THE ROLE OF ALKALI PROMOTERS IN SELECTIVE CATALYTIC COUPLING OF METHANE

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ABSTRACT

The role of alkali promoters in increasing the hydrocarbon selectivity of catalytic methane coupling is under investigation for series of unpromoted and alkali-promoted alkaline earth and rare earth oxides. Multilayer quantities of CO_2 and fractional monolayer quantities of O_2 and H_2O evolved during temperature-programmed desorption (TPD) experiments immediately following the stationary-state oxidative dimerization of methane by Na/CaO and Li/MgO. These results suggest that a relatively passive and protective layer of molten alkali carbonate with surface hydroxide and surface oxide components is formed on the promoted CaO and MgO surfaces during partial oxidation. Isotope exchange experiments with deuterium-labeled methane in the absence of gas phase oxygen showed high rates of H-D exchange on both the unpromoted and the Na-promoted CaO catalysts, indicating that the formation of methyl radicals may not limit the rate of production of higher hydrocarbons. The presence of an adsorbed species that released methane at moderate temperature, about 550 K, was also revealed in the TPD experiments following methane dimerization. Methyl (or methoxy) and hydroxyl entities coadsorbed on the carbonate layer are suggested as the source of methane observed in these TPD experiments.

INTRODUCTION

An increase in the worldwide supply of natural gas, increasing restrictions on the flaring of remote natural gas, and the high cost of synthesis gas conversion provide great incentives to develop processes that directly and economically convert methane to readily transportable and higher value products.[1-3] Hydrocarbon formation through the selective oxidation of only the excess hydrogen in the methane molecule is thermodynamically favorable, while direct thermal conversion of methane to higher hydrocarbons is thermodynamically unfavorable and energy intensive. However, the partial oxidation of methane is difficult because of the relatively high reactivity of useful products and the very

favorable thermodynamics for deep oxidation to carbon dioxide. Successful processes for direct methane conversion into higher hydrocarbons must therefore use highly selective catalysts that strongly inhibit total oxidation, yet retain the capability of activating the stable methane molecule.

Several classes of catalysts have significant selectivity for methane activation, including alkaline earth oxides, rare earth oxides, manganese oxide, and oxides of the soft metals such as lead, cadmium, bismuth, and antimony. Alkali promoters are widely used with methane activation catalysts,[4-8] and often increase selectivity without a corresponding increase in the methane conversion rate. Thus, alkali may act more to suppress hydrocarbon oxidation than to promote methane conversion. In the present, work we have used fixed-bed reactor kinetic studies, methane H-D exchange reaction experiments, and post-reaction temperature-programmed desorption (TPD) examination to study the mechanism of methane oxidative dimerization by a variety of unpromoted and alkali-promoted alkaline earth oxide and rare earth oxide catalysts.

EXPERIMENTAL RESULTS

Catalyst Preparation

Samples of alkali-promoted alkaline earth oxide catalysts were prepared from high-purity CaO, MgO, $Ba(OH)_2$, Na_2CO_3, K_2CO_3 and Li_2CO_3 (Johnson Matthew, Puratronic®, > 99.99%). The preparation consisted of adding appropriate amounts of the alkali carbonate and alkaline earth oxide or hydroxide to a small quantity of distilled water and boiling for 1 hour. The resulting slurry was then air dried overnight at 423 K. Various mole fraction compositions were prepared where the mole fraction of alkali metal is defined as the ratio of moles of alkali metal to the sum of the moles of alkali metal and the moles of alkaline earth oxide. BET (N_2) surface area measurements were performed on these catalysts following a standard pretreatment. Complex rare earth oxide catalysts, such as $LaAlO_3$ and La_2O_3, were prepared by precipitation of nitrate salt solutions with tetramethyl ammonium hydroxide, followed by centrifugation and drying. These catalysts were calcined in air at 873 K and characterized by x-ray diffraction and BET surface area measurements prior to the kinetic studies.

