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Synergy between Stable Carbonates and Yttria in Selective Catalytic Oxidation of Methane

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The use of yttria as an oxidative coupling of methane catalyst leads to relatively high carbon monoxide selectivity. This behavior, identical to that found with thoria, is believed to be due to the absence of carbonate formation and the stability of surface superoxide on these two oxides. The addition of high temperature stable alkaline earth carbonates decreases CO synthesis activity while increasing overall catalytic activity.

Several criteria for obtaining active and selective oxidative coupling of methane (OCM) catalysts have been recently suggested.1) These criteria are: basicity,2) absence of reducible surface cations,2) high temperature p-type semiconducting oxides, high temperature stable carbonates, low catalyst porosity and hydration resistance. ThO_2, although lacking high temperature stable carbonates, adheres to the other criteria and is relatively selective toward the formation of C_{2+} products.3) A synergistic effect between ThO_2 and alkaline earth or rare earth oxides was found and attributed to the addition of a cation capable of forming a stable carbonate.3) Surface carbonate is thought to decrease the formation of catalytically generated CO by destroying surface superoxide through formation of a peroxycarbonate intermediate.4)

Yttria, like thoria, is a basic,5) high temperature p-type semiconducting oxide6) which does not possess highly stable surface carbonates.7) Surface O_2^- species can be formed on yttria upon heating above 100 °C under oxygen.8) The formation of O_2^- is readily obtained on decarbonated surfaces. In addition to these similarities, the catalytic behavior of yttria and thoria was found to be very similar.

The relative selectivities toward CO and CO_2 are generally not regarded in detail. We have found, however, that ThO_2 leads to an anomalously high CO selectivity compared to CO_2.3,9) This behavior was attributed to the presence of surface O_2^- and the lack of stable surface carbonates on pure ThO_2. In view of the similarity to thoria, yttria was examined for OCM catalytic activity.

Several OCM catalysts having different carbonate stabilities were investigated in order to examine the influence of carbonate stability on catalytic activity and selectivities. The reactor design and operating conditions used in this study are the same as those previously reported.3) Silica grains were used before the catalyst bed to preheat the gas mixture, but were not used in the post-catalytic zone, tests 1-10. All of the catalysts were pretreated in situ under the reaction mixture for 1 h with a 930 °C catalyst bed hot spot (hs) temperature to ensure stable catalytic activity during testing. The furnace temperature was then lowered to obtain an 880 ^{0}C hs, as this temperature had been found to be suitable for this reactor design.[10]

For the catalytic tests reported here, the mass of the catalyst was adjusted in order to obtain similar O_2 conversions between sets of experiments, for example tests 1, 5-7 and 11-12 ($\approx$ 75%) and tests 8-10 ($\approx$ 94%), see Table 1. Tests 11-14, carried out in the presence of silica grains in the post-catalytic zone, have been included as comparative examples. The low activity of both $SrCO_3$ and $BaCO_3$ near 880 ^{0}C required that the hs temperature be raised to 906 ^{0}C to obtain comparable and reproducible results. This is probably due to the high temperature required to initiate carbonate decomposition, thereby creating sites for oxygen adsorption. It was observed that a small increase in the furnace temperature, at or near 880 ^{0}C with pure $SrCO_3$, led to very irradic change in catalyst activity. This was not the case for strontium containing mixed oxide/carbonates.

Table 1. Oxidative coupling of methane over various catalytic compositions[a]

Test	Catalyst	Weight	Temp[b]	Conv./(%)		Selectivity/(%)			$C_2^=/C_2$
		g	^{0}C	CH_4	O_2	C_{2+}	CO	CO_2	ratio
1	$CaCO_3$	0.5	818	10.3	79.7	62.6	15.2	22.2	1.18
2	$SrCO_3$[c]	0.3	868	13.3	88.0	70.2	11.9	17.9	1.88
3	$BaCO_3$[c]	0.3	856	11.1	68.3	73.7	12.6	13.8	1.56
4	Y_2O_3	0.4	807	12.6	86.9	67.4	20.0	12.5	1.60
5	Y_2O_3	0.2	828	11.3	76.4	66.3	24.0	9.7	1.90
6	ThO_2	1.0	821	10.1	73.7	64.1	21.9	14.1	1.26
7	$CaCO_3$-Y_2O_3[d]	0.3	826	11.1	74.5	69.0	18.0	13.0	1.51
8	$SrCO_3$-Y_2O_3[d]	0.3	778	14.7	92.0	77.4	6.8	15.8	1.13
9	Sr/Y_2O_3[e]	0.3	786	14.6	94.5	74.9	7.4	17.7	1.13
10	$BaCO_3$-Y_2O_3[d]	0.3	772	14.7	94.3	76.7	5.6	17.7	1.02
11	ThO_2[f]	1.0	802	10.5	74.4	62.0	23.5	14.4	0.83
12	$SrCO_3$-ThO_2[d,f]	1.0	807	12.0	74.1	75.0	9.2	15.8	0.97
13	La_2O_3[f]	0.3	759	14.1	99.6	69.7	10.4	20.0	0.76
14	$SrCO_3$-La_2O_3[d,f]	0.3	759	15.4	99.6	77.8	4.4	17.8	0.76

a) Methane and oxygen flow rates were 1000 and 100 ml/min respectively. b) Corresponds to the tubular furnace temperature required to obtain an 880 ^{0}C catalyst bed hot spot. c) Hot spot 906 ^{0}C. d) Mechanical mixtures of 1:1 mole alkaline earth carbonate and either $Y_2(C_2O_4)_3 \cdot 9H_2O$, ThO_2, or $La_2O_2CO_3$ calcined at 570 ^{0}C in air for 2 h. e) Prepared by impregnation of Y_2O_3 by a solution of $Sr(NO_3)_2$ then thermal decomposition at 570 ^{0}C in air for 2 h; atomic ratio Sr:Y=1:10. f) Tests 11-14 were carried out with quartz grains in the post-catalyst region of the reactor. This leads to decreased residence time in the reactor and therefore decreased ethylene to ethane ratios.

