JOURNAL OF CATALYSIS **114**, 422–432 (1988)

Oxidative Coupling of Methane over Sodium Promoted Praseodymium Oxide

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Received February 2, 1988; revised June 29, 1988

Unpromoted and alkali-promoted lanthanide oxides were evaluated in the oxidative coupling of methane to higher hydrocarbons. Methane conversion was carried out catalytically and in a redox mode by cycling methane and air independently over the lanthanide oxides. The sodium-promoted nonstoichiometric oxide, 4% Na on Pr_6O_{11}, was most active and selective, giving in the redox mode 21% methane conversion and 76% C_2^+ selectivity at 800°C and 1.4 WHSV (weight hourly space velocity, g CH_4/g cat. hr). At comparable conversion catalytic methane conversion had a C_2^+ selectivity of 64%. This selectivity deficit with respect to redox is attributed to an additional destructive route of the methyl radical, namely the reaction with molecular oxygen to yield a methylperoxy intermediate. Process variable studies support a mechanism whereby methane is activated at the metal oxide surface to form a methyl radical and in the gas phase C_2^+ hydrocarbon building occurs. © 1988 Academic Press, Inc.

INTRODUCTION

Methane is an abundant resource, making up greater than 60% of the composition of natural gas. There is a strong economic incentive to convert methane to useful products. Due to methane's high molecular stability, its conversion to higher hydrocarbons is a challenge. Recent advances have been made in the noncatalytic approach to C_2^+ hydrocarbons (*1, 2*). Other current reports have demonstrated the catalytic conversion of methane to C_2^+ products over reducible and nonreducible metal oxides. Of particular interest is the use of lanthanide sesquioxides, namely lanthanum (*3*) and samarium oxides. The performance of samarium oxide was shown to be improved upon by the addition of a lithium promoter (*4*).

This work demonstrates the use of alkali-promoted praseodymium oxide as both a redox agent and a catalyst for methane conversion. Compared to catalytic data obtained over lanthanide sesquioxides, the catalyst of 4% Na on Pr_6O_{11} is at least twice as productive at comparable C_2^+ selectivity and reaction temperature. Process variable studies suggest that methyl radical formation occurs at the metal oxide surface. Higher hydrocarbons form through gas-phase reactions, with ethane as the primary product.

EXPERIMENTAL

Catalyst Preparation

The lanthanide oxides Pr_6O_{11}, Tb_4O_7, CeO_2, La_2O_3, and Nd_2O_3 of 99.9% purity were obtained from Alfa Products. Elemental analysis indicated no cross contamination of the metal oxides. For example, Pr_6O_{11} contained no detectable amounts of La, Ce, Nd, Sm, or Tb. The lanthanide oxides were calcined at 900°C for 16 hr prior to use. The alkali-promoted lanthanide oxides were prepared by incipient wetness impregnation of the metal oxides with aqueous solutions of the acetate or pyrophosphate salts. This was followed by drying at 110°C for 2 hr and calcining at 900°C for 16 hr. The weight percent alkali loadings were measured by AA (atomic adsorption). The binary oxides, Na_2PrO_3 and Li_2PrO_3, were prepared by dry mix-ball milling the

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TABLE 1

Redox Runs over Lanthanide Oxides[a]

Catalyst[b]:	Pr_6O_{11}	Tb_4O_7	CeO_2
% CH_4 conv.	99	74.6	39
% C_2 + sel.	0	0.4	0
% Sel. to			
CO	0.3	0	0
CO_2	98.8	96.8	99
Coke	0.9	2.8	1

[a] Conditions: 825°C, 600 GHSV, 0.2 WHSV, 2-min cumul. CH_4.

[b] Less than 10% CH_4 conv. for UO_3, ThO_2, La_2O_3, Nd_2O_3.

stoichiometric amounts of Na_2O with Pr_6O_{11} and Li_2O with Pr_6O_{11}. These dry mixes were calcined at 950°C for 16 hr. Formation was verified by XRD (X-ray diffraction). The supported reagents of sodium–praseodymium oxides on silica, alumina, and magnesia were prepared by multiple incipient wetness impregnations of the supports with aqueous solutions of $Pr(OAc)_3 \cdot 3H_2O$ followed by drying at 110°C and calcining at 900°C for 16 hr. The calcined and supported praseodymium oxides were subsequently impregnated with aqueous sodium acetate solutions to incipient wetness, dried at 110°C, and calcined at 900°C.

