

## Oxidative Coupling of Methane

### II. Composite Catalysts of Basic Materials

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Composite catalysts consisting of Li, Na, and K carbonates, hydroxides, oxides, and sulfates supported on CaO and in some instances on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, MgO, and CaSO<sub>4</sub> have been tested for the oxidative coupling of methane to C<sub>n</sub> hydrocarbons ( $n \geq 2$ ). Normalized reaction conditions were generally  $T = 740^\circ\text{C}$ ,  $P_{\text{CH}_4}^\circ = 0.67$  bar,  $P_{\text{O}_2}^\circ = 0.074$  bar, and  $P_{\text{N}_2}^\circ = 0.26$  bar. Maximum selectivities of up to 80% were obtained depending on catalyst composition and preparation. CaO proved to be a suitable support for the alkali compounds. Selectivity was affected by time of catalyst-precursor calcination, the atmosphere surrounding the catalyst precursor during calcination, and whether the precursor was used in the form of granulates or in the final pellet shape applied for catalyst testing. © 1989 Academic Press, Inc.

#### INTRODUCTION

The requirement of high surface basicity in the oxidative coupling of methane for achieving good C<sub>n</sub> hydrocarbon ( $n \geq 2$ ;  $n = \text{"2+"}$ ) selectivities has been discussed previously (1-3). This may be attributed to electronic changes of the surface. According to the acid-base theory the charge distribution on a metal oxide surface may be severely perturbed by doping with metal ions of a different valence (4). This has been well investigated, particularly for acid catalysts (5). Matsuda *et al.* (6) found evidence indicating that this approach may also be applied to basic catalysts; these authors have shown that the basicity of MgO increases when doped with sodium compounds. We assumed that these findings with respect to formation and stabilization of surface basicity are more general and applied them in the preparation of catalysts for oxidative methane coupling. Against this background, the present paper deals with the improvement of C<sub>2+</sub> selectivity by the use of catalysts exhibiting high surface basicity which was achieved by

dispersing alkali compounds on mainly basic support materials. In particular, the effect of chemical composition and preparation of the catalysts on C<sub>2+</sub> selectivity was studied.

#### EXPERIMENTAL

Alkali compound/CaO catalysts were prepared by the incipient wetness method (cp. (1)), i.e., impregnating the pore volume of calcium hydroxide, used as a precursor of the catalytically active CaO support, with aqueous solutions of alkali compounds. Nitrates decomposing into the respective oxides by thermal treatment, hydroxides, sulfates, and carbonates of lithium, sodium, and potassium were applied. If aqueous solutions of sufficient alkali compound concentrations could not be prepared, i.e., for LiOH, Li<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, and K<sub>2</sub>SO<sub>4</sub>, these materials were mechanically mixed with CaO in the presence of water. Alkali compound/MgO and alkali compound/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared similarly; instead of the alkaline earth metal hydroxide magnesium hydroxide carbonate and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> were used. Drying and calcination conditions were partly varied; they are described further below, along

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with the respective results. All the chemicals including  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ , which were also tested as catalysts, were used as commercially received. All catalysts were pressed to  $3 \times 3$ -mm cylindrical pellets.

Procedures of catalyst testing and characterization correspond to those outlined in preceding papers (2, 3). The experimental conditions applied for catalytic evaluation of the various materials were always, if not otherwise noted,  $T = 740^\circ\text{C}$ ,  $P_{\text{CH}_4}^\circ = 0.67$  bar,  $P_{\text{O}_2}^\circ = 0.074$  bar,  $P_{\text{N}_2}^\circ = 0.26$  bar; gas flow was adjusted in such a way that the degree of oxygen conversion amounted generally to more than 80%.

## RESULTS AND DISCUSSION

The catalytic performance of unsupported alkali compounds and the selection of suitable support materials for such compounds are first reported and discussed. Subsequently, the effects of catalyst preparation, i.e., conditions of drying and calcination of various catalyst precursors based on a calcium oxide support, are described. Finally, the selectivity as achieved with various alkali compounds on calcium oxide is addressed.

