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The Role of Sodium Carbonate and Oxides Supported on Lanthanide Oxides in the Oxidative Dimerization of Methane

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The addition of Na_2CO_3 to three representative lanthanide oxides, La_2O_3, CeO_2, and Yb_2O_3, has a marked effect on the catalytic properties of these materials for the oxidative dimerization of methane. The effect is most dramatic for CeO_2, which, upon addition of Na_2CO_3, is transformed from a total oxidation catalyst to one which is reasonably selective for the conversion of CH_4 to C_2H_4 and C_2H_6. Results obtained by X-ray photoelectron spectroscopy and ion scattering spectroscopy show that a sodium carbonate/sodium oxide phase largely covers the lanthanide oxide surface, thus the catalytic properties are those of the sodium phase, rather than those of the lanthanide oxide. Indeed, the specific activities of the Na^+/Ln_xO_y catalysts and of pure Na_2CO_3 were the same within a factor of 2.5, with Na^+/Yb_2O_3 at the high end of the range. The specific activities of pure lanthanide oxides were considerably greater than those of the modified catalysts. Although Na_2CO_3 is the principal compound present on the surface of the Na^+/Ln_xO_y catalysts, it is probable that Na_2O_2 is responsible for the activation of CH_4.

INTRODUCTION

The lanthanide oxides differ greatly with respect to their ability to catalyze the oxidative dimerization of methane (*1, 2*); however, when these oxides are modified with alkali metal ions, their differences are often less apparent. The properties of these oxides in the partial oxidation of methane have been reviewed recently by Hutchings *et al.* (*3*). Since the goal of most of the previous research has been to optimize the selectivity or the yield of ethane and ethylene (C_2 products), the reaction have often been carried out under conditions of high oxygen conversion, making it difficult to extract intrinsic activities from the data.

We have shown that the large differences in C_2 selectives observed among various members of the lanthanide oxide series result mainly from secondary reaction between $CH_3\cdot$ radicals and the metal oxide (*4*). Those oxides which have accessible multiple cationic oxidation states (CeO_2, Pr_6O_{11}, and Tb_4O_7) react with $CH_3\cdot$ radicals, presumably by the reaction

$$M^{(n+1)+}O^{2-} + CH_3\cdot \rightarrow M^{n+}(OCH_3)^- \quad (1)$$

and the resulting surface methoxide ions provide a route to the formation of CO_2. In the absence of such secondary reactions, the $CH_3\cdot$ radicals couple to form the desired C_2 products.

When CeO_2 is modified by the addition of Na_2CO_3, it ceases to be a good radical scavenger, and becomes an effective catalyst for the production of gas phase $CH_3\cdot$ radicals (*4*). These changes are paralleled by its transformation from a total CH_4 oxidation catalyst to one that is effective in the oxidative coupling reaction. Similar changes in selectivity have been reported by Gaffney *et al.* (*5*) for the catalytic properties of Pr_6O_{11} before and after its modification with sodium salts.

Quite different behaviors are exhibited by the other members of the lanthanide oxide

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series, of which La_2O_3 and Yb_2O_3 are examples of the extremes. Lanthanum oxide is very effective in the formation of gas phase $CH_3 \cdot$ radicals, and, consistent with this fact, it is a poor radical scavenger (*4*). Ytterbium oxide is neither a good radical producer nor a good radical scavenger.

In our previous study, it was noted that a sodium carbonate/sodium oxide phase largely covered the CeO_2 surface and that the specific activity of nominally pure Na_2CO_3 for the generation of $CH_3 \cdot$ radicals approached that of the Na^+/CeO_2 catalyst (*4*). These preliminary observations suggested that the lanthanide oxide may serve primarily as a support for an active form of sodium oxide. In order to determine the validity of this hypothesis, three diverse members of the lanthanide oxide series (La_2O_3, CeO_2, and Yb_2O_3), both with and without added sodium, were evaluated with respect to their catalytic performances and their abilities to generate gas-phase $CH_3 \cdot$ radicals. With the sodium-modified catalysts, care was taken to operate under conditions of moderate CH_4 and O_2 conversions, so that the specific activities of the catalysts could be compared.

