and subsequent α-hydrogen bond scission as suggested by Muetterties and co-workers.[26,50] A small fraction of the 2,6-lutidine appears to react by the same pathway. The evolution of methane at 280 K may correspond to a nucleophilic attack at the α-carbon and C–C bond scission. This leads to the formation of a methyl-substituted α-pyridyl species. The methyl group stabilizes this species relative to the α-pyridyl species so the reaction temperature increased to 535 K relative to 490 K for the hydrogen-substituted derivative. The methyl-α-pyridyl led to the formation of picoline, in analogy with the observation that the α-pyridyl led to pyridine formation. Reflection infrared spectroscopy did not detect the ring vibrations for the methyl-α-pyridyl species, but as most of the 2,6-lutidine desorbed intact the surface coverage may have been below the detection limit.

The evolution of light gases at 635 K from 2,6-lutidine was similar to the results observed for pyridine, but the temperature was shifted higher by 35 K for the lutidine species. The methyl group stabilized the intermediate, leading to these reaction products. It is suspected that the intermediate accounting for these products is a oligimer of the α-pyridyl species, though more studies are needed to clarify this.

The interactions of pyrimidine with Ni(100) were similar to the results obtained with pyridine. Molecular desorption of pyrimidine was observed at 255 K, a slightly lower temperature than observed for pyridine. Both pyrimidine and pyridine displayed orientation changes near 300 K as detected by RAIS. The α-pyrimidyl species formed from pyrimidine reacted at 475 K, showing the second nitrogen destabilized the species slightly relative to pyridine. The second nitrogen atom also altered the TPR product distribution. Hydrogen cyanide evolved during pyrimidine TPR at 650 K, whereas ethene evolved from pyridine at this temperature.

Conclusions

The reactions of a variety of organonitrogen compounds on a Ni(100) surface have been examined. All the species appeared to interact initially with the surface via an electrophilic interaction between the HOMO of the organonitrogen reagent and the LUMO (empty d orbitals) of the metal. Specifically, this led to

adsorption of reagents as follows:

(1) Monomethylamine adsorbed by bonding between the Ni and the lone electron pair on the nitrogen.

(2) Aniline adsorbed with its ring parallel to the Ni surface, forming a π-bond between the ring and the surface and a bond between the nitrogen lone electron pair and the surface.

(3) Pyridine adsorbed with the ring parallel to the surface, forming a π-bond.

After the initial electrophilic interaction a nucleophilic interaction between the HOMO of the surface and the LUMO of the nitrogen compound proceeded. This resulted in C–N bond scission with monomethylamine, polymerization of aniline, and the formation of α-pyridyl species with pyridine.

The bonding of pyridine to the surface could be influenced by methyl group substituents. Specifically, methyl groups in the 3,5-positions appeared to force pyridine to adsorb via the nitrogen lone pair of electrons. The methyl groups reduced the stability of π-bonded pyridine and increased the electron density in the ring stabilizing the nitrogen-bound pyridine. Methyl groups in the 2,6-positions reduced the stability of π-bonded pyridine but also sterically hindered adsorption at the nitrogen lone pair of electrons.

Aniline and 3,5-lutidine were both activated for electrophilic addition reactions. This increased activity for electrophilic addition led to the surface polymerization of these species. The conformation of the surface polymers appeared to be controlled by the initial electrophilic interaction of the species with the surface; poly(aniline) had its ring parallel to the surface, whereas poly(lutidine) had its ring perpendicular to the surface. These surface polymers were thermally very stable, pyrolyzing above 900 K.