### Unsupported Alkali Compounds

$\text{C}_{2+}$  selectivities of sodium and potassium carbonates amounted to 51 and 34%, respectively (cp. Table 1).  $\text{K}_2\text{CO}_3$  was transformed during the oxidative coupling reaction into  $2\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$  as established by X-ray diffraction. Both carbonates have

shown very low activity as may be derived from the modified reaction time  $W/F$  ( $W$ , weight of catalyst;  $F$ , volumetric flow rate) necessary to achieve a given conversion (to facilitate the comparison of the activities of the various catalysts, a pseudo-first-order rate constant for oxygen consumption—as explained in (1)—is also given in Table 1 and the subsequent Tables 2, 4, and 6). The reaction temperature applied was just below the respective melting points of the two solids resulting in very low surface areas ( $<1 \text{ m}^2/\text{g}$ ) due to sintering. For these reasons sodium and potassium carbonate, and most probably also similar alkali compounds, are not suited to being catalytic components unless a support is used.

### Selection of a Support for Alkali Compounds

The catalytic results obtained after various periods of operation with (a) various nonacidic support materials ( $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaSO}_4$ ,  $\text{CaO}$ ) impregnated with sodium hydroxide as an alkali probe compound and (b)  $\alpha\text{-Al}_2\text{O}_3$  impregnated with  $\text{LiOH}$ ,  $\text{KOH}$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{Na}_2\text{CO}_3$  are shown in Table 2. Phase compositions determined by X-ray diffraction for some of the catalysts are added as footnotes to Table 2, indicating that obviously some of the alkali compounds, i.e.,  $\text{KOH}$  and  $\text{NaOH}$ , do not exist as XRD-detectable crystallites.

All  $\alpha\text{-Al}_2\text{O}_3$ -supported alkali compound catalysts lost  $\text{C}_{2+}$  selectivity with time of

TABLE 1

Activity (Oxygen Conversion  $X$  Related to Modified Reaction Time  $W/F$  or Pseudo-First-Order Rate Constant  $k$ ) and Selectivity of Sodium Carbonate and Potassium Carbonate Catalysts

Catalytic material	Activity			Selectivity			
	$W/F$ (g · s/ml)	$X_{\text{O}_2}$ (%)	$k$ (ml/g · s)	$\text{C}_2\text{H}_6$ (%)	$\text{C}_2\text{H}_4$ (%)	$\text{C}_{3+}$ (%)	$\Sigma\text{C}_n\text{H}_m$ (%)
$\text{Na}_2\text{CO}_3$	46.4	71	0.03	19	27.8	4.2	51
$\text{K}_2\text{CO}_3$	4.1	97	0.86	22.8	10.8	0.4	34

TABLE 2

Activity (Oxygen Conversion  $X$  Related to Modified Reaction Time  $W/F$  or Pseudo-First-Order Rate Constant  $k$ ) and Selectivity  $S$  of Various Supported Alkali Compound Catalysts at Different Times of Operation  $t_{op}$

Support	Alkali Cpd. (wt%)	Activity			Selectivity				
		$W/F$ (g · s/ml)	$X_{O_2}$ (%)	$k$ (ml/g · s)	$C_2H_6$ (%)	$C_2H_4$ (%)	$C_{3+}$ (%)	$\Sigma C_nH_m$ (%)	$t_{op}$ (h)
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	0	1.1	99	4.2	14	31	1.1	47	2.0
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	2 NaOH	6.3	100	>1	24	26	3.4	54	1.0
		1.4	99	3.3	13	30	0.2	43	2.0
		0.8	90	2.9	11	29	0.5	40	4.0
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	7 NaOH <sup>a</sup>	6.0	90	0.4	21	26	3.1	50	2.0
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	13 NaOH <sup>b</sup>	7.0	100	>1	14	21	1.0	36	1.0
		3.5	98	1.1	10	18	0.3	29	2.5
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	7 LiOH	6.9	100	>1	24	26	4.2	54	1.0
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	17 KOH <sup>c</sup>	2.9	79	0.5	9	22	—	31	3.0
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	21 Na <sub>2</sub> SO <sub>4</sub>	3.1	100	>2.2	21	34	1.3	56	1.5
		1.9	93	1.4	19	37	1.6	59	2.5
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	17 Na <sub>2</sub> CO <sub>3</sub>	7.0	100	>1	17	21	2.1	40	1.5
		4.2	94	0.7	12	22	0.9	35	3.0
MgO	0	0.2	93	13.3	18	27	1.8	47	1.0
MgO	0.001 NaOH	1.0	98	3.9	15	20	1.4	37	0.2
		1.0	97	3.5	9	15	0.1	24	1.0
MgO	0.01 NaOH	1.0	100	>7	20	29	2.0	52	0.4
		0.4	98	9.8	16	28	1.6	45	2.2
MgO	43 NaOH <sup>d</sup>	0.2	82	8.6	17	36	1.7	55	1.0
		0.2	78	7.6	16	36	2.0	54	2.0
CaSO <sub>4</sub>	0	4.9	53	0.15	22	28	2.6	53	2.0
CaSO <sub>4</sub>	8 NaOH	6.9	92	0.37	25	29	6.3	61	2.5
CaO	0	0.1	94	28	18	33	3.2	55	3.0
CaO	0.001 NaOH	0.2	97	17.5	15	37	2.0	54	1.0
CaO	6 NaOH <sup>e</sup>	0.2	88	10.6	15	43	2.6	60	5.0
CaO	12 NaOH	2.6	93	1	28	32	5.3	66	7.0