EXPERIMENTAL

Catalyst preparation. The starting materials were Na_2CO_3 (99.999%), La_2O_3 (99.99%), CeO_2 (99.9%), and Yb_2O_3 (99.9%), and were obtained from Aldrich Chemical Co. The sodium-doped lanthanide oxide catalysts, Na^+/Ln_xO_y, were made by dissolving sodium carbonate in deionized water, adding the appropriate amount of Ln_xO_y to the solution, and then evaporating the water with vigorous stirring until a thick paste was formed. The paste was dried at 120°C overnight and then calcined at 700°C in air for 10 h. This calcination step is necessary to achieve stable activities of the catalysts. Before contacting with reactant, the catalysts were pretreated in flowing O_2 at temperatures close to or greater than the operational temperatures, e.g., 780°C for Na^+/CeO_2. The sodium content is expressed as the weight percentage of sodium in the lanthanide oxide, and was determined using inductively coupled plasma (ICP) emission spectroscopy. Pure La_2O_3, CeO_2, and Yb_2O_3 were treated in the same manner, but without the addition of sodium.

Catalytic experiments. The catalytic data were obtained using conventional flow reactors constructed of alumina (Omegatite 450, 99.8% Al_2O_3). One reactor was 3.2-mm i.d. in the region where the catalyst was located, and immediately below the catalyst bed a four-holed alumina insert (3.2-mm o.d., 0.5-mm-diameter holes) was used to reduce the time that the product stream remained in the heated region of the system. A 0.050 g catalyst bed was supported between thin layers of quartz wool. Above the catalyst was a layer of quartz chips that served to preheat the gases and to minimize the purely homogeneous reactions. Blank runs, in which the catalyst was replaced by quartz chips, showed negligible conversion in the oxidation of methan. A bare thermocouple coated with a thin layer of an inert cement was placed inside the catalyst bed via two of the holes in the exit tube.

A second reactor was 10-mm i.d., and a two-holed alumina insert (6.4-mm o.d., 1.5-mm-diameter holes) was placed below the catalyst bed, as shown in Fig. 1. Except for larger dimensions and a larger catalyst bed (0.50 g), this reactor was essentially the same as the one described above. A coated thermocouple located in the center of the catalyst bed was used to measure the temperature (T_{in}) during reaction, and a bare thermocouple on the outside of the reactor was used to control the temperature (T_{out}).

The system was allowed to reach steady state, which was usually ca. 10 h after initial exposure to the reactants, before the data reported here were obtained. Product gas analyses were performed using a conventional gas chromatographic (GC) technique. A thermal conductivity detector was used to analyze for CH_4, O_2, C_2H_4, C_2H_6, CO, and CO_2, while propane and butane

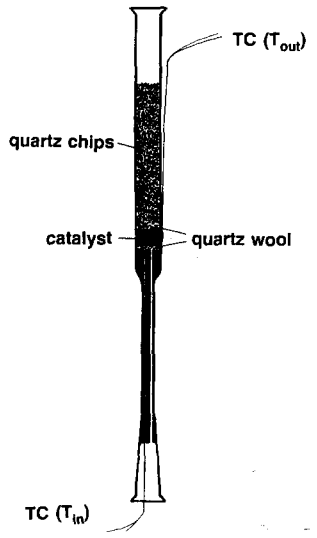

FIG. 1. Alumina reactor used to obtain the data at high levels of oxygen conversion.

were analyzed using a flame ionization detector. The gases used to make up the feed gas were CH_4 (Matheson, 99.97%), O_2 (Matheson, 99.6%), and He (Airco, 99.99%).