Methane Activation by the Lanthanide Oxides

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The catalytic production of gas-phase methyl radicals from methane over the lanthanide oxides was measured by using a matrix isolation electron spin resonance (MIESR) technique. The results show that metal centers with multiple stable oxidation states are not a requirement for activity. The oxide with the greatest activity per gram was hydrothermally treated La_2O_3, which was ca. 5 times more active than the next highest oxide. Hydrothermally treated La_2O_3 and Sm_2O_3 have the largest activities per square meter. Results obtained in a conventional flow reactor for selected oxides indicate that the CH_4 conversions per square meter are in the order $Nd_2O_3 > La_2O_3 > Sm_2O_3 > Dy_2O_3 > CeO_2$. Oxidative coupling of CH_4 results in C_2H_6 and C_2H_4 (C_2 compounds), and the combined C_2 yields follow the same order with $Dy_2O_3 \gg CeO_2$. The MIESR and flow reactor results are in qualitative agreement, with the exception of Nd_2O_3.

Introduction

Considerable progress has been made in understanding the mode by which methane is activated for the oxidative addition to metal centers and for the generation of methyl radicals.[1-3] The latter

reaction forms the basis for the high-temperature catalytic oxidation of CH_4, both to oxygenates (methanol and formaldehyde)[4] and to higher hydrocarbons (mainly ethane and ethylene).[5-8]

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Keller and Bhasin[5] proposed a mechanism for the oxidative coupling of CH_4 over metal oxides in which methyl radicals formed through a surface reaction coupled on the surface, whereas Lunsford and co-workers[7] proposed a mechanism in which surface-generated methyl radicals were released into the gas phase where they coupled to form ethane. While the formation of surface-generated methyl radicals is an accepted part of both mechanisms, it remains to be demonstrated whether subsequent surface reactions or gas-phase reactions of the methyl radicals constitute the major pathway for the oxidative coupling of methane. It should be noted that the existence of surface-generated gas-phase $CH_3\cdot$ radicals has been clearly shown by Driscoll et al.[3] using a matrix-isolation electron spin resonance (MIESR) technique.

Recently Otsuka et al.[8,9] examined the abilities of the lanthanide oxides to catalyze the oxidative coupling of CH_4 to form C_2H_6 and C_2H_4. They reported that Sm_2O_3, which gave a C_2 selectivity of 93%, was much more active than the other members of the series in the production of C_2 compounds. However, all of the lanthanide oxides except for Ce, Pr, and Tb gave high C_2 selectivities (>75%).

The marked variations which occur throughout the lanthanide oxides provide one an opportunity to explore the relationship between activity, C_2 selectivity, and the formation of gas-phase methyl radicals. In addition, it was of interest to relate this rate data to the physical and chemical properties encountered in the series. Examples of properties which may be of importance are basicity, crystal structure, crystal defects, oxygen mobility, and redox potentials. It was previously demonstrated that the first member of this series, La_2O_3, is quite effective for radical formation,[11] and in this paper we report on the activities of the complete series for gas-phase methyl radical formation. Conventional flow reaction studies also were carried out on selected oxides.

Experimental Section

The MIESR system used in this study has been described in detail previously.[3,10] Briefly, the reactant gases are passed through a heated catalyst bed into a low-pressure ($\sim$1 Torr) quartz flow reactor. The effluent gases then pass through a leak into a low-pressure ($\sim$2 $\times$ 10^{-5} Torr) collection region and are frozen on a sapphire rod maintained at 14 K. After a collection period the rod with the matrix is lowered into an ESR cavity and the spectrum is recorded.

The lanthanide oxides were obtained from Aldrich Chemical Co. (La_2O_3 99.99%; CeO_2 99.9%; Pr_6O_{11} 99.9%; Nd_2O_3 99.9%; Sm_2O_3 99.9%; Eu_2O_3 99.99%; Ho_2O_3 99.9%; Er_2O_3 99.99%; Tm_2O_3 99.99%; Yb_2O_3 99.9%; Lu_2O_3 99.99%) and Alfa Products (Gd_2O_3 99.9%; Tb_4O_7 99.9%; Dy_2O_3 99.9%). The oxides were used as received and after a hydrothermal treatment. In the hydrothermal treatment the original oxides were heated overnight in vacuo at 900 °C and then under flowing H_2O-saturated argon (300 mL min^{-1}) for 4 h at 100 °C followed by 8 h at 25 °C.