<sup>a-e</sup> Crystallized phases identified by XRD: <sup>a</sup> $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\beta$ -NaAlO<sub>2</sub>,  $\beta''$ -NaAl<sub>5</sub>O<sub>8</sub>; <sup>b</sup> $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\beta$ -,  $\gamma$ -NaAlO<sub>2</sub>,  $\beta'$ -NaAl<sub>5</sub>O<sub>8</sub>,  $\beta''$ -NaAl<sub>11</sub>O<sub>17</sub>; <sup>c</sup> $\alpha$ -Al<sub>2</sub>O<sub>3</sub>; <sup>d</sup>MgO, Na<sub>2</sub>CO<sub>3</sub>; <sup>e</sup>CaO, Na<sub>2</sub>CO<sub>3</sub>.

operation. This may probably be attributed to the formation of acidic  $\beta$ -alumina phases as established by XRD patterns of the NaOH/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst after operation. Also, NaOH/MgO catalysts lost selectivity with time. Apart from the time-dependent catalytic performance, the NaOH/MgO catalyst exhibited a rather surprising result (cp. Table 2): small amounts of sodium hydroxide on MgO (0.001 wt%) led to a significant decrease in C<sub>2+</sub> selectivity in comparison to the pure MgO; only when the NaOH loading was very high (43%) did selectivity exceed that of pure MgO. Cata-

lysts consisting of CaO- and CaSO<sub>4</sub>-supported NaOH showed an increase in C<sub>2+</sub> selectivity with an increasing amount of NaOH; their performance did not change significantly with time. Since the NaOH/CaO catalysts compared to all the other catalyst compositions resulted in high activity (low values of  $W/F$  to achieve nearly complete oxygen conversion or high  $k$  values, respectively) and also good selectivities, this type of catalyst was used for further studies. The extent to which C<sub>2+</sub> selectivity and activity were affected by catalyst preparation, different alkali com-

TABLE 3

Effect of Duration  $t_{\text{dry}}$  and Temperature  $T_{\text{dry}}$  of Drying and Pelletizing Pressure  $P_{\text{pellet}}$  on Activity ( $X_{\text{O}_2}$  at  $W/F = 0.59 \text{ g} \cdot \text{s/ml}$ ) and Selectivity  $S$  of a  $\text{Li}_2\text{O}$  (2 mole%)/CaO Catalyst

$T_{\text{dry}}$ (°C)	$t_{\text{dry}}$ (h)	$P_{\text{pellet}}$ (bar)	$X_{\text{O}_2}$ (%)	$\text{C}_2\text{H}_6$ (%)	$\text{C}_2\text{H}_4$ (%)	$\text{C}_{3+}$ (%)	$\Sigma\text{C}_n\text{H}_m$ (%)
105	2	60	89	37.9	33.3	8.8	80
130	2	60	79	39.1	32.4	8.5	80
130	70	30	84	32.5	35.8	8.7	77
130	70	60	78	35.9	34.1	8.0	78
130	70	120	78	36.9	33.5	7.6	78

Note. Conditions of subsequent calcination after drying correspond to normalized reaction conditions; catalytic results were taken after 22 h of operation.

pounds, and their proportion of the total catalyst was investigated.

