# Quantitative Studies of Methyl Radicals Reacting with Metal Oxides

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The reactive sticking coefficients of CH<sub>3</sub><sup>•</sup> radicals, produced by the thermal decomposition of azomethane, were determined over ZnO, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Sr/La<sub>2</sub>O<sub>3</sub>, and Li/MgO at 650 °C. The intrinsic sticking coefficients ranged from  $6 \times 10^{-8}$  for La<sub>2</sub>O<sub>3</sub> activated at 900 °C to  $3 \times 10^{-5}$  over ZnO. In the presence of even 0.1 mTorr of O<sub>2</sub> the sticking coefficient for the La<sub>2</sub>O<sub>3</sub> sample increased to  $3 \times 10^{-6}$ . Although the other nonreducible oxides exhibited similar behaviors, the magnitude of the effect was not as great. Methyl radicals are believed to react via electron transfer at the surface. The electron transfer may be either to metal ions, in the case of reducible oxides, or to O<sub>2</sub>, in the case of nonreducible oxides. Reactions of CH<sub>3</sub><sup>•</sup> radicals with several high surface area, porous silicas and zeolites were also studied. The sticking coefficient on a highpurity silica was found to be  $1 \times 10^{-8}$  at 200 °C. An analysis of the stable products indicated that the reaction of CH<sub>3</sub><sup>•</sup> radicals with these surfaces exceeded the coupling reactions that might have occurred at the surfaces. That is, the surfaces did not function as an effective "third body" in the coupling reaction.

### Introduction

Recent interest in the catalytic conversion of methane has focused attention on both the formation and reactions of methyl radicals on surfaces.<sup>1-5</sup> These radicals, for example, play a role in the catalytic oxidative coupling of CH<sub>4</sub> to form  $C_2H_6$  and subsequently  $C_2H_4$ . The  $C_2H_6$  is produced as surface-generated CH<sub>3</sub> radicals couple, primarily in the gas phase.<sup>3</sup> The radicals also may undergo secondary reactions with the surface through electron transfer reactions. Metal oxides having cations with multiple accessible oxidation states are most susceptible to reduction by CH<sub>3</sub> radicals.<sup>5</sup> The reaction may be expressed as

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

from which it is evident that methoxide ions are formed. Spectroscopic evidence supports the reduction of the metal ions and the formation of methoxide ions. Depending on the nature of the metal oxide, the methoxide ions may be converted into CO or CO<sub>2</sub>, via formate ions, or they may decompose to yield HCHO. The former reaction occurs over CeO<sub>2</sub><sup>5</sup> and the latter over MoO<sub>3</sub><sup>6</sup> and V<sub>2</sub>O<sub>5</sub>.<sup>7</sup> If water is present, the surface methoxide ions may react to produce methanol.<sup>6,7</sup>

In the initial quantitative study of CH<sub>3</sub><sup>•</sup> radicals reacting with a series of metal oxides, the radicals, produced by the reaction of CH<sub>4</sub> and O<sub>2</sub> over one oxide (Sm<sub>2</sub>O<sub>3</sub>), were allowed to react over a second oxide.<sup>5</sup> Most of the data were obtained with the second oxide at about 480 °C. With this reaction system it was not possible to eliminate the effects of small amounts of O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, *etc.*, that were produced over the Sm<sub>2</sub>O<sub>3</sub> as well as CH<sub>4</sub> that was present in a large excess. The results of Wang *et al.*<sup>8</sup> suggested that surface carbonate ions, formed from CO<sub>2</sub>, might significantly decrease the activity of a Li/MgO surface. This decrease in activity of CH<sub>3</sub>• radicals with the Li/MgO catalyst was used to explain the positive effect that CO<sub>2</sub> has on C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> selectivity during the coupling reaction.