ESR experiments. The matrix isolation electron spin resonance (MIESR) system used in this study has been described in detail previously (*6*). A flow reactor containing a layer of the catalyst of interest was coupled to the MIESR system. The gases exiting from the catalyst were allowed to leak into a low pressure collection region where part of the methyl radicals were frozen onto a cold (14 K) sapphire rod. The rod was then lowered into the ESR cavity, and the spectrum was recorded. This system was used to determine the activities of the Na^+/Ln_xO_y catalysts, as well as those of the pure compounds, for the formation of gas phase $CH_3 \cdot$ radicals. The catalysts studied in the MIESR system were steady-state catalysts from the conventional reactors. A typical procedure for the MIESR experiment involved retreating the sample at elevated temperatures in O_2 for 1 h, evacuating the gas phase for 10 min, and then admitting the reactants. The time interval between the introduction of reactants and the beginning of a collection of $CH_3 \cdot$ radicals was 1 h. The relative concentration of the gas phase $CH_3 \cdot$ radicals was determined from the signal intensity of the ESR spectrum of the $CH_3 \cdot$ radicals.

Characterization techniques. Powder X-ray diffraction (XRD) patterns were obtained with a computer-controlled Seifert-Scintag Pad II automated powder diffractometer, using Cu$K\alpha$ radiation. The crystalline phases present in the catalysts were determined after various treatments.

The near-surface compositions of the Na^+/Ln_2O_3 catalysts were determined by X-ray photoelectron spectroscopy (XPS) on a Hewlett–Packard Model HP5950A instrument, using monochromatic Al$K\alpha$ excitation. Used catalyst samples were further heated *in vacuo* at 250–300°C for about 10 h to remove adsorbed water and weakly bound carbon dioxide. The samples were then pressed into wafers and loaded into the spectrometer without exposure to the atmosphere. The regions scanned covered the 1*s* binding energies of oxygen, carbon, and sodium, as well as the 3*d* binding energies of La and Ce and the 4*d* binding energy of Yb. Adventitious carbon with an assigned binding energy of 285 eV was used as an internal standard to determine the binding energies of the other species. Ion scattering spectroscopy (ISS), which is highly surface sensitive technique, was used to determine the composition of the top layer of a used Na^+/CeO_2 catalyst. ISS data were obtained on a Leybold MAX-200 spectrometer at a fixed retardation ratio of 4, using 2.3 keV $^4He^+$ ions.

The surface areas of the catalysts were determined using a dynamic BET system from Quantachrome Corp., with nitrogen as the adsorbate. For those materials of low surface area (< 0.5 m^2/g), such as Na_2CO_3, a 2 to 3-g sample was used in the measurement to reduce the error caused by the low surface area. In addition, the surface area of the sample tube used in the measurements was determined and subtracted from the val-

ues obtained for those materials. Although the systematic error may be somewhat larger, the relative errors (repeatability) for surface areas measured in the same system were approximately ± 0.02 m^2/g for samples having an area < 0.5 m^2/g and ± 0.04 m^2/g for samples having an area > 0.5 m^2/g.

RESULTS AND DISCUSSION

Characterization. Both the fresh and used Na^+/Ln_xO_y catalysts exhibited the same XRD patterns, and the only crystalline phases detected in the catalysts were the corresponding lanthanide oxides; no new crystalline species, such as Na_2CeO_3 or $NaYbO_2$, were found. It is a little surprising that crystalline phases due to sodium carbonate or the oxides of sodium were not observed by XRD, when one considers the amount of Na_2CO_3 added to the catalysts. Failure to observe a phase that corresponds to a sodium compound suggest that the sodium carbonate existed as very small crystallites or as a thin layer on the surfaces of the lanthanide oxides. These results may be contrasted with those obtained on a used Na^+/CaO catalyst, for which a distinct Na_2CO_3 phase was observed (*7*).

As an example of the XPS results, the spectra of 4% Na^+/CeO_2 which had been used in a catalytic test are shown in Fig. 2. In this O 1*s* region, three peaks may be resolved, at binding energies of 529, 532, and 534 eV. Comparison of these results with the XPS spectra of CeO_2, Na_2CO_3, $NaHCO_3$, and Na_2O_2 indicate that the peaks at 529 and 532 eV may be assigned to O^{2-} and to oxygen in CO_3^{2-}, respectively. The broad peak at 532 eV may include contributions from OH^- and even O_2^{2-} oxygen. The broader shoulder at 534 eV is tentatively assigned to oxygen present in HCO_3^- ions. The presence of CO_3^{2-} is supported by a C 1*s* peak at 289 eV. The HCO_3^- species, if present, should have resulted in a C 1*s* line at 289 eV, but this peak may have been below the limits of detection (*8*).