#### Catalyst Preparation

The precursors of composite catalysts consisting of an alkali compound, i.e., NaOH and  $\text{Li}_2\text{O}$ , respectively, and CaO were prepared by incipient-wetness impregnation of calcium hydroxide. The effects of the subsequent steps, i.e., drying, calcination, and pelletization, on  $\text{C}_{2+}$  selectivity and activity are described.

The selectivity of a  $\text{Li}_2\text{O}$  (2 mole%)/CaO catalyst which was pelletized with a pres-

sure of 60 bar and subsequently calcined under reaction atmosphere (cp. above) was not significantly affected by temperature and duration of drying (Table 3: cp. first with second row and second with fourth row, respectively); since the ratio of ethylene to ethane depends at least partly on postcatalytic reactions its change should not be considered to be significant. Activity is slightly higher at a drying temperature of 105°C than of 130°C as illustrated by the oxygen conversion obtained (Table 3: cp. first with second row).

The pressure of pelletization which was varied between 30 and 120 bar did not affect the coupling selectivity to any significant degree (Table 3: cp. third to fifth row).

The effect of precursor-calcination conditions (shape of catalyst precursor, i.e., particulate or pelletized, temperature, duration, and ambient gas atmosphere) on activity and selectivity was studied for two materials, NaOH (6 mole%) and  $\text{Li}_2\text{O}$  (2 mole%), both supported on  $\text{Ca}(\text{OH})_2$  which was transformed to CaO during calcination.

*NaOH/CaO.* The catalyst precursor was used (a) as particulate material which was pelletized after calcination and (b) as pellets prepared immediately after drying. The results which are summarized in Table 4 are described in the following.

TABLE 4

Effect of Calcination Conditions Applied to Particulate and Pelletized NaOH (6 mole%)/ $\text{Ca}(\text{OH})_2$  on Its Catalytic Activity and Selectivity

No.	Activity			Selectivity				Form of material	Calcination conditions					
	$W/F$ ( $\text{g} \cdot \text{s/ml}$ )	$X_{\text{O}_2}$ (%)	$k$ ( $\text{ml/g} \cdot \text{s}$ )	$\text{C}_2\text{H}_6$ (%)	$\text{C}_2\text{H}_4$ (%)	$\text{C}_{3+}$ (%)	$\Sigma\text{C}_n\text{H}_m$ (%)		$T$ (°C)	$t_{\text{calc}}$ (h)	$P_{\text{O}_2}$	$P_{\text{CH}_4}$ (mbar)	$P_{\text{H}_2\text{O}}$	$P_{\text{N}_2}$
1	0.22	88	9.6	42.8	14.6	2.6	60	Particulate	800	22	210			790 <sup>c</sup>
2	0.75	98	5.2	39.2	23.5	6.3	69	Particulate	800	14	210			790 <sup>c</sup>
3	0.24	98	16.3	42.1	24.0	7.9	74	Pellet	800	22	210			790 <sup>c</sup>
4	0.24	98	16.3	43.2	23.8	7.0	74	Pellet	740	<sup>a</sup>	75	670	—	255
5	0.13	98	30	44.2	25.2	7.6	77	Pellet	<sup>b</sup>	<sup>b</sup>	75	670	—	255
6	0.17	91	14	42.5	24.7	5.8	73	Pellet	<sup>b</sup>	<sup>b</sup>	—	—	126	874
7	0.17	100	>40	43.2	22.0	6.8	72	Pellet	<sup>b</sup>	<sup>b</sup>	—	874	126	—
8	0.17	78	8.9	46.2	22.6	7.2	76	Pellet	<sup>b</sup>	<sup>b</sup>	—	1000	—	—
9	0.17	83	10.4	42.8	23.9	7.3	74	Pellet	<sup>b</sup>	<sup>b</sup>	—	—	—	1000
10	0.18	75	7.7	44.0	23.3	6.7	75	Pellet	<sup>b</sup>	<sup>b</sup>	220 <sup>d</sup>	—	—	780 <sup>d</sup>

<sup>a</sup> During oxidative coupling.

<sup>b</sup> Calcination: 1 h at 500°C; 1 h at 600°C; 0.5 h at 700°C.

<sup>c</sup> Including constituents of ambient air except oxygen.