The methane (99.97%) and oxygen (99.6%) were obtained from Matheson Gas while the argon (99.99%) and helium (99.99%) were from Airco. The methane was used as received. The argon and oxygen were passed through molecular sieve traps to remove traces of H_2O. For all the MIESR experiments the following flow rates were employed: Ar (3.80 mL min^{-1}), CH_4 (1.08 mL min^{-1}), and O_2 (0.023 mL min^{-1}).

The original oxide samples were pretreated in vacuo for 0.5 h each at 250, 500, and 600 °C, and then overnight at 750 °C. The hydrothermally treated samples were activated in a similar manner except the overnight treatment at 750 °C was omitted. The samples were then conditioned in flowing O_2 (300 mL min^{-1}) at 600 °C for 2.5 h. Reactant gas flow was initiated with the catalyst at 600 °C and three matrices were prepared and analyzed in the
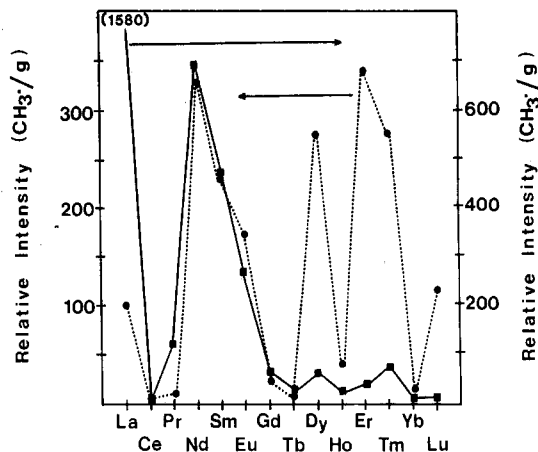

Figure 1. Relative intensities of $CH_3\cdot$ radical production per gram for original ($\cdots$) and hydrothermally (—) treated lanthanide oxides.

MIESR system over an 8-h period. Each collection period was 30 min. The spectra obtained for second and third matrices were compared to assure steady-state conditions. An agreement of at least 15% in $CH_3\cdot$ radical production was the criterion employed. All of the results reported in this paper are based on values obtained from the third matrix. When successive experiments were carried out on the same catalyst (original and hydrothermal), a reproducibility of ca. 25% for $CH_3\cdot$ radical production was obtained.

For comparison with results from the conventional flow reactor the temperature program was modified for the hydrothermally treated samples. After the radicals were collected with the catalyst at 600 °C the temperature was raised to 700 °C and maintained overnight. Radicals were collected with the catalyst at temperatures of 700 °C and then 600 °C.

The flow reactor experiments were carried out in a fixed bed reactor which operated at atmospheric pressure. Hydrothermally treated oxide samples (5 mg) were pretreated in flowing O_2 (50 mL min^{-1}) at 450 °C for 2 h. Then the reactant mixture ($He/CH_4/O_2$ = 19.7/12.3/1; total flow = 50 mL min^{-1}) was introduced and the temperature was raised to 700 °C and maintained overnight. The conversion and selectivities were measured at 700 and 600 °C using standard GC techniques.[4]

The surface areas of the catalysts were measured by a volumetric BET method using Kr as the gaseous adsorbate. For the original oxides and hydrothermally treated oxides the surface areas were determined on fresh samples that were pretreated in vacuo as outlined for the MIESR studies. In addition, some of the catalysts were treated with oxygen; however, this step showed no effect on the surface areas. When comparisons were made between results obtained with the flow reactor and the MIESR system, the surface areas were determined on the used catalysts.

Results and Dicussion

As previously reported by Lin et al.,[11] high surface area La_2O_3 is an excellent catalyst for the formation of gas-phase methyl radicals from methane. This result is confirmed by the data of Figure 1 which gives the relative steady-state production of $CH_3\cdot$ radicals per gram of catalyst for the original lanthanide oxides and the hydrothermally treated oxides. The hydrothermally treated La_2O_3 has a much higher activity per gram than any of the other oxides.