Fixed-Bed Reactor Studies of Methane Activation

Isothermal reaction kinetics for methane activation by the alkali-promoted alkaline earth oxide catalyst were examined over a period of time (15 to 72 h) sufficient to establish stationary-state conditions.

catalytic rates were measured using a fixed-bed microreactor system. Approximately 50-mg samples were loaded in 4-mm-ID quartz reactors. The reaction products were analyzed by gas chromatography using a 6-ft Carbosieve® column with a flame ionization detector. The chromotographs were calibrated using a certified standard blend of reactant and product gases. The methane conversion and product selectivities were based on the number of moles of carbon reacted per unit time. C_{2+} yield is defined as the product of methane conversion and selectivity. Product distributions for the series of alkali-promoted alkaline earth oxides at 1000 K ranged from total combustion (for CaO) to 74% C_{2+} (for Li/MgO). The highest methane activation rate was observed for the Na/CaO catalyst.

The results of our kinetic studies are best understood as competition between oxidative coupling of the methane and its complete oxidation to CO_2. Both reactions show a positive reaction order with respect to CH_4; however, the coupling reaction was inhibited by increasing oxygen partial pressure. Thus, with low oxygen partial pressure, methane conversion was not altered by P_{O_2}, but the selectivity for C_2H_6 and C_2H_4 decreased with increasing P_{O_2}.

Extrapolation of our results to zero oxygen partial pressure predicts that selectivities to C_2H_6 approaching 100% are inherently possible in alkali-promoted catalyst systems. Similar results in this range of low oxygen partial pressures were reported by Ito, et al.[5] When the degree of methane conversion is high, both C_2H_4 and C_2H_6 are observed. The beneficial effect of low O_2 partial pressure on C_{2+} selectivity has long been noted, and is the basis for the redox processes involving the sequential partial oxidation of methane and regeneration of the oxide with air, as demonstrated in the work of Jones, et al.[9] and Keller and Bhasin.[10]

Temperature-Programmed Desorption Studies

The temperature-programmed desorption (TPD) technique was to identify adsorbate binding states as well as bulk phases in the alkali-enriched alkaline earth oxide catalysts. After reaction at elevated temperature, the catalyst was cooled to room temperature in the reactive gas mixture. A stream of pure helium was then passed through the reactor and the catalyst was heated to 1300 K at a rate of 1 K s^{-1}. Desorption and decomposition products were continuously monitored by on-line mass spectrometry. The principal ion masses corresponding to CH_4, H_2O, C_2H_x, CO, C_3H_x, O_2, CH_3OH, and CO_2 were continuously scanned (Figure 1 and Table 1). Variable amounts of O_2, which evolve at high temperatures (>1000 K), small amounts of H_2O, and large quantities of CO_2 indicative of bulk carbonate decomposition were observed. All catalysts unexpectedly exhibited methane desorption at low temperature (650 ± 50 K) in submonolayer quantities.