The particulate material was calcined for 14 and 22 h, respectively, in ambient air at 800°C; the 22-h calcination resulted in a significantly lower selectivity for C<sub>2</sub> and C<sub>3+</sub> hydrocarbons (cp. No. 1 and No. 2). If pelletization was carried out before rather than after calcination, C<sub>2</sub> and C<sub>3+</sub> selectivities were markedly improved (cp. No. 1 and No. 3).

To suggest a preliminary explanation of these effects, reference is made to hitherto unpublished work (7) showing that C<sub>2+</sub> selectivity increases with the surface concentration of sodium on CaO. Since NaOH may evaporate during calcination at 800°C due to its vapor pressure, it is tentatively assumed that the loss of NaOH is more marked for the particulate (No. 1) than for the pelletized (No. 3) material due to the different lengths of the diffusion paths in the two materials. This proposition would also account for the decrease in selectivity when the duration of calcination of the particulate material was increased. (Another explanation based on a pore structural effect may not be ruled out when pore diffusion affects selectivity (11).)

No effect on C<sub>2+</sub> selectivity was observed when the catalytic material was exposed to either ambient air or the mixture of reactants during calcination at 800°C (cp. No. 3 and No. 4). When the final calcination temperature was lowered to 700°C (applying a temperature program (cp. footnote *b* of Table 4)) a slight increase in coupling selectivity was observed (cp. No. 4 and No. 5). When the pellets were calcined in either N<sub>2</sub> or a mixture of N<sub>2</sub> and O<sub>2</sub> using the temperature program mentioned, no effect on C<sub>2+</sub> selectivity was observed (cp. No. 9 and No. 10); selectivity increased slightly when methane was used instead (cp. No. 8). By adding water vapor to CH<sub>4</sub> or N<sub>2</sub>, C<sub>2+</sub> selectivity decreased by about 2% (cp. No. 6, 7 and No. 8, 9).

In summary it can be derived that best total coupling selectivities to C<sub>2+</sub> hydrocarbons resulted when pellets were first prepared from the precursor material after

drying and then subsequently exposed to reactive conditions up to 700°C or to methane alone before the final reaction temperature of 740°C was established. There is no final explanation for these phenomena but it may be tentatively suggested that some kind of carbon overlayer is built up in the presence of methane during calcination by which either coupling is favored or total oxidation is suppressed; further work is needed for further elucidation of this proposition. There was no marked effect on C<sub>3</sub> selectivity except when condition No. 1 was applied (see above); all other changes are considered to be in the range of experimental accuracy (the average C<sub>3</sub> values of No. 2 to No. 10 amount to 7 ± 0.7).

Some random changes in activity were observed when the different calcination conditions were applied; an appropriate interpretation appears impossible at present.

*Li<sub>2</sub>O/CaO*. The effect of temperature, gas atmosphere, and duration of calcination on catalytic activity and coupling selectivity has also been investigated for pelletized Li<sub>2</sub>O/Ca(OH)<sub>2</sub> material. The conditions applied and the results obtained are summarized in Table 5. Although there are some changes in activity, i.e., oxygen conversion at a set reaction time *W/F*, it is believed that they are of minor importance with respect to catalyst evaluation. There are, however, marked effects on C<sub>2+</sub> and C<sub>3+</sub> selectivity: When calcination is carried out at 740°C (a) under reduced pressure (1 to 5 mbar) for 2 h (cp. No. 7) and (b) under ambient air for 24 h (cp. No. 8), selectivity is reduced to 73 and 67%, respectively, compared to all the other conditions (cp. No. 1 to No. 6) for which the selectivity amounts to 76 to 79%; selectivity is highest, i.e., 78–79% in the presence of the mixture of reactants (No. 1 to No. 4).