When the activities per gram of the original oxides and the hydrothermally treated oxides are compared from CeO_2 to Tb_4O_7, the trends are the same with a maximum occurring at Nd_2O_3. For the oxides of La to Tb the hydrothermally treated material is either much more active or essentially the same (CeO_2) as the original material, whereas from Dy to the end of the series the trend is reversed.

Although most rate data in heterogeneous catalysis are reported per unit surface area, it is not clear that the surface generation of gas-phase radicals should be viewed on this basis. First, the number of active sites for radical formation is not necessarily linear

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TABLE I: Catalytic Activity and Selectivity for the Oxidative Coupling of CH$_4$ to C$_2$H$_6$ and C$_2$H$_4$ on Lanthanide Oxide Catalysts

catalyst[a]	temp, °C	rate, μmol CH$_4$ min^{-1} m^{-2}	conversion, %		selectivity, %				C$_2$ yield, %
			CH$_4$	O$_2$	CO$_2$	CO	C$_2$H$_4$	C$_2$H$_6$	
La$_2$O$_3$	600	360	0.57	10.3	55.6	16.4	0	28.0	0.16
	700	1600	2.51	25.8	23.0	26.6	6.72	43.8	1.27
CeO$_2$	600	76	0.14	3.44	100	0	0	0	0
	700	500	0.93	22.6	100	0	0	0	0
Nd$_2$O$_3$	600	490	0.89	13.6	55.1	12.6	0	32.3	0.29
	700	2400	4.40	41.9	24.4	13.1	9.84	52.7	2.75
Sm$_2$O$_3$	600	330	0.47	6.20	35.0	37.4	0	27.6	0.13
	700	1200	1.72	12.8	11.8	32.2	5.65	50.3	0.96
Dy$_2$O$_3$	600	150	0.16	9.70	36.5	63.5	0	0	0
	700	790	0.83	11.2	25.5	40.6	0	34.0	0.28

[a] Experimental conditions: catalyst weight = 5 mg; atmospheric pressure; reactant ratio of CH$_4$/O$_2$/He = 12.3/1/19.7; flow rate = 50 mL min^{-1}.
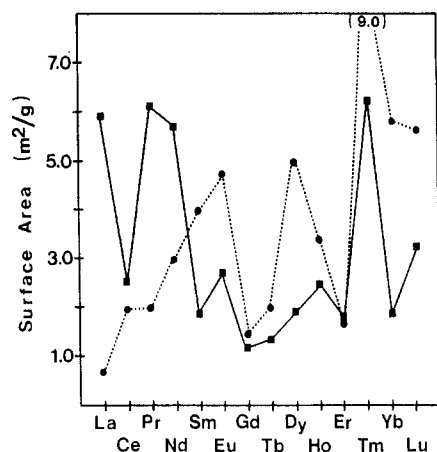

Figure 2. Surface areas of original (···) and hydrothermally (—) treated lanthanide oxides.
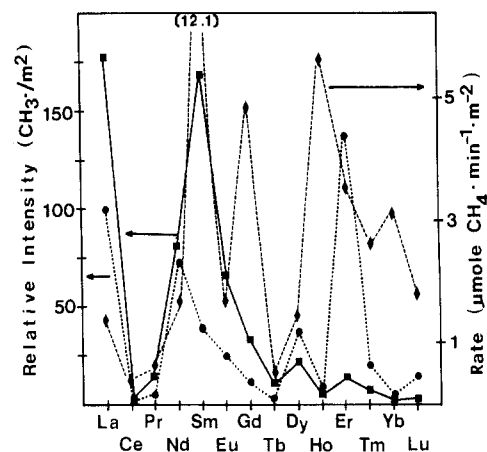

Figure 3. Relative intensities of CH$_3$· radical production per square meter for original (···) and hydrothermally (—) treated lanthanide oxides. Results on the rate of CH$_4$ conversion obtained by Otsuka et al.[8,9] (- - -) are also shown.

with respect to surface area, and, second, the collection efficiency is probably inversely proportional to the surface area. Nevertheless, the surface areas were determined for the oxides in the series, and the data are depicted in Figure 2.