From the areas under the Na 1*s* and the Ln 3*d* and 4*d* peaks, with appropriate corrections for cross sections, the atomic ratios of the metal ions in the near-surface region were determined for the used catalysts, and these are compared with the bulk atomic ratios from ICP analyses in Table 1. Clearly, the Na : Ln ratios are greater at the surface than in the bulk for all three catalysts, with the ratio being greatest for the 4% Na^+/CeO_2 catalyst. The ISS results shown in Fig. 3 confirm that a phase containing sodium ions completely covered the used 4% Na^+/CeO_2 catalyst. Initially, almost no Ce ions were detected on the surface; only Na^+ ions were observed. After several minutes of ion etching, however, the underlying Ce ions began to appear. These ISS results are con-

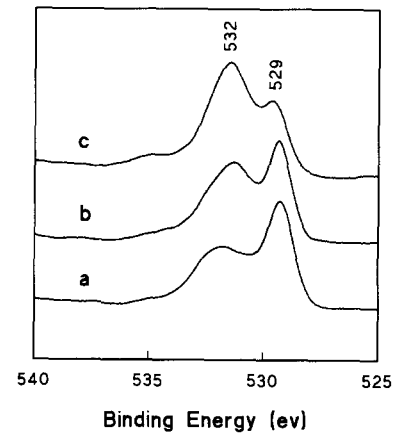

FIG. 2. XPS spectra in the O(1s) region of 4% Na^+/CeO_2 catalyst after (a) calcination in air at 700°C for 16 h, (b) further calcination in O_2 at 780°C for 2 h, and (c) use as a catalyst at 780°C for 17 h.

TABLE 1

Na : Ln Atomic Ratios Determined by XPS and ICP[a]

Catalyst	Na : Ln at surface (XPS)	Na : Ln in bulk (ICP)
4% Na^+/La_2O_3	1.0	0.29
4% Na^+/Yb_2O_3	0.9	0.26
4% Na^+/CeO_2	3.7	0.24

[a] Used catalysts: Na/La_2O_3, 730°C for 10 h; Na/Yb_2O_3, 760°C for 11 h; Na/CeO_2, 780°C for 17 h.

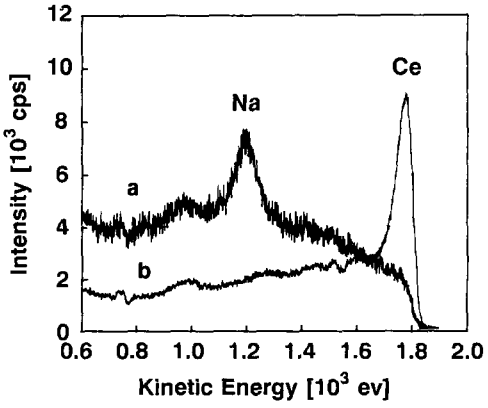

FIG. 3. ISS spectra of (a) pure CeO_2 and (b) a used 4% Na^+/CeO_2 catalyst.

sistent with the previous catalytic experiments which demonstrated that the addition of Na_2CO_3 transformed CeO_2 from a totally nonselective CH_4 oxidation catalyst to one which gave ca. 60% selectivity to higher hydrocarbons (*4*). Moreover, it was observed that CeO_2 was transformed from a good $CH_3 \cdot$ radical scavenger to a good generator of gas phase $CH_3 \cdot$ radicals.

A calculation of a hypothetical *uniform* layer of Na_2CO_3 on a 4% Na^+/CeO_2 catalyst shows that the thickness would be about 400 Å, which corresponds to about 90 layers of the carbonate. Obviously, if such a uniform layer existed, then no Ce would have been evident in the XPS spectrum. We conclude, therefore, that the used Na^+/CeO_2 catalyst was completely, but nonuniformly, covered with sodium compounds that include sodium carbonate and sodium oxides, particularly under reaction conditions.