Reactor Apparatus

The catalysts, 1 to 10 ml of 14- to 30-mesh pellets, were charged to 14-mm-i.d. quartz tubes containing quartz thermowells and were supported on quartz plugs. The reaction tubes were electrically heated to reaction temperatures under a flow of air. The reported reaction temperatures represent the highest temperature realized across the catalyst bed under the run conditions. In a typical redox sequence the air was purged from the reactor with nitrogen before the methane sequence began. Methane conversion redox runs were typically 1 to 10 min in length. During this time instantaneous, or on-line, samples were taken. The total cumulative effluent was also collected in a gas bag. The end of the methane redox run was followed by a nitrogen purge. The redox agent was then reoxidized with air at reaction temperature. This also served to burn off carbonaceous material. The regeneration gases were also collected in a gas bag so that a coke yield could be calculated. During the catalytic runs with a feed of 50% air in methane, gaseous effluents were sampled instantaneously after at least 30 min under each set of run conditions to allow performance to stabilize. Under the reaction conditions employed, oxygen conversion was always greater than 90%.

GC Method

Samples were analyzed for carbon monoxide, carbon dioxide, methane, ethane, ethylene, oxygen, and nitrogen on a TCD-GC (thermal conductivity detector–gas chromatograph). The parallel columns used for this one-injection analysis were of molecular sieve and Porapak Q. The C_2 through C_7 hydrocarbon products were analyzed on a Porapak Super Q column in a FID-GC (flame ionization detector–gas chromatograph). The carbon oxides formed upon regeneration after a redox run were included in the total product yields that were summed to give the methane conversion and normalized to give product selectivities. Results are reported on a carbon mole percent basis. Selectivity to desired products, C_2–C_7 hydrocarbons, will be referred to as C_2^+.

REDOX RESULTS

Initial evaluation of the lanthanide oxides was carried in a redox mode by cycling methane and air independently over the metal oxide. Under the reaction conditions given in Table 1, methane conversions of less than 10% were obtained for La_2O_3, Nd_2O_3, and Eu_3O_4, whereas Pr_6O_{11}, Tb_4O_7, and CeO_2 were highly reactive giving at least 39% methane conversion. For the latter three reagents greater than 96% of the product was CO_2. Addition of sodium

TABLE 2

Redox Runs over Sodium-Promoted Lanthanide Oxides[a]

Catalyst:	4% Na on Pr_6O_{11}[b]	4% Na on Tb_4O_7[b]	4% Na on CeO_2[c]
% CH_4 conv.	27.5	20.1	1.8
% C_2 + sel.	70.3	59.0	47.7
Productivity g product/ g cat. hr	0.14	0.08	0.003
% Sel. to			
C_2H_4	33.8	32.7	31.8
C_2H_6	24.3	18.3	15.9
C_3	7.0	4.6	0
C_4	2.5	1.7	0
C_5	0.3	0.2	0
C_6	2.0	1.3	0
C_7	0.3	0.2	0
CO	0	0	0
CO_2	28.8	40.3	38.4
Coke	0.8	0.7	13.9

[a] Sodium-promoted lanthanide oxides mentioned in Ref. (*17*).

[b] Conditions: 775°C, 2400 GHSV, 0.7 WHSV, 2-min cumul. CH_4.

[c] Conditions: 775°C, 1200 GHSV, 0.37 WHSV, 2-min cumul. CH_4.

markedly improved C_2^+ selectivity as shown in Table 2. Carbonate formation is a potential problem in masking true C_2^+ selectivities. After 200 hr of continuous cycling a 1000-fold stoichiometric excess of methane had passed over the reagent of 4% Na on Pr_6O_{11} that would have been necessary for sodium carbonate formation. During this time, conversion and selectivity remained constant, eliminating the possibility of carbonate formation. XRD analysis gave no evidence of sodium or sodium–praseodymium oxides. Ion probe mapping analysis indicated that sodium was evenly dispersed on praseodymium oxide. The surface areas of the calcined lanthanide oxides ranged from 3 to 6 m^2/g, whereas the alkali-doped systems, which underwent sintering, had surface areas of 0.7 to 1.9 m^2/g.

Substitution of the sodium promoter with lithium and potassium was investigated at an equivalent alkali : praseodymium atomic ratio, namely 1 : 3.2. The potassium system had activity equivalent to that of the sodium system but was less selective. The lithium system had C_2^+ selectively comparable to that of sodium system but was half as active. The data are summarized in Table 3. A similar study on alkali-doped magnesia showed no chemical periodicity in the catalytic conversion of methane. Sodium-promoted magnesia gave the highest C_2^+ yield (*5*).

Studies on the optimization of sodium

TABLE 3

Alkali Promoters on Pr_6O_{11}[a]

Wt% promoter:	4% Na	6.6% K	1.2% Li
Effective ionic radius	Na^{+1}, 0.99 Å	K^{+1}, 1.38 Å	Li^{+1}, 0.59 Å
% CH_4 conv.	27.5	28.6	8.2
% C_2 + sel.	70.3	50.9	89.4
Productivity g product/ g cat. hr	0.14	0.12	0.06
% Sel. to			
C_2H_4	33.8	29.2	38.5
C_2H_6	24.3	15.9	36.2
C_3	7.0	3.4	8.6
C_4	2.5	1.2	3.1
C_5	0.3	0.1	0.3
C_6	2.0	1.0	2.4
C_7	0.3	0.1	0.3
CO	0	0	0
CO_2	28.8	47.7	10.5
Coke	0.8	1.4	0
Rel. sel.	1.0	0.7	1.0

[a] Conditions: 775°C, 2400 GHSV, 0.7–0.8 WHSV, 2-min cumul. redox run.