It should be emphasized that the samples as received were activated at 750 °C overnight, but the hydrothermally treated samples were heated first to 900 °C to remove carbonates, then reacted with water, and finally heated to only 600 °C in an attempt to minimize sintering as the hydroxide decomposed. In the early members of the series (La$_2$O$_3$ to Nd$_2$O$_3$) the surface areas indeed were larger for the hydrothermal samples, but such was not the case in the later members. Rosynek and co-workers[12] have shown that La$_2$O$_3$ will undergo complete hydrolysis to La(OH)$_3$ with subsequent decomposition resulting in a high surface area La$_2$O$_3$. Touret et al.,[13] however, have claimed that complete hydrolysis of the last members of the series, Dy$_2$O$_3$ through Lu$_2$O$_3$, is not possible because of the decreasing basicity across the series.

It is also significant that all of the lanthanide trihydroxides crystallize in the hexagonal structure, but the oxides exist in two crystalline forms in the 600–700 °C temperature range. The sesquioxides of La, Pr, and Nd are hexagonal while the oxides of Sm through Lu are cubic. The surface areas, in turn, may be influenced by the presence or absence of a structural change as the trihydroxides decompose.

When compared on the basis of surface area the CH$_3$· radical production, as depicted in Figure 3, shows that La$_2$O$_3$ remains the most active of the as received oxides, and the next maximum remains at Nd$_2$O$_3$. But with the hydrothermally treated oxides the second maximum shifts to Sm$_2$O$_3$, which was the most active and selective catalyst reported by Otsuka et al. (Figure 3). With several of the other oxides the agreement with Otsuka's results was not nearly so good. For example, hydrothermally treated La$_2$O$_3$ was still very active for the formation of CH$_3$·, but according to Otsuka et al. the overall conversion of CH$_4$ on this

material was relatively small. In addition, Gd$_2$O$_3$ was moderately good for methane conversion, but it was not very effective in generating CH$_3$· radicals.

If one excludes the oxides that exhibit multiple oxidation states (CeO$_2$, Pr$_6$O$_{11}$, and Tb$_4$O$_7$), then a qualitative relationship exists between the basicity of the hydrothermally treated oxides and their ability to generate methyl radicals (Figure 3). That is, La$_2$O$_3$ through Eu$_2$O$_3$ were active, whereas, Dy$_2$O$_3$ through Lu$_2$O$_3$ were relatively inactive. The basicity may, in turn, influence the formation of surface oxygen species, such as superoxide or peroxide ions, which are capable of activating methane.

It is clear that sample pretreatment has a significant effect on the production of methyl radicals, regardless of the basis for comparison. Moreover, even the source of the oxide had a marked effect on its ability to generate CH$_3$· radicals. As received Er$_2$O$_3$ from another source (Alfa, 99.9%) had an activity per unit surface area which was approximately 20% of the value indicated in Figure 3. Thus, it is not surprising that differences exist between the overall catalytic conversions reported by Otsuka et al. and our results on the formation of CH$_3$· radicals.

The results of the two studies, however, do agree on one important point, which is the low activities of CeO$_2$, Pr$_6$O$_{11}$, and Tb$_4$O$_7$. Since these lanthanide ions are unique in that they exhibit multiple oxidation states, this factor must not be important in the activation of methane.