It was found that the atomic ratios, determined from the XPS spectra, strongly depended on the nature of the support and on the previous history of the catalyst. The changes in surface stoichiometry of 4% Na^+/CeO_2 catalyst and a 4% Na^+/Yb_2O_3 catalyst were determined as a function of the catalyst treatment. After calcination in air at 700°C for 16 h, both catalysts exhibited a Na : Ln ratio of about 1.2. After being used in the catalytic reaction for 17–20 h at 780°C, the Na : Ln ratio increased to 3.7 for Na^+/CeO_2, but decreased to 0.5 for Na^+/Yb_2O_3 It is not clear whether the decrease observed with the latter catalyst resulted from loss of Na_2CO_3 from the surface or whether agglomeration, rather than spreading of the Na_2CO_3/Na_2O_2, occurred. In either case, it is evident that CeO_2 has a stronger affinity than Yb_2O_3 for surface sodium compounds.

The effect of sample treatment on the spreading of Na_2CO_3, and perhaps of Na_2O_2, over CeO_2 is also evident in the O 1*s* spectra of Fig. 2. Exposure of the catalyst to O_2 and then to reactants at 780°C caused an increase in intensity of the peak at 531–532 eV, relative to the peak at 529 eV. Moreover, there was a distinct shift of the broad maximum at about 532 eV to a sharper maximum at 531 eV. This shift is consistent with the partial transformation of Na_2CO_3 (532 eV) to Na_2O_2 (531 eV) (*9*). These results support the postulate that CeO_2, which has an O^{2-} peak at 529 eV, is covered by sodium compounds which are characterized by O 1*s* peaks at 531–532 eV.

Catalytic results. Prior to carrying out specific activity measurements the three lanthanide oxide catalysts, with and without added sodium carbonate, were studied under nearly oxygen-limiting conditions, and the results are summarized in Table 2. The sodium-modified catalysts are characterized by C_2^+ selectivities of 52–57% and by productivities which compare favorably with most of the more active catalysts that have been reported (*3*). The productivities given here and elsewhere may be misleading, however, since the systems are nearly oxygen limited. Pure La_2O_3 was somewhat less selective than 4% Na^+/La_2O_3, while pure CeO_2, as noted previously, produced mainly CO_2 and H_2O. The conversions and selectivities for Na^+/La_2O_3 are comparable to those reported previously by DeBoy and Hicks (*10*) at somewhat greater temperatures and space velocities. We are not aware of any comparable study of Na^+/Yb_2O_3.

In contrast to this work, 4% Na^+/CeO_2

TABLE 2

Performances of Na_2CO_3, Ln_xO_y, and Na^+/Ln_xO_y Catalysts

Catalyst[a]	O_2 Conv. %	CH_4 Conv. %	C_2^+ Sel. %	Partial pressure, Torr					C_2^+ Prod.[b]
				C_2H_4	C_2H_6	C_4H_{10}	CO	CO_2	
Na_2CO_3	10	5.3	47.8	0.9	3.2	0.1	2.8	6.6	0.08
La_2O_3	>99	25.1	46.2	10.4	9.9	0.8	7.8	43.2	0.38
CeO_2	100	13.7	1.2	0.0	0.3	0.0	0.0	51.0	0.01
Yb_2O_3	83	20.1	40.3	6.5	7.3	0.5	9.0	34.8	0.27
4% Na^+/La_2O_3	73	21.8	56.8	9.6	12.2	1.0	2.2	34.0	0.41
4% Na^+/CeO_2	81	21.7	52.7	8.2	12.1	0.8	0.0	39.3	0.38
4% Na^+/Yb_2O_3	81	21.9	52.3	8.3	12.1	0.8	2.3	38.2	0.38

[a] 0.50 g of 20–40 mesh catalyst chips was loaded into an 11 mm i.d. Al_2O_3 reactor. Total flow rate = 84 ml/min; $CH_4:O_2$ = 5.5:1; $P(CH_4)$ = 0.5 atm; T_{in} = 775°C; P_{total} = 1 atm.