The results shown in Table 1 clearly indicate that oxides which do not possess stable carbonates (tests 4-6 and 11) or which are not substantially carbonated at the temperature of the reaction (tests

1 and 7) exhibit high CO selectivities. On the other hand, mixtures of Y_2O_3 or ThO_2 with a high temperature stable carbonate (tests 8-10, 12) exhibit substantially lower CO selectivities and higher C_{2+} selectivities. The addition of either barium or strontium oxide/carbonate to an irreducible oxide, possessing an oxidation state other than 2+ and unable to form stable carbonates, results in a decrease in CO synthesis activity with little or no increase in the CO_2 synthesis activity of the oxides. Note also that pure Y_2O_3, resulting from the decomposition of $Y_2(C_2O_4)_3 \cdot 9H_2O$ (tests 4 and 5), $BaCO_3$ and $SrCO_3$ have lower catalytic activities than the mixed oxide/carbonates (tests 8-10). This can be seen by the higher methane and oxygen conversions and lower tubular furnace temperature required for the mixed oxide/carbonates. This indicates a true synergy between high temperature stable alkaline earth carbonates and yttria.

The relative order of carbonate stability for the alkaline earth oxides is known to increase with increasing cationic radius. If we now add the other oxides used in this study the general order becomes: $ThO_2 \approx Y_2O_3 < MgO < CaO < La_2O_3 < SrO < BaO$. Li, Na, and K oxides are also capable of forming highly stable carbonates. The apparent importance of high temperature stable carbonates would appear to be one of the key factors for the requirement of at least one of either Li, Na, K, La, Sr, or Ba cations in active and selective catalysts for the oxidative coupling of methane.

Carbonate incorporation into basic oxide OCM catalysts has an influence on: 1) the CO selectivity,3) 2) the XPS O1s binding energy,4) 3) the EPR signal of surface superoxide 9) and 4) the temperature of maximum CO_2 thermal decomposition with respect to the pure carbonate compound.7,11,12) The temperature of maximum CO_2 thermal decomposition has been found to decrease when a carbonate is mixed with a basic oxide, such as with $(Ca,Mg)CO_3$ in Dolomite,11) $CaCO_3$-$Y_2O_3$7) and CaO-$BaCO_3$.12) A possible explanation for these results may be a transfer of carbonate, or CO_2, from the carbonated species to the oxide which subsequently decomposes.

The decomposition of surface carbonates should be an advantage under catalytic operation. This would tend to increase anion vacancy sites which are required for oxygen adsorption. The decomposition of bulk forming carbonates would also increase crystal disorder and perhaps catalyst surface area. The presence of gas phase CO_2 is known to increase selectivity toward C_{2+} products at low concentration and enter into competition with oxygen for surface sites, thereby decreasing catalytic activity, at higher concentration.13,14) The addition of substantial quantities of CO_2 to methane-oxygen gas mixtures may be very beneficial for oxide mixtures containing components which form low temperature stable carbonates, but which are not carbonated in the high temperature ranges required for elevated OCM catalytic activity. By increasing the partial pressure of CO_2, mixed oxides containing Ca or Mg, and free of Li, Na, K, La, Sr, and Ba, may become more active and selective OCM catalyst due to partial carbonatation of the surface. Such an effect has been observed for pure MgO at 800 ^{0}C.14)

The superoxide ion has been proposed as the oxygen species responsible for the generation of methyl radicals from methane based on EPR studies of CaO-Y_2O_3.7) This, however, is not in agreement with this study nor the observations that peroxides possessing surface O_2^- are ineffective for methane activation15) and that pure ThO_2, which possess surface superoxide, is less selective than ThO_2 with added $SrCO_3$ or $BaCO_3$, which do not possess surface superoxide.3,9) The coexistence of both paramagnetic and diamagnetic oxygen species in and on basic oxides requires that a combination of EPR, XPS, thermal desorption and catalytic testing be used to better understand the interplay of the various oxygen species present on these mixed oxide/carbonates.

ThO_2, Y_2O_3, and rigorously decarbonated La_2O_3 are known to form surface O_2^- ions upon heating in oxygen. The addition of a more stable carbonate forming cation to these oxides improves the C_{2+} selectivity while decreasing the CO selectivity. Synergy between a highly stable carbonate and an irreducible oxide leads to very effective OCM catalysts. Although the carbonate is inactive, its presence is required to improve catalyst selectivity. The role of carbonate may be related to its ability to alter the relative stability of the various oxygen species found on the surface thus reducing CO formation. The peroxycarbonate anion has been previously suggested as the intermediate responsible for the alteration in surface oxygen species.4)

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