In order to examine more closely the relationship between CH$_3$· formation and overall catalytic behavior, without the complications which arise because of sample source or pretreatment conditions, flow reactor studies were carried out on some selected lanthanide oxides. High CH$_4$:O$_2$ ratios, comparable to those employed in the MIESR experiments, were adopted, but conditions where chosen to assure that the O$_2$ conversion was less than 50%. Hydrothermally treated samples were chosen, and as noted previously the oxides used in both systems were heated overnight at 700 °C prior to collecting the data for comparison. Surface areas

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TABLE II: Comparison of MIESR Results with Flow Reactor Results

catalyst	temp, °C	flow reactor results[a]		rel[b] conv, m^{-2}	(rel C$_2$ yield)$^{1/2,b}$ m^{-2}	MIESR results[a]	
		rel conv, g^{-1}	(rel C$_2$ yield)$^{1/2}$, g^{-1}			rel activity, g^{-1}	rel activity,[c] m^{-2}
La$_2$O$_3$	600	23	36	23	36	23	23
	700	100	100	100	100	100	100
CeO$_2$	600	6	0	5	0	0	0
	700	37	0	33	0	<1	<1
Nd$_2$O$_3$	600	35	48	31	42	17	19
	700	175	147	154	129	53	56
Sm$_2$O$_3$	600	19	32	20	34	7	13
	700	69	87	74	94	33	61
Dy$_2$O$_3$	600	6	0	10	0	3	5
	700	33	47	51	73	15	29

[a] Relative conversion, (C$_2$ yield)$^{1/2}$ and CH$_3$• radical formation based on an assigned value of 100 for La$_2$O$_3$ at 700 °C. [b] Surface areas for flow reactor catalysts in m^2 g^{-1}: La$_2$O$_3$ = 2.4, CeO$_2$ = 2.8, Nd$_2$O$_3$ = 2.8, Sm$_2$O$_3$ = 2.2, Dy$_2$O$_3$ = 1.6. [c] Surface areas for MIESR catalysts in m^2 g^{-1}: La$_2$O$_3$ = 3.0, CeO$_2$ = 2.4, Nd$_2$O$_3$ = 2.8, Sm$_2$O$_3$ = 1.6, Dy$_2$O$_3$ = 1.6.

of the catalysts used in the flow reactor and in the MIESR experiment are given in a footnote in Table II.

The CH$_4$ reaction rate, CH$_4$ conversion, C$_2$ selectivities and C$_2$ yields at 600 and 700 °C are given in Table I. (The actual temperature sequence was 700 °C and then 600 °C.) The CH$_4$ conversions per square meter are in the order Nd$_2$O$_3$ > La$_2$O$_3$ > Sm$_2$O$_3$ > Dy$_2$O$_3$ > CeO$_2$. The C$_2$ yields follow the same order except Dy$_2$O$_3$ >> CeO$_2$. These results, as in the case of the MIESR results, do not agree with those of Otsuka et al.[8,9] in that they found Sm$_2$O$_3$ to be the best catalyst, both with respect to activity and C$_2$ yield. Also, the CH$_4$ reaction rates for all oxides tested are much greater than those reported by Otsuka.

The temperature effect on C$_2$ selectivity, as reported by Lin et al.,[11] is clearly positive for all oxides tested except CeO$_2$. The C$_2$ selectivities approximately doubled when the temperature increased from 600 to 700 °C, while the CH$_4$ conversions increased by factors of 4 or 5.

The inability of CeO$_2$ to form any C$_2$ compounds and the absence of CO in the products are attributed to a rapid surface reaction of any CH$_3$• radicals. In these surface reactions the CH$_3$• radicals apparently are converted to CO$_2$. Evidence for this was obtained from MIESR experiments in which first a layer of La$_2$O$_3$ catalyst was followed by a layer of quartz powder. In a second experiment the quartz powder was replaced by a layer of CeO$_2$ catalyst. When the quartz powder was in place a relative intensity for CH$_3$• radical production of 100 was obtained. The addition of the CeO$_2$ layer resulted in a decrease in the CH$_3$• intensity to almost zero. This demonstrates that CeO$_2$ acts as a CH$_3$• radical trap in that it removes CH$_3$• radicals from the gas phase by some type of surface reaction.