[b] C_2^+ productivity: g(CH_4 to C_2^+)/g(catalyst)/h.

has been reported to be quite a poor catalyst in the redox mode (*5*). We tested our Na^+/CeO_2 catalyst in the redox mode and found it to be nearly as productive as in the co-feed mode. This discrepancy in results probably arises from variations in the method of preparation, including the calcination temperature. CeO_2 has been used in automotive emission control catalysts because of its ability to store and release oxygen in a redox process (*11, 12*), and it has been reported that the oxygen storage capacities of CeO_2 and of noble metal/CeO_2 catalysts change with pretreatment temperature. For example, a general decrease in the oxygen storage capacity of the catalysts was observed when the calcination temperature was increased from 600 to 800°C (*11*). The poor redox mode performance of the 4% Na^+/CeO_2 catalyst reported previously (*5*) may have resulted from its calcination at 900°C for 16 h before testing.

The sodium-promoted catalysts and pure Na_2CO_3 were also studied under nearly differential conditions so that their specific activities could be more meaningfully compared, and the results are reported in Table 3. Results for the pure lanthanide oxides are also reported in Table 3, but over these catalysts the reactions were oxygen limited. Obviously, the conditions chosen for the data of Table 3 were not those that would give maximum C_2^+ selectivities or yields. Here, it should be noted that C_2H_4 and C_2H_6 were the major C_2^+ products, and the amount of higher hydrocarbons was less than 5% of the total. From the results in Table 3, it is apparent that the addition of sodium carbonate to a lanthanide oxide decreased both the percent conversion and the specific activity per unit surface area.

In Table 3, the specific activities are compared for four Na^+/Ln_xO_y catalysts and for nominally pure Na_2CO_3 under the same conditions. Although the total activities of these catalysts (based on CH_4 conversion) varied by a factor of more than 40, the specific activities varied by a factor of only 2.5. If one considers the catalysts 4% Na^+/CeO_2, 10% Na^+/CeO_2, and Na_2CO_3, the specific activities were virtually identical. These results are consistent with the observation that sodium compounds essentially cover the CeO_2 surface, and therefore the observed reaction rate might be expected to reflect the activity of this sodium carbonate/sodium oxide phase. The specific activity of the Na^+/La_2O_3 catalyst was slightly greater than those of the latter three catalysts, but was substantially less than that of the pure La_2O_3. We conclude, therefore, that the activity of this catalyst was also largely a result

TABLE 3
Catalytic Properties of Ln_xO_y, Na_2CO_3, and Na/Ln_xO_y for Methane Coupling

Catalyst	CH_4 Conv.[a] (%)	C_2^+ Prod.[b]	Surface Area (m_2/g)	Specific Activity (per unit area)	$[CH_3 \cdot]$[c]
La_2O_3	21.9[d]	3.08	2.2	(10.0)[d]	4.4
CeO_2	11.0[d]	0.0	2.5	(4.6)[d]	0.0
Yb_2O_3	17.3	1.97	1.8	9.6	1.1
Na_2CO_3	0.2	0.02	0.08	3.0	3.7
4% Na/La_2O_3	6.1	0.75	1.5	4.1	3.3
4% Na/CeO_2	2.5	0.23	0.84	3.0	3.6
4% Na/Yb_2O_3	8.7	0.95	1.3	6.5	4.6
10% Na/CeO_2	3.5	0.28	1.2	2.9	2.3

[a] 0.050 g catalyst chips in a 3-mm i.d. Al_2O_3 reactor; WHSV = 25.7 h^{-1}; $P(CH_4)$ = 0.5 atm; $CH_4 : O_2$ = 5 : 1; Temperature = 730°C; Pressure = 1 atm.

[b] C_2^+ productivity, g(CH_4 to C_2^+)/g(catalyst)/h.

[c] Relative rate of $CH_3 \cdot$ radical formation, $m^{-2} \cdot s^{-1}$: 0.30 g catalyst; P = 1.5 Torr; T = 730°C; Flow rates, (ml/min) : He 3.9; CH_4 1.2; O_2 0.028.

[d] Under O_2-limited conditions.

of the sodium carbonate/sodium oxide phase. The specific activity of the Na^+/Yb_2O_3 catalyst was somewhat greater than expected on the basis of the Na_2CO_3 activity, which might indicate an incomplete coverage of Yb_2O_3 by the sodium compounds.