Using the same line of argument as that in the preceding case and taking into account that the lithium compound is stabilized under reactive conditions due to carbonate formation as has been shown by

TABLE 5

Effect of Calcination Conditions Applied to Pelletized  $\text{Li}_2\text{O}$  (2 mole%)/ $\text{Ca}(\text{OH})_2$  on Its Catalytic Activity ( $X_{\text{O}_2}$  at  $W/F = 0.59 \text{ g} \cdot \text{s ml}^{-1}$ ) and Selectivity  $S$

No.	$X_{\text{O}_2}$ (%)	$S(\text{C}_2\text{H}_6)$ (%)	$S(\text{C}_2\text{H}_4)$ (%)	$S(\text{C}_{3+})$ (%)	$S(\Sigma\text{C}_n\text{H}_m)$ (%)	Conditions of calcination
1	78	35.9	34.1	8.0	78	$T = 740^\circ\text{C}$ ; reaction atmosphere <sup>a</sup>
2	77	38.7	31.1	8.2	79	2 h/400°C, 2 h/500°C, 2 h/600°C, 2 h/740°C; reaction atmosphere <sup>a</sup>
3	73	38.9	30.8	8.3	78	2 h/500°C, 2 h/600°C, 740°C; reaction atmosphere <sup>a</sup>
4	85	33.9	35.3	8.8	78	2 h/600°C, 2 h/740°C; reaction atmosphere <sup>a</sup>
5	76	37.7	31.2	8.1	77	2 h/400°C, 2 h/500°C, 2 h/600°C, 2 h/740°C; nitrogen
6	83	37.7	29.8	8.5	76	2 h/400°C, 2 h/500°C, 2 h/600°C, 2 h/740°C; synthetic air
7	78	38.1	28.5	6.4	73	2 h/740°C; vacuum (ca. 1 to 5 mbar)
8	72	39.6	22.2	5.2	67	24 h/740°C; ambient air

<sup>a</sup>  $P_{\text{CH}_4} = 0.67 \text{ bar}$ ,  $P_{\text{O}_2} = 0.074 \text{ bar}$ ,  $P_{\text{N}_2} = 0.26 \text{ bar}$ .

Ross and associates (8), one can easily explain the results.

During calcination procedures No. 1 to No. 4 carbon dioxide is formed—at least at higher temperatures when lithium losses would become significant—whereby lithium oxide is stabilized. In experiments No. 5 and No. 6 there is no reactive atmosphere and, hence, no  $\text{CO}_2$  present but the duration of calcination at elevated temperatures ( $740^\circ\text{C}$ ) is short, presumably resulting in only low losses of lithium; the opposite is true for condition No. 8 where temperature treatment at  $740^\circ\text{C}$  lasted 24 h in a nonreactive atmosphere, i.e., ambient air, most probably resulting in a significant loss of lithium. Finally, with treatment No. 7 somewhere between No. 8 and No. 9 the vaporization of the lithium oxide is certainly favored by the reduced pressure. Since  $\text{C}_{2+}$  selectivity depends similarly on the lithium concentration of the catalyst surface as shown for sodium (cp. above)

the different selectivities obtained can be understood by the above reasoning.

No significant changes in catalyst activity were caused by the different conditions of calcination.

#### *Different Alkali Compounds on CaO*

Catalytic results obtained with catalysts consisting of different alkali compounds, i.e., carbonates, sulfates, hydroxides, and oxides of lithium, sodium, and potassium, loaded in varying amounts on CaO are shown in Table 6. The catalyst precursors were dried 2 h at  $130^\circ\text{C}$ , subsequently pelletized, and finally calcined under standard reaction conditions. The results were obtained after 1 to 2 h of catalyst operation. When the hydrocarbon selectivities are compared the errors (standard deviations) associated with the various data must be taken into account:  $\text{C}_2$ , ca. 2%;  $\text{C}_3$ , 1 to 1.5%;  $\text{C}_4$ , 1 to 1.5%; total hydrocarbons, 2 to 2.5%.

TABLE 6

Activity (Oxygen and Methane Conversion Related to Modified Reaction Time or Pseudo-First-Order Rate Constant  $k$ ) and Selectivity of Alkali Compounds on CaO

