,¹ Li⁺–MgO,² Na⁺–MgO,³ Sm₂O₃,⁴ LaAlO₃,⁵ La₂O₃,⁶ and Li⁺–Sm₂O₃)⁷ have been reported to be effective catalysts for the title reaction. Among these, alkali doped MgO has been reported to show the highest yield for C₂ compound formation.^{2,3} We studied the title reaction over a simple alkaline earth oxide and carbonate and these catalysts promoted with alkali, although alumina supported alkali earth oxides have been reported to have low activities.⁸

Reactions were performed in a conventional flow reactor (8 mm o.d.) at temperatures between 673 to 1073 K, and CH₄, air, and He flow rates of 1.5 ml min⁻¹ (4.02 mmol h⁻¹), 3.75 ml min⁻¹, and 50 ml min⁻¹ respectively. The CH₄:O₂ ratio was 2:1 (2CH₄ + O₂ = C₂H₄ + 2H₂O). Commercial BaO and CaO were crushed and sieved to a suitable size (20 mesh). Hydrated and dried SiO₂ (Cab-O-Sil) was also crushed and sieved (20 mesh). ZnO (Kadox), anatase TiO₂ (MCB), MgO (Soekawa), BaCO₃, and SrCO₃ were mixed with water to make a slurry, partly dried, and the paste was extruded using a plastic syringe. SrO was made by baking Sr(OH)₂·8H₂O at 673 K for 4 h. Alkali metal nitrates were added to BaCO₃ or SrCO₃ in water, and the samples were dried and weighed. The reagents which are not cited were obtained through Kanto

Chemical Co. The sample (2 g) was evacuated or heated in a He flow at 773 K for 1 h and at 1073 K for 2 h and used for the reaction. The alkali metal nitrates (promoters) are considered to be decomposed to the oxides or the hydroxides during the pretreatment.

In Table 1 we summarize our results of the reaction for the various oxides, carbonates, and the promoted catalysts at the CH₄:O₂ ratio of 2.0:1. The yield and the selectivity are defined as (2 × moles C₂ hydrocarbons produced)/(moles CH₄ in the feed) and (2 × moles C₂ hydrocarbons produced)/(moles CH₄ reacted), respectively. Oxides of alkali earth elements are more effective than the other oxides studied here. The effectiveness of these catalysts increases with increasing atomic number (BaO ≈ SrO > CaO > MgO). The highest yields of C₂ products over SrO and BaO without alkali promoters were 16.3 and 16.6% respectively at 1073 K. However, BaO and SrO gave no CO₂ as a product during several hours of the reaction because these oxides are partly converted into their carbonates under the reaction conditions. (The decomposition temperatures of carbonates are 1613 and 1633 K for SrCO₃ and BaCO₃ respectively.) Another problem with BaO and SrO is the corrosion of the glass reactor.

In order to overcome these problems, we studied oxidative

Table 1. Activity and selectivity of the oxidative dimerization of CH₄ at 1023 and 1073 K.^a

Catalyst (2 g)	1023 K Yield for C ₂ compounds (%)	Selectivity for C ₂ compounds (%)	1073 K Yield for C ₂ compounds (%)	Selectivity for C ₂ compounds (%)
MgO	4.4	11.7	—	—
CaO	9.4	28.9	12.8	39.1
SrO	10.0	39.0	16.3	52.7
SrCO ₃	8.5 (4.4) ^b (2.5) ^{b,c}	22.7 (98.0) ^b (99.5) ^{b,c}	— (6.4) ^b	— (92.7) ^b
SrCO ₃ –2 mol% K ⁺ ^d	5.0	46.5	11.5	55.5
SrCO ₃ –10 mol% K ⁺	4.1	43.9	8.7	58.2
SrCO ₃ –10 mol% Rb ⁺	4.0	30.5	10.1	37.1
BaO	15.2	45.4	16.6	44.6
BaCO ₃	15.3 (5.1) ^b	46.3 (82.5) ^b	18.2 (7.1) ^b	48.4 (90.5) ^b
BaCO ₃ –2 mol% Li ⁺	15.3	44.3	18.5	49.6
BaCO ₃ –2 mol% Na ⁺	16.3	43.5	15.5	42.5
BaCO ₃ –2 mol% K ⁺	17.0	37.6	20.2	42.0
BaCO ₃ –2 mol% Rb ⁺	17.6	41.8	17.1	37.9
ZnO	0.1	1.0	—	—
TiO ₂	0.0	0.0	—	—
ZrO ₂	0.2	1.0	—	—
SiO ₂	0.4	2.0	—	—
SiO ₂ –200 mol% Sr ²⁺	2.2	13.3	7.6	25.4

^a CH₄:O₂ = 2.0:1; selectivity = (2 × moles C₂ hydrocarbons produced)/(moles CH₄ reacted). ^b CH₄:O₂ = 37.9:1; selectivity = (moles carbon in C₂ hydrocarbons)/(moles carbon in all the products). ^c Reaction at 973 K. ^d Percentage molar ratio of a promoter against an unpromoted oxide or a carbonate.

dimerization over BaCO_3 and SrCO_3 . The activities and the kinetic behaviour of these carbonates are almost identical to those of their oxides. The carbonates of Sr and Ba prove to be the most effective catalysts. The yield of C_2 hydrocarbon is 18.2% over BaCO_3 at 1073 K, which compares well with the best values reported previously: (19.4, 21, and 22.4% over 7 wt% Li^+-MgO ,² 10 mol% $\text{Li}^+-\text{Sm}_2\text{O}_3$,⁷ and 15 mol% Na^+-MgO ³ catalysts). These carbonates are also considered to have radical centres which abstract hydrogen from CH_4 at the elevated temperature.² Since BaCO_3 and SrCO_3 are thermally stable and not corrosive, they should be the favoured catalysts for industrial use. Although the alkali promoted MgO has been reported to be the most effective catalyst,^{2,3} the alkali elements in the MgO might be lost during a long run at high temperature.

The promoter effect of alkali in the BaCO_3 and SrCO_3 catalysts was also studied as is shown in Table 1. In the case of BaCO_3 , the activity of C_2 formation was improved. The highest C_2 yield (20.2%) was observed over 2 g of 2 mol% K^+-BaCO_3 at 1073 K with a C_2 selectivity of 42%. In the case of SrCO_3 , the activity is depressed a little, whereas the selectivity is improved. The maximum C_2 selectivity observed was 58.2% for 2 g of 10 mol% K^+-SrCO_3 at 1073 K at a $\text{CH}_4:\text{O}_2$ ratio of 2.0:1.

When the $\text{CH}_4:\text{O}_2$ ratio was increased from 2.0:1 to 37.9:1 (flow rate of CH_4 , air, He = 12.9, 1.70, 50 ml min^{-1}), the selectivity for C_2 compounds increased for the carbonate catalysts, as is shown in Table 1. In particular, SrCO_3 improved in selectivity from 25.6 to 98.0% at 1023 K and even

to 99.5% at 973 K, a value higher than any previously reported.¹⁻⁷

In summary, for stable compounds which contain no additives BaCO_3 and SrCO_3 were found to be among the most effective catalysts for the oxidative dimerization of methane. These carbonates can be improved in their activity and selectivity when they are doped with alkali.

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