The abilities of the catalysts to generate gas phase $CH_3 \cdot$ radicals also parallel the specific activities of the Na_2CO_3 and the Na^+/Ln_xO_y catalysts; thus, we conclude that a mechanism involving the role of surface-generated gas-phase radicals is common to all of these catalysts. The agreement between the CH_4 conversion and the $CH_3 \cdot$ radical production over the pure lanthanide oxides is not as good, however, and may reflect the oxygen-limiting conditions. As observed previously, CeO_2 did not produce any gas phase $CH_3 \cdot$ radicals, which is consistent with the absence of C_2^+ products.

Although the Na^+/Ln_xO_y catalysts were largely covered by a sodium carbonate/sodium oxide phase, we believe that the sodium oxide component, probably Na_2O_2, is responsible for the activation of CH_4. A representation of such a catalyst is given in Fig. 4. Here, Na_2O is in equilibrium with Na_2O_2 through the reaction

$$Na_2O + \tfrac{1}{2}O_2 \rightleftharpoons Na_2O_2 \qquad (2)$$

Otsuka and co-workers (*13*) have provided convincing evidence that Na_2O_2 is capable of stoichiometrically converting CH_4 to C_2 products at temperatures as low as 400°C. By contrast, the formation of Na_2CO_3 via the equilibrium reaction

$$Na_2O + CO_2 \rightleftharpoons Na_2CO_3 \qquad (3)$$

has an adverse effect both on the generation of $CH_3 \cdot$ radicals and on the conversion of CH_4 (*14*, *15*). In view of the similarity in specific activities of Na_2CO_3, Na^+/CeO_2, and Na^+/La_2O_3, one may conclude that the

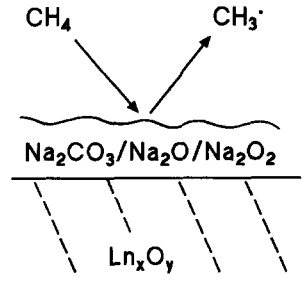

FIG. 4. Scheme of Ln_xO_y catalyst covered with sodium compounds.

lanthanide oxide does not significantly influence this equilbrium.

In many respects, the concepts introduced here extend and confirm the model developed by Gaffney *et al.* (*5*) to explain the catalytic properties of Na^+/Pr_6O_{11}. According to that model, CH_4 is activated by Na_2O_2, and the regeneration of Na_2O_2 is facilitated by a rapid $Pr^{3+} \rightleftharpoons Pr^4$ redox couple. In view of this study and our previous paper (*4*), it also seems that the presence of a sodium carbonate/sodium oxide phase on the surface prevents $CH_3 \cdot$ radicals from reacting with Pr_6O_{11}, which would result ultimately in the formation of CO_2.

Finally, it should be pointed out that the present model does not preclude the activation of CH_4 by centers of the type $[Na^+O^-]$ that are formed, for example, when Na^+ substitutes for Ca^{2+} ions in CaO (*7*). Important distinctions between the predominance of $[Na^+O^-]$ or Na_2O_2 as centers for the activation of CH_4 can be made on the basis of (i) a suitable match between the guest and host ionic radii and (ii) the temperature at which good C_2 selectivity is attained. The formation of centers of the type $[M^+O^-]$ requires that the ionic radius of the alkali metal ion be less than or equal to the size of the metal ion in the host oxide. Furthermore, the presence of Na_2O_2 under steady-state reaction conditions requires that the equilibrium of reaction (*3*) be shifted to the left. Thus, Na_2O, and presumably Na_2O_2, is favored by higher temperatures. The importance of these factors is illustrated by the two catalysts Li^+/MgO and Na^+/MgO. The former is characterized by $[Li^+O^-]$ centers and high C_2 yields at temperatures $\leq 720°C$ (*16*). Moreover, the conversion of Li_2O to Li_2CO_3 has almost no effect on C_2 productivity (*17*). By contrast, Na^+/MgO has no $[Na^+O^-]$ centers because of the mismatch in ionic size, and the catalyst changes from a poor one for oxidative coupling at $\leq 700°C$ to a relatively good one at 750°C (*18, 19*).

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