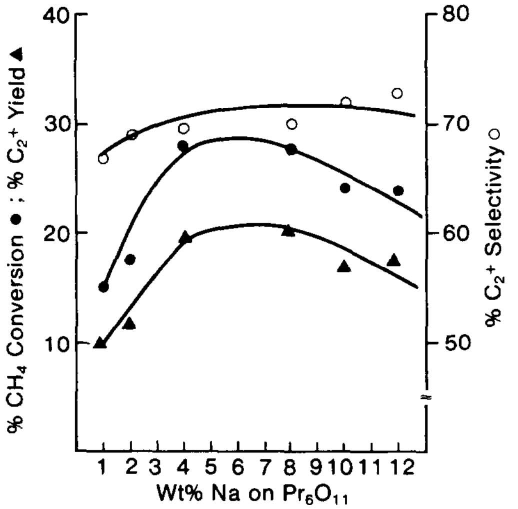

FIG. 1. Methane conversion to C_2^+ hydrocarbons. Two-minute cumulative redox runs at 775°C and 2400 GHSV over Na on Pr_6O_{11}; % CH_4 conversion, ●; % C_2^+ yield, ▲; % C_2^+ selectivity, ○.

loading were carried out with reagents of 1 to 12% sodium on Pr_6O_{11} as shown in Fig. 1. Optimal percentage methane conversion and percentage C_2^+ yield were realized at 4 to 8 wt% sodium. The percentage C_2^+ selectivity was only slightly affected during the loading study, varying from 67 to 72%. Note that 4 wt% sodium is equivalent to 23 mol% sodium. A similar loading study of lithium on samarium oxide gave optimal C_2 yield at 20 mol% lithium and an identical alkali : lanthanide atomic ratio of 1 : 3.2 (*6*).

TABLE 4

Promoter Study[a]

Wt% promoter on Pr_6O_{11}	% CH_4 conv.	% C_2^+ sel.	Radius (Å)
4% Na	28	70	Na^{+1}, 0.99
None	35	2	
16.4% Ag	41	1	Ag^{+1}, 1.02
4.2% Mg	40	3	Mg^{+2}, 0.90
6.8% Ca	20	13	Ca^{+2}, 1.00
15.9% Bi	32	16	Bi^{+3}, 0.99
13.7% Sr	13	24	Sr^{+2}, 1.16
9.4% In	1.5	28	In^{+3}, 0.92

Note. Promoter: Pr atomic ratio 1 : 3.2.
[a] 775°C, 2400 GHSV, 2-min cumul. redox run.

Other metals with effective ionic radii close to that of sodium and praseodymium, namely 0.99 Å, were evaluated at a dopant : praseodymium atomic ratio of 1 : 3.2. For all the doped reagents listed in Table 4 the C_2^+ selectivity never exceeded 28%. A similar study was carried out on promoted magnesia catalysts. At comparable doping levels of 2 to 20 wt%, alkali metals were most effective for C_2^+ formation. Transition metals (Groups 5A, 6A, 7A, 8, and 1B) and 2A (Ca, Sr, Ba), 3A (Y, La), 4A (Zr), 2B (Zn), 3B (Al, In), and 4B (Pb) group additives had a less significant effect on C_2 formation (*7*).

The reagent of 4% Na on Pr_6O_{11} generated a conversion–selectivity curve similar to that of 15% Mn, 5% $Na_4P_2O_7$ on SiO_2 (*2*) (see Fig. 2), but its longevity was much shorter. At 775°C and 0.7 WHSV (weight hourly space velocity) redox performance was maintained for 200 hr at 21% conversion and 79% C_2^+ selectivity. From 200 to 400 hr deactivation occurred and results leveled out to 6% conversion and 91% C_2^+ selectivity. This performance was maintained for 850 hr (see Fig. 3). Deactivation was largely attributed to a 53 wt% sodium loss. Note that in the sodium loading study, catalysts of 1 to 2 wt% sodium were signifi-

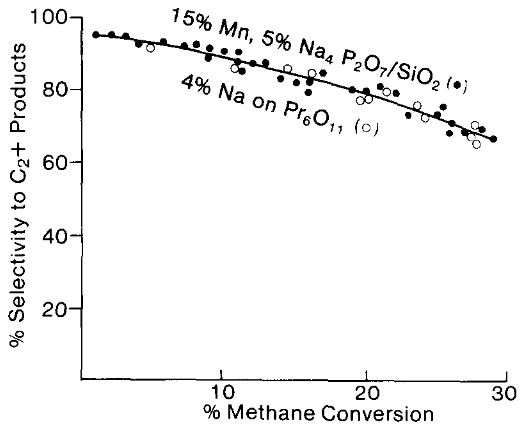

FIG. 2. Methane conversion to higher hydrocarbons. 15% Mn, 5% $Na_4P_2O_7/SiO_2$ (●): 1- and 2-min cumulative redox runs at 700 to 850°C and 0.51 to 1.02 WHSV. 4% Na on Pr_6O_{11} (○): 1- and 2-min cumulative redox runs at 700 to 825°C and 0.70 to 1.40 WHSV.