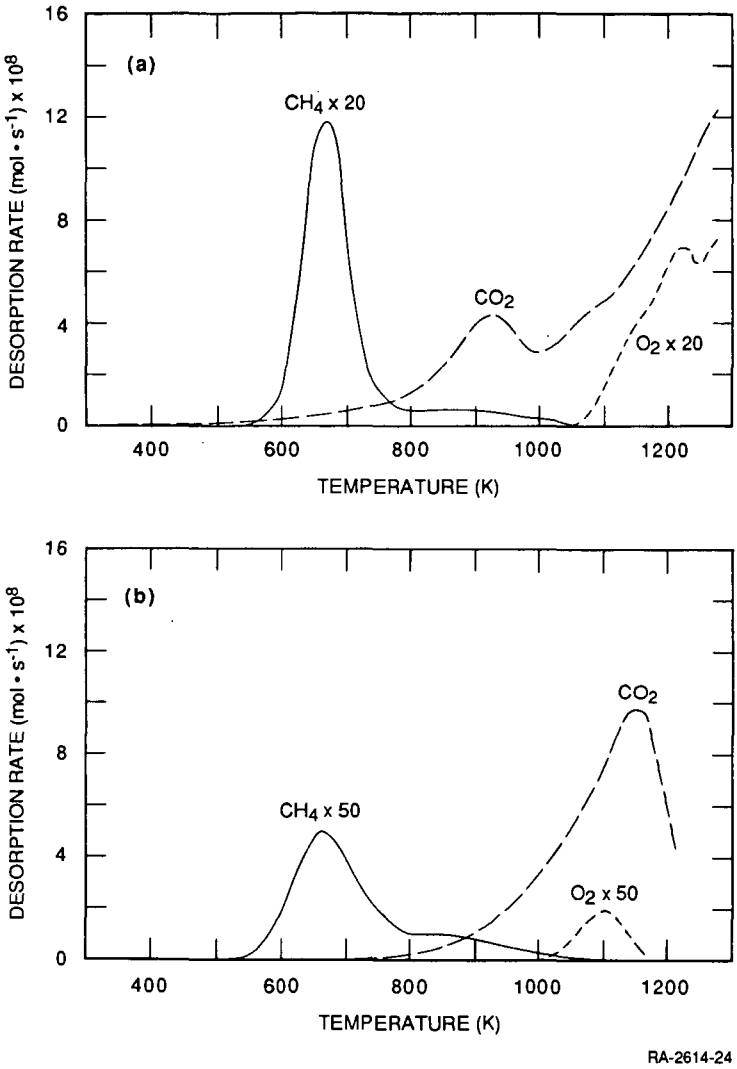

Figure 1. Temperature programmed desorption from alkali-metal-promoted alkaline earth catalysts.

(a) 30 mol % Li/MgO.
(b) 30 mol % Na/CaO.
(1 K • s^{-1} heating rate; 0.5 ml • s^{-1} He flow rate)

Table 1

TEMPERATURE-PROGRAMMED PRODUCT ANALYSIS[a]

Catalysts	Conc. of Sites (μmol g^{-1})	Amount of Desorbed Product[c] (μmol g^{-1})			
		CH_4	H_2O	O_2	CO_2
0.01 Na/CaO	96	3.5 (600)	312 (700)	1.1 (1175)	27.9 (800)
0.30 Na/CaO	46	1.7 (675)	10.5 (400+)	0.6 (1100)	583 (1150)
0.30 Li/CaO	17	0.4 (700)	0.8 (broad)	11.0 (>1100)	3.4 (>1100)
0.30 Li/MgO	40	12.9 (675)	15.8 (broad)	12.6 (1225)	683 (925, >1300)

[a]TPD conditions: 0.5 cm^3 s^{-1} He flow rate, 1 K s^{-1} heating rate, 0.04 g of catalyst.

[b]Number of surface sites estimated assuming site density of 1 x 10^{19} sites m^{-2} for the catalyst surface area following pretreatment at 973 K in air for 48 hours.

[c]Number in parenthesis refers to temperature of desorption peak maxima (K).

The quantities of evolved water vapor for 30 mol% Na/CaO and 30 mol% Li/MgO and oxygen for 30 mol% Li/CaO and 30 mol% Li/MgO approached the estimated surface cation density based on the BET surface area measurements, assuming 1.0 x 10^{19} sites m^{-2}. The CO_2 evolved for the 0.01 and 0.3 Na/CaO and 0.3 Li/MgO samples was almost equal to the quantity of carbonate expected if all alkali was converted to the carbonate during reaction. Thermodynamic calculations predict the formation of bulk carbonates under reaction conditions, despite the low CO_2 selectivity of the alkali/alkaline earth oxide catalysts. The nearly one-fourth monolayer quantities of desorbing oxygen and water vapor (the latter presumably from hydroxyl species) may arise from chemisorbed species or possibly from gas dissolved in the bulk carbonate.