Alkali compound (mole%)	Activity				Selectivity								
	W/F (g · s/ml)	X <sub>O<sub>2</sub></sub> (%)	X <sub>CH<sub>4</sub></sub> (%)	$k$ (ml/g · s)	C <sub>2</sub> H <sub>6</sub> (%)	C <sub>2</sub> H <sub>4</sub> (%)	ΣC <sub>2</sub> (%)	C <sub>3</sub> H <sub>8</sub> (%)	C <sub>3</sub> H <sub>6</sub> (%)	ΣC <sub>3</sub> (%)	ΣC <sub>4</sub> (%)	ΣC <sub>n</sub> H <sub>m</sub> (%)	CO <sub>x</sub> (%)
1.2% Li <sub>2</sub> CO <sub>3</sub>	0.37	92	15	6.8	27	40	67	2.3	2.5	4.8	4.2	76	24
3.0% Li <sub>2</sub> CO <sub>3</sub>	0.36	91	16	6.7	27	41	68	2.3	2.5	4.8	4.0	77	23
5.8% Li <sub>2</sub> CO <sub>3</sub> <sup>a</sup>	0.44	93	16	6.0	30	38	68	2.6	2.6	5.2	4.6	77	23
1.2% Na <sub>2</sub> CO <sub>3</sub>	0.14	86	16	14.0	24	44	68	—	4.6	4.6	5.4	78	22
3.5% Na <sub>2</sub> CO <sub>3</sub>	0.14	83	15	12.7	25	42	67	—	4.6	4.6	5.3	78	22
6.2% Na <sub>2</sub> CO <sub>3</sub> <sup>a</sup>	0.81	91	12	3.0	29	33	62	2.6	1.2	3.8	2.9	70	30
1.5% K <sub>2</sub> CO <sub>3</sub>	0.36	98	15	10.9	22	41	63	—	3.6	3.6	5.6	72	28
3.7% K <sub>2</sub> CO <sub>3</sub>	0.14	91	14	17.2	20	42	62	—	3.3	3.3	5.0	72	28
7.1% K <sub>2</sub> CO <sub>3</sub> <sup>b</sup>	0.38	96	13	8.5	22	43	65	—	3.6	3.6	1.8	70	30
2.3% LiOH	0.62	87	15	3.3	30	39	69	3.3	2.1	5.4	2.7	77	23
5.7% LiOH	0.63	100	16	>11	31	36	67	3.4	1.7	5.1	4.5	77	23
11.0% LiOH <sup>a</sup>	1.37	96	16	2.3	34	29	63	5.9	—	5.9	6.6	76	24
2.6% NaOH	2.59	100	16	>3	29	34	63	3.5	1.7	5.2	4.8	74	26
6.0% NaOH	0.15	90	14	15.4	24	43	67	—	4.5	4.5	2.5	74	26
11.9% NaOH <sup>a</sup>	0.96	93	15	2.8	30	36	66	5.3	—	5.3	4.1	75	25
2.6% KOH	0.26	95	15	11.5	22	43	65	—	3.8	3.8	3.5	73	27
5.5% KOH	0.26	89	13	8.5	20	44	64	—	3.5	3.5	2.3	70	30
11.3% KOH <sup>b</sup>	1.93	96	14	1.7	30	30	60	4.8	—	4.8	7.5	72	28
1.4% Li <sub>2</sub> O	0.37	92	14	6.8	28	39	67	2.5	2.3	4.8	3.4	75	25
3.0% Li <sub>2</sub> O	0.38	97	14	9.2	24	40	64	—	4.0	4.0	3.4	72	28
6.0% Li <sub>2</sub> O <sup>a</sup>	0.36	99	14	12.8	24	41	65	—	3.9	3.9	3.4	72	28
1.3% Na <sub>2</sub> O	0.36	97	17	9.7	27	40	67	2.7	2.8	5.5	5.5	78	22
3.0% Na <sub>2</sub> O	0.36	95	16	8.3	25	40	65	—	4.8	4.8	5.6	72	28
8.7% Na <sub>2</sub> O <sup>a</sup>	0.72	96	14	4.5	29	35	64	4.1	1.4	5.5	6.7	73	23
1.2% K <sub>2</sub> O	0.25	93	15	10.6	24	42	66	—	3.9	3.9	2.5	74	26
2.9% K <sub>2</sub> O	0.25	83	14	7.1	23	42	65	—	4.2	4.2	2.9	72	28
6.0% K <sub>2</sub> O <sup>b</sup>	0.43	94	14	6.5	21	42	63	—	3.7	3.7	2.3	69	31
1.4% Li <sub>2</sub> SO <sub>4</sub>	0.91	100	16	>7.6	35	31	66	5.8	—	5.8	4.3	76	24
3.4% Li <sub>2</sub> SO <sub>4</sub>	1.40	99	16	3.3	33	32	65	5.3	—	5.3	5.1	76	24
6.5% Li <sub>2</sub> SO <sub>4</sub> <sup>c</sup>	0.95	93	14	2.8	30	38	68	3.6	6.0	4.6	2.2	74	26
1.4% Na <sub>2</sub> SO <sub>4</sub>	0.24	95	14	12.5	24	40	64	—	3.7	3.7	4.3	73	27
3.5% Na <sub>2</sub> SO <sub>4</sub>	0.19	92	16	13.3	26	45	71	—	4.8	4.8	2.2	78	22
5.2% Na <sub>2</sub> SO <sub>4</sub> <sup>d</sup>	0.20	82	15	8.6	27	42	69	—	4.9	4.9	4.0	78	22
1.2% K <sub>2</sub> SO <sub>4</sub>	0.22	85	15	8.6	27	42	69	2.5	2.3	4.8	2.4	76	24
3.4% K <sub>2</sub> SO <sub>4</sub>	0.18	80	14	8.9	24	46	70	—	4.2	4.2	2.0	76	24
5.2% K <sub>2</sub> SO <sub>4</sub>	0.23	92	15	11.0	27	42	69	—	4.2	4.2	2.8	76	24