TABLE 5

Redox of Selective Phases

Catalyst	WHSV	% CH_4 conv.	% C_2^+ sel.	Rel. sel.	$\frac{\text{g } CH_4 \text{ conv.}}{\text{g cat. hr}}$
Na_2 PrO_3[a]	0.44	14.3	92.8	1.13	0.06
Li_2PrO_3[a]	0.42	11.1	98.6	1.16	0.05
4% Na on Pr_6O_{11}[b]	0.70	27.5	70.3	1.0	0.19
1.2% Li on Pr_6O_{11}[b]	0.78	8.2	89.4	1.0	0.06

[a] 825°C, 1200 GHSV, 2-min cumul. redox run.
[b] 775°C, 2400 GHSV, 2-min cumul. redox run.

cantly less active than those of 4 to 8 wt% sodium.

Alkali-promoted praseodymium reagents gave XRD patterns of PrO_2, $PrO_{1.83}$, and PrO_x ($x < 1.83$). In no case were alkali or mixed alkali–praseodymium oxide compounds observed. Two binary oxides, Na_2 PrO_3 and Li_2PrO_3, were prepared for evaluation. These compositions, which were confirmed by XRD, proved to be highly selective reagents at moderate methane conversion. Their selectivity surpassed that of the bulk alkali-promoted reagents as shown in Table 5, but their activities were lower. Again, the possibility of carbonate formation was eliminated by carrying out a sufficient number of redox cycles.

The possibility of reducing catalyst cost by supporting the active components on a carrier was investigated. Sodium–praseodymium oxides supported on silica, alumina, and magnesia were inferior to the nonsupported oxides. XRD analysis indicated formation of praseodymium silicate and aluminate. Praseodymium oxide was only a minor component at best. Thus the majority of praseodymium was locked into a fixed oxidation state and was unable to participate in the redox chemistry as shown in Table 6. Methane conversion was 13% or less for redox runs with the supported oxides whereas for the nonsupported oxide, methane conversion was 36%.

Methane conversion over the reagent of 4% Na on Pr_6O_{11} was carried out over 1- through 10-min cumulative redox runs at 775°C and 0.8 WHSV as shown in Fig. 4. The cumulative methane conversion decreased from 26 to 14% and the cumulative

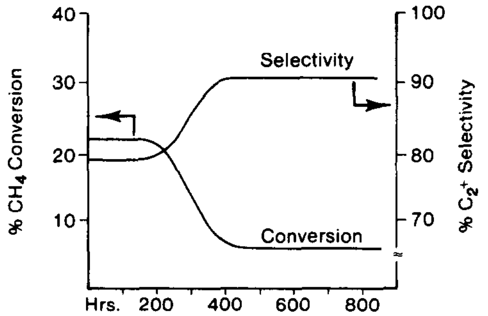

FIG. 3. Life study. Two-minute cumulative redox runs at 775°C and 2400 GHSV over 4% Na (NaOAc) on Pr_6O_{11}.

TABLE 6

Supported Systems

Catalyst[a]	% CH_4 conv.	% C_2^+ sel.	XRD
1% Na on 20% Pr on silica	2	0	$Pr_8Si_6O_{24}$
1% Na on 20% Pr on alumina	6	13	$PrAlO_3$ (major) Pr_6O_{11} (minor)
1% Na on 20% Pr on MgO	13	30	Pr_6O_{11} $Ca_2Pr_8(SiO_4)_6O_2$ $Pr_8Si_6O_{24}$
4% Na on Pr_6O_{11}[b]	36	61	$PrO_{1.83}$

[a] 825°C, 600 GHSV, 0.7 WHSV, 2-min cumul. redox run.
[b] 825°C, 2400 GHSV, 0.7 WHSV, 2-min cumul. redox run.

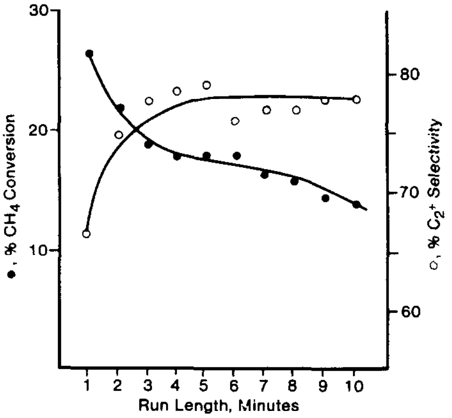

FIG. 4. Effect of reaction time. Cumulative redox results at 775°C and 2400 GHSV over 4% Na on Pr_6O_{11}.