Isotopic Exchange

The extent of hydrogen exchange between CD_4 and CH_4 on calcium oxide catalysts was investigated by injecting an aliquot consisting of a dilute

mixture of CD_4 and CH_4 into a stream of helium and through the catalyst bed at elevated temperatures. The degree of H-D exchange in the methane components of the effluent gas was measured by on-line mass spectrometry. Several pulses of a mixture containing 2.0 μmol CH_4 and 0.6 μmol CD_4 were injected over a temperature range from 300 to 1200 K for CaO and Na-promoted CaO catalysts and for an empty reactor containing the thermocouple assembly. Ion current for masses 15 though 20 amu corresponding to CH_3^+, CH_4^+, CDH_3^+, $CD_2H_2^+$, CD_3H^+ and CD_4^+ ions respectively, were scanned during each pulse.

Both pure CaO and sodium promoted calcium oxide showed substantial activity for hydrogen exchange with CD_4. The extent of H exchange between CH_4 and CD_4 was taken as the conversion of CD_4 since the equilibrated population of CD_4 would be very small (< 1% of the total methane) given the low D/H ratio (D/H = 0.3). At 980 K, 6% of the CD_4 was converted to $CD_{4-x}H_x$ on Na/CaO (Figure 2) while about 60% was converted on CaO. Under these conditions, stationary-state methane conversion with the Na/CaO catalyst was about 5%. Similarly exchange measurements have been reported[11] for MgO and Al_2O_3. Based on CD_4 conversion in the blank reactor, less than 15% of the observed exchange with Na/CaO was attributed to homogeneous gas phase reaction or to reactions occurring on the thermocouple assembly or reactor wall surfaces.

Apparently the hydrogen exchange reaction and the coupling reaction occur similtaneously. The temperature of the onset of hydrogen exchange (800 to 900 K) is approximately the same as the appearance of C_{2+} and CO_2 reaction products during the temperature programmed oxidative coupling of methane over 0.3 Na/CaO and the onset of H_2O and CO_2 evolution during the TPD experiments.

CONCLUSIONS

The kinetics of methane activation were examined for a series of CaO catalysts promoted by lithium, sodium, and potassium oxide/carbonate salts. The methane conversion activity and higher hydrocarbon selectivity follow the order Na > Li > K with respect to promoter. This result is in accord with the idea that cation size, and presumably intersolubility of alkali-alkaline earth cations, influences the nature and surface density of active sites.

The sodium-promoted CaO catalyst system showed high intrinsic C_2H_6 selectivity (> 80 mol% carbon basis in the limit of low conversion and low oxygen partial pressure), good activity (about twice the methane conversion rate per unit area relative to lithium-promoted magnesia under