The ratios of water to molecular H$_2$ in the product stream were determined for the Nd$_2$O$_3$ and CeO$_2$ catalysts. The values were obtained by experimentally measuring the H$_2$ and using mass balance of H to obtain the ratios. For Nd$_2$O$_3$ the H$_2$O/H$_2$ ratio was 4 while for CeO$_2$ the ratio was 3.

In order to compare the MIESR results with results obtained in the flow reactor, relative values for CH$_4$ conversion, (C$_2$ yield)$^{1/2}$ and CH$_3$• intensity (activity) are given in Table II. Since the CH$_3$• intensity represents the radicals formed on the surface and released into the gas phase, it is expected that the CH$_3$• intensities should follow the same trend as the CH$_4$ conversions. Likewise, it is expected that the rate of C$_2$ product formation would be proportional to the square of the CH$_3$• radical concentration. Thus the CH$_3$• intensity should follow the same trend as the square root of the C$_2$ yield.

When comparing the flow reactor and MIESR results the values per square meter should be used since the surface areas of the catalysts were slightly different for the two systems. The values obtained for the relative conversion per square meter, the (C$_2$ yield)$^{1/2}$, and the CH$_3$• radical formation per square meter for La$_2$O$_3$, Sm$_2$O$_3$, and Dy$_2$O$_3$ are in fair agreement. The results show

approximately the same temperature effect and same order of activity for these oxides. As expected there is no agreement for CeO$_2$ because of the rapid reaction of CH$_3$• radicals with the surface.

For Nd$_2$O$_3$ the abnormally large activity and C$_2$ yield is difficult to explain. The results from the flow reactor indicate that Nd$_2$O$_3$ is the most active catalyst, while the MIESR results have La$_2$O$_3$ as the most active. There are two different explanations that can be postulated based on this result. If methyl radicals formed on the Nd$_2$O$_3$ surface were to undergo surface coupling reactions or other surface reactions not present on the other oxide surfaces, the MIESR experiment would predict too low an activity for Nd$_2$O$_3$. This explanation does not agree with the fact that Nd$_2$O$_3$, La$_2$O$_3$, and Sm$_2$O$_3$ exhibit almost the same C$_2$ selectivities (Table I). If the pathway for the formation of C$_2$ compounds was different for Nd$_2$O$_3$, it would be expected to have a different C$_2$ selectivity. However, the larger CO$_2$:CO ratio for Nd$_2$O$_3$ is evidence of a possible surface reaction.

Another possible explanation assumes that the active sites on the Nd$_2$O$_3$ surface are situated closer together than on the other oxide surfaces. Thus, over the Nd$_2$O$_3$ a larger local concentration of gas-phase CH$_3$• radicals may exist. If this were true a larger fraction of the CH$_3$• radicals would be lost to the coupling reaction than for the other oxides, and the MIESR experiment would indicate too low an activity for CH$_3$• radical formation over Nd$_2$O$_3$.

Conclusions

The complex pattern observed in the catalytic activities of hydrothermally treated lanthanide oxides for the abstraction of hydrogen atoms from methane can best be related to basicity of the oxides, with the more basic oxides being active. Exceptions are found for those metals which have multiple stable oxidation states, such as cerium oxide. Surface reactions of CH$_3$• radicals occur on CeO$_2$, but these are not coupling reactions. Thus, metal centers having multiple oxidation states are not a prerequisite for the oxidative coupling of methane. The MIESR and flow reactor results show qualitative agreement, except for Nd$_2$O$_3$, which supports the role of gas-phase CH$_3$• radical coupling in the catalytic conversion of CH$_4$ to C$_2$H$_6$ and C$_2$H$_4$. Pretreatment of the oxides, and even the source of the oxides, has a marked effect on activity, which may explain the qualitative differences obtained in this study and those previously reported by Otsuka et al.[8,9]