C_2^+ selectivity increased from 67 to 78%. At the end of the 10-min cumulative run 86% of the active oxygen derived from the reduction of Pr_6O_{11} to Pr_2O_3 was consumed. XRD analysis of the spent catalyst confirmed that the reduced form was the sesquioxide, Pr_2O_3.

A series of redox runs was carried out at residence times varying from 0.047 to 0.004 s over 4% Na on Pr_6O_{11}. Decreasing the residence time caused percentage methane conversion to fall from 14 to 2.5%. The percentage C_2H_6 selectivity increased from 48 to 71%, while selectivities to C_2H_4, CO_x, and C_{3-7} all fell below 12% (see Fig. 5).

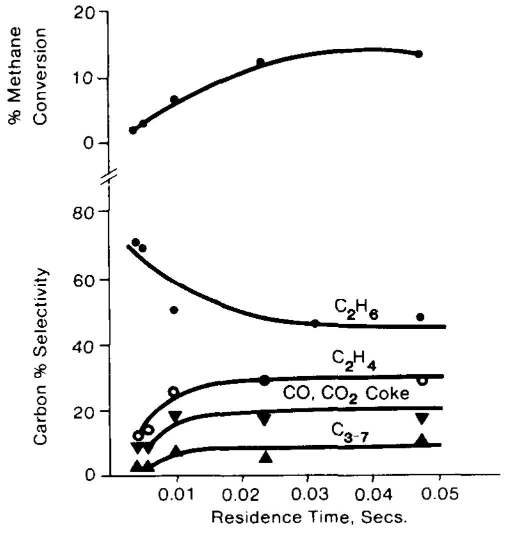

FIG. 5. One-minute cumulative redox runs at 775°C over 4% Na on Pr_6O_{11}.

CATALYTIC CONVERSION RESULTS

Catalytic oxidative coupling of methane was carried out over 4% Na on Pr_6O_{11}. Activity comparable to that realized in redox was obtained at a run temperature 100°C higher (see Table 7). Also, at comparable conversion the catalyst had a 12 to 15% C_2^+ selectivity deficit with respect to redox. As was found in the catalytic oxidative coupling of methane over supported sodium–manganese oxide catalysts (*8*), optimal C_2^+ selectivity was obtained at higher run temperatures. It should be noted that in the absence of alkali promoter, the praseodymium catalyst gave 15% conversion and 20% C_2^+ selectivity under the catalytic reaction conditions of Table 7. The conversion–selectivity curves for catalytic and redox

TABLE 7

Redox vs Cofeed over 4% Na on Pr_6O_{11}

	Redox[b]	Cofeed[c]
Temp. (°C)[a]	800	900
% CH_4 conv.	21.3	21.8
% C_2^+ sel.	76.4	63.9
Productivity g product/ g cat. hr	0.23	0.20
% Sel. to		
C_2H_4	25.8	28.8
C_2H_6	38.0	31.9
C_3	7.3	2.6
C_4	2.6	0.3
C_5	0.3	0.1
C_6	2.1	0.2
C_7	0.3	0.1
CO	0	0.5
CO_2	22.7	35.6
Coke	0.4	0

[a] 4800 GHSV, 1.4 WHSV.

[b] 2-min cumul. redox run.

[c] Catalytic methane conversion mentioned in Ref. (*19*).

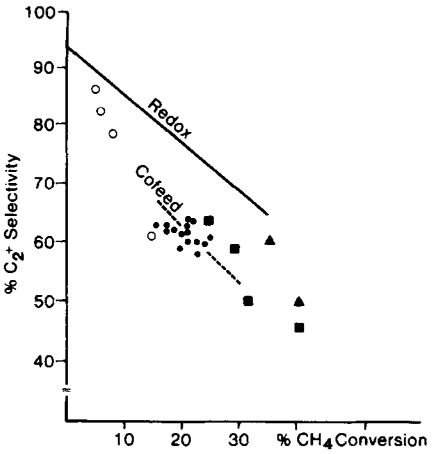

FIG. 6. Redox vs cofeed over 4% Na on Pr_6O_{11}. Redox conditions: 1- and 2-min cumulative redox runs at 700 to 850°C and 0.70 to 1.40 WHSV. Cofeed conditions: 50% air in CH_4 at 825 to 925°C and 0.40 to 1.60 WHSV after 30 min at steady state. Other cofeed lanthanide oxide systems: ○, Sm_2O_3 (*9*); ▲, Li/Sm_2O_3 (*5*); ■, $LiCl/Sm_2O_3$ (*20*).

results obtained over 4% Na on Pr_6O_{11} are shown in Fig. 6. Both have approximately the same slope; the catalytic conversion–selectivity curve is displaced 15 C_2^+ selectivity points below that of the redox curve.