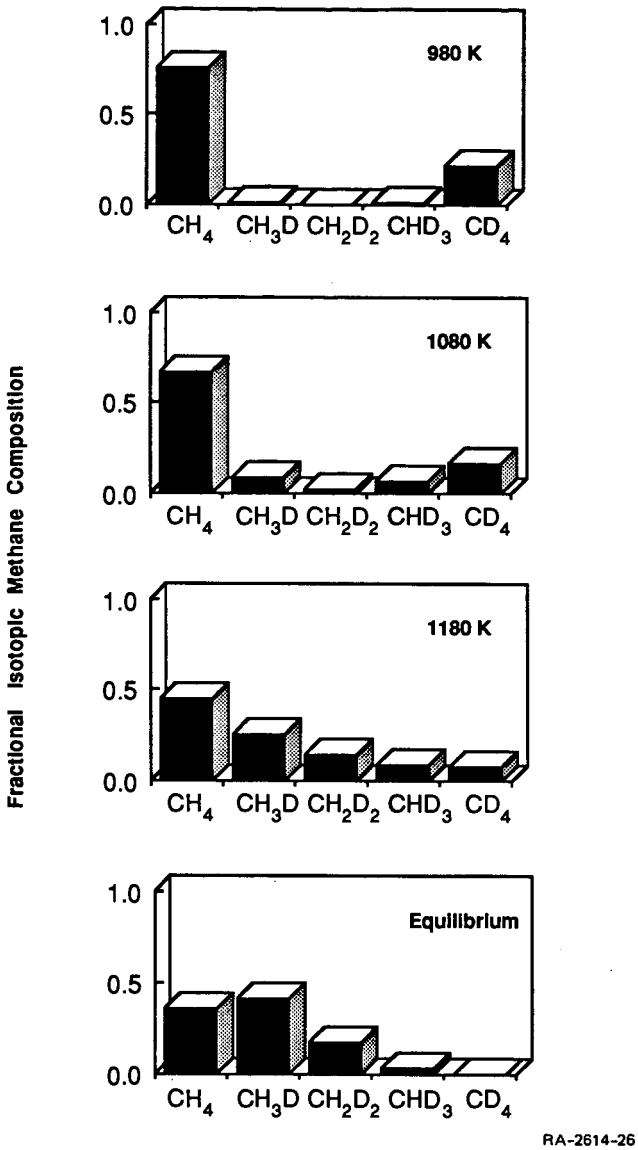

Figure 2. Isotopic concentration of methane pulses over 30 mol% Na/CaO at various temperatures. (Pulse composition: 2.1 micromoles CH_4, 0.6 micromole CD_4)

identical reaction conditions), and good stability (no observable decrease in rate and selectivity after 72 hours). Our results are in substantial agreement with published work.

Detailed reaction order experiments showed that the rate of methane conversion was linear with methane partial pressure as expected and independent of oxygen partial pressures, whereas the C_2 selectivity varied as the square root of methane partial pressure and the inverse square root of oxygen partial pressure. This result shows that operation at moderate pressure (especially with fixed low oxygen partial pressure) with Na/CaO and presumbaly other alkali-promoted alkaline earth oxide catalyst would increase the hydrocarbon yield. Other kinetic studies showed the weak dependence of C_2 selectivity of CO_2 partial pressure and the strong correlation between ethene/ethane product ratio and methane conversion.

ESR experiments were performed in situ at temperatures up to 920 K to detect thermally induced radical oxygen anion species in the presence of oxygen, methane, or a reacting gas mixture. Signals attributable to O^- or $[A^+O^-]$ centers were photoinduced at 78 K but rapidly disappeared at higher temperatures (temperatures below 300 K). This result indicates that O^- centers are not sites for methane activation by selective dimerization catalysts.

TPD experiments indicate that the alkali components after extended reaction exist in the form of (probably molten) carbonate salts on MgO and CaO catalysts. Minor, perhaps fractional, monolayer quantities of oxygen and hydroxyl species were also shown to be present on the working catalysts. Other TPD experiments presented tantalizing evidence for an organic intermediate which was stable at temperatures below 550 K, but which decomposed into methane at 750 K in the absence of oxygen.

A picture of the working alkali-promoted alkaline earth methane dimerization catalysts and the reaction mechanism is emerging from the present work and the numerous methane activation studies under way throughout the world. Recent evidence presented by the Texas A&M group[12-15] convincingly confirms that a free radical mechanism involving gas phase recombination of methyl radicals as a primary step can explain the hydrocarbon product distribution for oxidative methane dimerization. The initial step is the abstraction of a hydrogen atom by an active surface oxygen species with subsequent release of a methyl radical into the gas phase. The high exchange rates we observed between CD_4 and CH_4 suggest that the production of methyl radicals is relatively rapid. Methyl radicals are easily oxidized so that the catalyst surfaces must have a very low concentration of reducible oxygen. The working catalyst may be passivated by the formation of a molten or glassy layer of alkali

carbonate over MgO or CaO surfaces. The carbonate layer may contain surface oxygen or hydroxyl species. The location (gas/alkali carbonate interface, bulk alkali carbonate, or alkali carbonate/alkaline earth oxide interface) and the nature (O^-, O_2^-, or O^{-2}) of the active site is still uncertain. Additional research now under way should clarify both the mechanism and nature of the active site for the initial methane activation step.

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