In the present study, azomethane  $(CH_3N=NCH_3)$  was used as the source of methyl radicals because this compound cleanly pyrolyzes to  $CH_3^{\bullet}$  and  $N_2$ . Thus, the intrinsic activity of an oxide with respect to  $CH_3^{\bullet}$  radicals could be determined, and

TABLE 1: Surface Areas of the Metal Oxides

oxide	surface area (m <sup>2</sup> /g)	oxide	surface area (m <sup>2</sup> /g)
ZnO	4.3	Sr/La <sub>2</sub> O <sub>3</sub>	7.6
$CeO_2$	15.4	$La_2O_3$	3.2
Li/MgO	1.2		

the effects of O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O, or CH<sub>4</sub> could be independently investigated. The oxides of interest were CeO<sub>2</sub>, ZnO, La<sub>2</sub>O<sub>3</sub>, Sr/La<sub>2</sub>O<sub>3</sub>, and Li/MgO. Among these, CeO<sub>2</sub> and ZnO are nonselective coupling catalysts, whereas La<sub>2</sub>O<sub>3</sub>, Sr/La<sub>2</sub>O<sub>3</sub>, and Li/MgO are selective catalysts for the formation of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. In addition, a cursory study was made of CH<sub>3</sub><sup>•</sup> radicals reacting on high surface are silica and zeolites, which typically are nonselective coupling catalysts.

## **Experimental Section**

The metal oxides used in this study either were obtained comercially or were prepared according to methods described previously. CeO<sub>2</sub> (Rhone-Poulenc, 99%), ZnO (New Jersey Zinc, super purity), La<sub>2</sub>O<sub>3</sub> (Aldrich, 99.9%), 1 wt % Sr/La<sub>2</sub>O<sub>3</sub> (provided by Amoco Oil), Na-Y zeolite (Union Carbide, LZ-Y52), NH<sub>4</sub>-Y zeolite (Union Carbide, LZ-Y62), Cab-O-Sil SiO<sub>2</sub> (Cabot), SiO<sub>2</sub>(57) (Davison, Grade 57 silica gel), and SiO<sub>2</sub>-(03) (Davison, Grade 03 silica gel) were used as received. A 4.1 wt % Li/MgO catalyst was prepared by adding MgO (Aldrich, 98%) to an aqueous solution of Li<sub>2</sub>CO<sub>3</sub> of appropriate concentration. The resulting material was dried in air at 140 °C and calcined at 750 °C for 16 h. The surface areas of the low surface area, nonporous materials are summarized in Table 1.

The synthesis of azomethane was carried out using a modification of the procedure described by Renaud and Leitch.<sup>9</sup> Briefly, 1,2-dimethylhydrazine, resulting from the neutralization of 1,2-dimethylhydrazine dihydrochloride (Aldrich, 99+%), was added slowly to a suspension of yellow mercuric oxide (Aldrich, 99.9%) in water at room temperature. This addition was conducted while purging the slurry with a slow stream of He to avoid any chance of an explosion. Azomethane was formed by heating the reagents in a water bath at 95 °C, and the product was collected in a trap cooled with a dry ice—acetone bath. Then, the azomethane was dried by passing the gas through a

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Figure 1. Knudsen cell used to study the reactions of  $CH_3$  radicals with metal oxides.

tube containing potassium hydroxide in a glass vacuum line. This drying procedure was performed three times, with the KOH being dried under vacuum at 25 °C each time. Gas impurities, primarily He, were removed by several freeze-pump-thaw cycles using liquid nitrogen. The purity of the final product was verified by mass spectrometry. The azomethane was transferred to a stainless steel cylinder and pressurized with Ar to a desired Ar/CH<sub>4</sub> ratio. Azomethane can be stored in this manner for several months without any degradation. The other gases, which included Ar (Airco, 99.99%), CH<sub>4</sub> (Matheson, 99.97%), O<sub>2</sub> (Matheson, 99.6%), CO<sub>2</sub> (Matheson, 99.99%), and N<sub>2</sub>O (Matheson, 99.9%), were used without further purification.