A life test was carried out with the catalyst of 4% Na as sodium pyrophosphate on Pr_6O_{11}. At 850°C and 0.9 WHSV with 50% air in methane initial catalytic results were 18% methane conversion and 63% C_2^+ selectivity. After 100 hr, steady-state results were 19% conversion and 54% selectivity. Selectivity loss occurred between 50 and 100 hr. The latter performance was maintained from 100 to 3200 hr (see Fig. 7). The C_2^+ yield decreased by 1% to give 10.3%, absolute. Note that the redox life study with sodium acetate-promoted praseodymium oxide underwent a 11.1% decrease in C_2^+ yield to give 5.5% absolute, by 400 hr. No crystalline sodium or phosphorus XRD phases were found in the fresh catalyst. The spent catalyst showed a 0.9 wt% incorporation of silicon from the quartz reactor; SiP_2O_7 was identified by XRD. Inclusion of phosphorus as sodium pyrophosphate led to greater performance stability. The effect of phosphorus may be related to enhanced sodium and surface area retention. Note that with the sodium pyrophosphate promoter the catalyst's surface area and sodium loading decreased by 13 and 30%, respectively, over 3200 hr, whereas with the sodium acetate promoter, the redox reagent's surface area and sodium loading decreased by 25 and 53%, respectively, over 850 hr.

A summary of the catalytic data obtained from the partial oxidation of methane over lanthanide oxides is given in Table 8. At a run temperature comparable to those reported in the literature, the sodium–praseodymium oxide catalyst was an order of magnitude more productive than lanthanum and samarium oxides. And at higher temperatures, where C_2^+ selectivity was optimal, the sodium–praseodymium oxide catalyst gave C_2^+ selectivity competitive with that of lithium–samarium oxide.

The catalytic activity of samarium oxide was evaluated at higher temperatures, oxygen partial pressures, and methane WHSV than those reported in the literature (*9*) as shown in Table 9. Under comparable conditions the catalyst of 4% Na on Pr_6O_{11} was considerably more active and selective than samarium oxide. For the latter catalyst percentage conversion, C_2^+ yield and C_2^+ selectivity increased with run temperature and maximized at 925°C, whereas for samarium oxide performance was relatively insensitive to temperature. From 700 to 950°C methane conversion varied from 12 to 14%

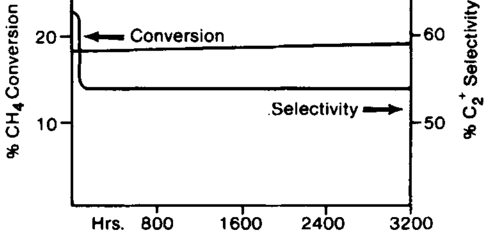

FIG. 7. Life study. 50% air in CH_4 at 850°C and 2400 GHSV over 4% $Na(Na_4P_2O_7)$ on Pr_6O_{11}.

TABLE 8

Methane Conversion over Lanthanide Oxides

Catalyst	Temp. (°C)	CH_4/O_2	CH_4 pressure (atm)	CH_4 (WHSV)	% CH_4 conv.	% C_2^+ sel.	Productivity g product / g cat. hr	Ref.
4% Na on Pr_6O_{11}	900	5	0.5	1.4	21.8	63.9	0.20	This work
	775	5	0.5	1.4	17.0	50.9	0.12	
La_2O_3	725	3.4	0.08	1.0	19.7	23.7	0.05	(*3*)
Sm_2O_3	750	5.2	0.18	0.18	15.1	60.6	0.016	(*9*)
Li/Sm_2O_3	750	2.5	0.05	0.20	35.0	60.0	0.042	(*5*)
$LiCl/Sm_2O_3$	750	2.5	0.10	0.10	31.1	49.7	0.015	(*20*)

and C_2^+ selectivity varied from 25 to 36%. The higher run temperatures gave a higher yield to CO_x. A control run with an empty alumina tube at identical flow rates and 925°C (0.4 s residence time) gave thermal results of 4.2% methane conversion and 50% C_2^+ selectivity.

DISCUSSION

As redox reagents the nonstoichiometric oxides, Pr_6O_{11} and Tb_4O_7, showed higher activity toward methane than the other lanthanide oxides investigated. Studies on the catalytic oxidation of nitric oxide (*10*) and butane (*11*) likewise found higher activity for Pr_6O_{11} and Tb_4O_7 than the other lanthanide oxides. There is no correlation between methane conversion and basicity (i.e., ionic radius). The higher reactivity of the nonstoichiometric oxides may be attributed to three factors: (i) rapid interconversion of oxidation states ($Ln^{3+} \rightleftharpoons Ln^{4+}$), (ii) rapid diffusion of O_2 in the bulk, and (iii) high Ln^{4+}/Ln^{3+} oxidation potentials.