<sup>a-c</sup> Phase composition by XRD: <sup>a</sup>CaO, Ca(OH)<sub>2</sub>; <sup>b</sup>CaO, Ca(OH)<sub>2</sub>, K<sub>2</sub>Ca(CO<sub>3</sub>); <sup>c</sup>CaO, Li<sub>2</sub>SO<sub>4</sub>-I; <sup>d</sup>CaO, Na<sub>2</sub>SO<sub>4</sub>-II; <sup>e</sup>CaO, K<sub>2</sub>SO<sub>4</sub> (arcanite).

The proportions of the various compounds loaded on CaO which were varied between approximately 1 and 10% did not significantly affect the total hydrocarbon selectivity. Among the various alkali compounds used, the best total hydrocarbon selectivities of 75 to 78% were obtained with Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, LiOH, Na<sub>2</sub>O, Li<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, and K<sub>2</sub>SO<sub>4</sub>; lower selectivities of approximately 72 to 75% were

achieved by using NaOH and Li<sub>2</sub>O; the lowest selectivities of about 70 to 72% resulted from K<sub>2</sub>CO<sub>3</sub>, KOH, and K<sub>2</sub>O.

Under all conditions the approximate C<sub>2</sub> hydrocarbon selectivities amounted to about 64 to 68% while for C<sub>3</sub> and C<sub>4</sub> hydrocarbons values of 4 to 5 and 2.5 to 4.5% were obtained.

The pseudo-first-order rate constant, a measure of catalyst activity, does not ex-

hibit any systematic or significant changes for the different catalyst compositions. There appears to be a slight decrease in the rate constant when the alkali loading is in the high region of approximately 6 to 11 mole% which is presumably due to a loss of surface area of the catalyst.

In general, no systematic pattern of the variations observed could be recognized or related to some fundamental properties of the various catalytic compounds. Also, the phase compositions which were determined by XRD for all the catalysts containing the highest alkali compound proportions could not give any respective indication (cp. footnote of Table 6); a solid solution of the alkali compounds in CaO could not be identified and can most probably be excluded since no significant deviations of the lattice constant of CaO were observed; it is therefore assumed that these compounds are amorphous.

#### CONCLUSIONS

In this study it was shown that composite catalysts consisting of alkali and alkaline earth compounds resulted in selectivities of up to 80% for the formation of C<sub>2+</sub> hydrocarbons by oxidative coupling of methane, which were higher than those of the individual compounds. This is in agreement with results obtained with the lithium/magnesium oxide system as reported by Lunsford and associates (9) and subsequently also by others (10). It is assumed that the improvement of the coupling selectivity may be ascribed to an increase in surface basicity which occurs when alkali cations are incorporated into the alkaline earth compound surface. In earlier work (2) it was shown that selectivity increases with increasing surface basicity.

Calcium hydroxide which is transformed to calcium oxide during heat treatment

proved to be a suitable support for alkali compounds. The selectivity of such catalysts was affected by the alkali compound used and the conditions of catalyst preparation, i.e., especially the time of calcination, the atmosphere surrounding the catalyst precursor during calcination, and whether the precursor was subject to calcination as granulates or in final pellet shape as used for the catalytic experiments.

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