Addition of sodium reduced the lanthanide oxide's activity and improved C_2^+ selectivity. With a more basic surface there was less of a tendency for interaction with olefinic and aromatic products. Once activated at these temperatures, such products are prone to coking or overoxidation by the oxidizing surface. Calculations indicate that monolayer sodium coverage on Pr_6O_{11} is achieved at 0.4 wt%. But it is conceivable that a substantial amount of sodium migrates into the Pr_6O_{11} lattice structure thus accounting for the optimal loading of 4 to 8 wt%.

The lanthanide oxides were evaluated by other investigators as catalysts in the oxidative coupling of methane. These studies did not access the redox capability of the metal

TABLE 9

Catalytic Methane Conversion

Catalyst	Temp. (°C)	CH_4 (WHSV/GHSV)	% CH_4 conv.	% C_2^+ sel.	Productivity g product / g cat. hr
4% Na ($Na_4P_2O_7$) on Pr_6O_{11}	925	4.5/9600	20.7	59.3	0.55
Sm_2O_3	925	3.1/9600	13.3	31.4	0.13
Empty tube	925	[a]	4.2	50.1	—

[a] Identical flow rates to those above.

oxides. In the case of lanthanum oxide, ESR studies suggested that the superoxide anion, O_2^-, was the active species (*12*). Interestingly, Campbell *et al.* (*13*) and Otsuka *et al.* (*9*) found that the catalysts, CeO_2, Pr_6O_{11}, and Tb_4O_7, were least reactive of the unpromoted lanthanide oxides toward methane. These latter two authors disagree on the order of catalytic activity. The former rates (*13*) $Nd_2O_3 > La_2O_3 > Sm_2O_3 > Dy_2O_3$, while the latter rates (*9*) $Sm_2O_3 > Ho_2O_3, Gd_2O_3 > Dy_2O_3, Nd_2O_3, La_2O_3$. Discrepancies may be attributed to metal oxide impurities and differences in catalyst pretreatment. Otsuka proposed that for samarium oxide the active oxygen species responsible for methane activation was a diatomic species such as O_2, O_2^-, or O_2^{2-} on the surface (*14*). Otsuka also proposed that the peroxide anion, O_2^{2-}, was the oxygen species responsible for methane activation in the catalytic oxidation of methane over sodium peroxide, Na_2O_2 (*15*). The stable metal oxide forms for the alkali promoters reported within are Li_2O (O^{2-}, oxide anion), Na_2O_2 (O_2^{2-}, peroxide anion), and KO_2 (O_2^-, superoxide anion).

The C_2^+ product distributions for the alkali-promoted lanthanide oxides listed in Tables 2 and 3 are very similar to one another. This similarity supports a mechanism whereby a methyl radical is generated at the metal oxide surface and hydrocarbon building steps occur in the gas phase. Also, the C_2^+ product slates obtained from both redox and catalytic runs over 4% Na on Pr_6O_{11} are similar to one another, as shown in Table 7. This similarity suggests that both processes have identical mechanisms for hydrocarbon building, namely the gas-phase coupling of methyl radicals. The $C_2^=/C_2$ ratio is higher for the catalytic vs redox process, largely due to the higher run temperature promoting thermal dehydrogenation and the additional route leading to olefin:

$$R^\cdot + O_2 \rightarrow \text{Olefin} + HO_2^\cdot$$

The product distribution vs residence time results summarized in Fig. 5 indicate that methyl radicals are the first species formed upon methane activation and that ethane is the initial hydrocarbon product formed.

The parallel conversion–selectivity curves of Fig. 6 show a constant 15% C_2^+ selectivity deficit for the catalytic vs redox process. This observation suggests that an additional primary reaction of the methyl radical with molecular oxygen to yield CO_x may be operative in the catalytic mode. The fact that the CO_x selectivity decreases with increasing temperature suggests that the primary reaction may be reversible. Lunsford *et al.* (*3*) used Eq. (1) to account for the lower CO_x selectivity at higher temperature. That is, the equilibrium concentration of the methylperoxy radical decreases with higher temperature,

$$CH_3^\cdot + O_2 \rightleftharpoons CH_3O_2^\cdot \rightarrow\rightarrow CO_x \qquad (1)$$

In the catalytic reaction carbon oxide formation occurs predominantly at the surface via allylic oxidation of olefins or coking of olefins and aromatics. The contribution to carbon oxide formation by reaction of methyl radical with molecular oxygen is minor. The general mechanism for the catalytic conversion methane is the following:

C–H Bond Activation

$$R\text{–H} + MO_x \rightarrow R^\cdot + MO_xH$$

Hydrocarbon Building

$$2R^\cdot \rightarrow R\text{–}R$$

$$R^\cdot + \text{Olefin} \rightarrow R\text{–Olefin} + H^\cdot$$

$$_n\text{Olefin} \overset{\Delta}{\rightleftharpoons} (\text{Olefin})_n$$

Dehydrogenation

$$R\text{–H} + MO_x \rightarrow \text{Olefin} + MO_{x-1} + H_2O$$

$$R\text{–H} \overset{\Delta}{\rightleftharpoons} \text{Olefins} + H_2$$

$$R^\cdot + O_2 \rightarrow \text{Olefin} + HO_2^\cdot$$

Oxide Formation

$$\text{Olefins} \xrightarrow{MO_x}\rightarrow CO, CO_2$$

$$CH_3^\cdot \xrightarrow{MO_x}\rightarrow CO + \tfrac{3}{2} H_2$$

$$CH_3^\cdot + O_2 \rightleftharpoons CH_3O_2^\cdot \rightarrow\rightarrow CO, CO_2$$

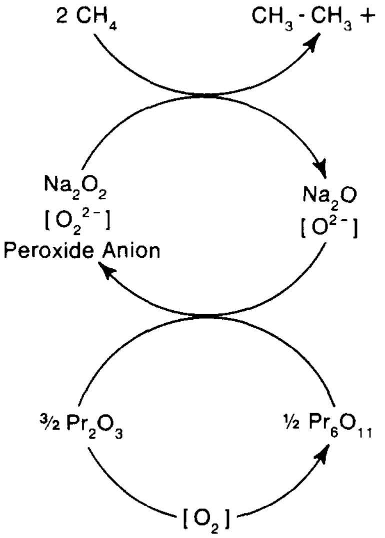

FIG. 8. Reaction scheme.

For the redox reaction a similar mechanism is proposed minus the reactions involving molecular oxygen.

In the overall reaction scheme shown in Fig. 8, methane is activated by a peroxide anion, O_2^{2-}, to yield the primary product ethane and the oxide anion, O^{2-}. Sodium oxide is regenerated back to sodium peroxide by praseodymium oxide. Molecular oxygen, supplied in a catalytic or redox mode, regenerates the co-catalyst Pr_2O_3 back to Pr_6O_{11}. The proposal that the peroxide anion serves to activate methane is precedented in Otsuka's catalytic methane coupling studies over sodium peroxide (*15*). Interestingly, all reported reagents and catalysts selective toward C_2^+ products in methane conversion contain an alkali component. Examples of selective catalysts are sodium permanganate on magnesia (*8*), lithium on magnesia (*16*), sodium on praseodymium oxide, and lithium on samarium oxide (*5*). It may be that for all these systems, the oxide, peroxide, or superoxide anion (depending on whether lithium, sodium, or potassium, respectively, is employed) serves to selectively activate methane. As shown in Table 1, in the absence of alkali little or no C_2^+ products form over the lanthanide oxide. The catalyst of 4% Na on Pr_6O_{11} has a C_2^+ activity rate superior to that of other lanthanide oxides. This may reflect the ability of praseodymium oxide to undergo a rapid $Ln^{3+} \rightleftharpoons Ln^{4+}$ oxidation state change and thus enhance the regeneration rate of sodium oxide. The lithium-promoted samarium oxide catalyst cannot benefit from this redox capability.

CONCLUSION

Unpromoted and alkali-promoted lanthanide oxides were evaluated in the oxidative coupling of methane to higher hydrocarbons. Methane conversion was carried out catalytically and in a redox mode by cycling methane and air independently over the lanthanide oxides. The sodium-promoted nonstoichiometric oxide, 4% Na on Pr_6O_{11}, was most active and selective toward C_2^+ products. A 2-min cumulative redox run at 800°C and 1.4 WHSV gave 21% methane conversion and 76% C_2^+ selectivity (0.23 g product/g cat. hr). In the catalytic reaction, activity comparable to that of redox was obtained at a run temperature 100°C higher. For example, at 900°C and 1.4 WHSV and a cofeed of 50% air in methane, 22% methane conversion and 64% C_2^+ selectivity were realized (0.20 g product/g cat. hr). At comparable conversion the catalytic results had a 12% C_2^+ selectivity deficit with respect to redox. This is attributed to an additional destructive route of the methyl radical, namely the reaction with molecular oxygen to yield a methylperoxy intermediate. Compared to other catalytic data obtained from the partial oxidation of methane over lanthanide oxides, as reported in the literature, the catalyst of 4% Na on Pr_6O_{11} is at least twice as active at similar run temperatures and has C_2^+ selectivity better than or competitive with that of the literature. The higher activity of 4% Na on Pr_6O_{11} may be attributed to the ability of praseodymium oxide to undergo a rapid $Ln^{3+} \rightleftharpoons Ln^{4+}$ oxidation state change and thus enhance the regeneration of the proposed active species, the peroxide anion

(O_2^{2-}). The reported samarium and lanthanum oxide-based catalysts do not benefit from this redox chemistry. Process variable studies support a mechanism whereby methane is activated at the metal oxide surface to form a methyl radical and in the gas phase C_2^+ hydrocarbon building occurs.

ACKNOWLEDGMENTS

The authors thank Beth A. Burnside for technical assistance and Barbara A. King for catalyst characterization.

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