In most of the studies described here, the  $CH_3^*$  radicals were detected using a matrix isolation electron spin resonance (MIESR) system described previously.<sup>10</sup> Gases that pass through a leak in a Knudsen cell (described below) traverse through a low-pressure region and are frozen in an Ar matrix on a sapphire rod at 14 K. After a collection period, the rod with the matrix is lowered into an ESR cavity, and spectra are recorded.

Methyl radicals, as well as stable products, were detected using a variable ionization energy mass spectrometer (VIEMS) similar to that described by Stair and co-workers.<sup>11</sup> A UTI-Model 100C quadrupole mass spectrometer was modified so that the energy range of impacting electrons was variable from 4 to 110 eV. Thus, by using a nominal electron-impact energy of 15 eV, it was possible to selectively ionize only CH<sub>3</sub><sup>•</sup> radicals. Stable reaction products, such as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and CO<sub>2</sub>, were detected using a normal electron-impact ionization energy of 70 eV.

A schematic diagram of the fused-quartz Knudsen cell is shown in Figure 1. The main body of the cell is an 18 mm i.d. cylindrical tube that is heated externally. The cell is connected via a valve to a pressure transducer. Two 1.0 mm i.d. capillary tubes allow gases to enter the cell. The exit from the cell is via a 1.1 mm i.d. hole which serves as the leak into the vacuum of the MIESR or VIEMS systems.

The CH<sub>3</sub> radicals were generated by the pyrolysis of azomethane in one of the capillary tubes at 910 °C. The decomposition of the azomethane was essentially complete at this temperature, in agreement with the results of Peng *et al.*<sup>12</sup> These radicals then entered the Knudsen cell that contained the catalyst at a temperature  $T_2$ . According to Benson *et al.*,<sup>13</sup> the pressure should be confined to a range such that the mean free path of molecules in the cell is at least 10 times greater than the diameter of the exit aperture, hence guaranteeing molecular effusion through the exit pinhole. Under this condition, the reactor will behave like a well-stirred reactor. In the following MIESR experiments, the pressure within the cell was kept at *ca.* 14 mTorr, resulting in a molecular mean free path of *ca.* 25 mm. Since the pressure after the leak was much less than 1 mTorr, no backflow occurred. The advantage of this reactor

system is that the residence times of the molecules within the cell could be determined accurately using Knudsen flow.

The samples typically were prepared by mixing the appropriate catalysts with a small amount of deionized water to form a thick slurry. The slurry was then mixed with 0.10 g of quartz wool. The quartz wool, coated with a catalyst, was placed inside the reactor. The catalyst was kept under vacuum for > 12 h at 25 °C and then was normally heated in flowing O<sub>2</sub> at a reduced pressure (0.2 mL min<sup>-1</sup> (STP)) for 40 min at 700 °C. One sample of La<sub>2</sub>O<sub>3</sub>, designated La<sub>2</sub>O<sub>3</sub>(900), was heated in flowing O<sub>2</sub> at 900 °C in order to remove additional carbonate from the surface. The sample was cooled in vacuo to the desired reaction temperature, and the reagent gases were admitted to the cell. A mixture of azomethane and Ar in a 1:37 ratio was fed through line 1 at a flow rate of 0.035 mL min<sup>-1</sup> (STP). The reaction was usually stabilized for 1 h before the first collection commenced in the MIESR system. The collection period was 15 min, and the time between successive collections was ca. 1.5 h.

To investigate the reactivity of CH3 radicals in porous materials, 100 mg of catalyst dispersed on quartz wool was slowly heated (ca. 10 °C min<sup>-1</sup>) to 400 °C under flowing O<sub>2</sub> at 40 mTorr and then was maintained at these conditions for 40 min. This thermal treatment converted the  $NH_4-Y$  zeolite to a H-Y zeolite. The loss of CH3 radicals as they reacted with the porous materials in the Knudsen cell was followed with both the MIESR and the VIEMS systems. The azomethane: Ar ratios were 1:40 and 1:74 in the VIEMS and the MIESR systems, respectively. No other gases were introduced via the other inlet. Because of constraints introduced by the mass spectrometer, the total pressure in the Knudsen cell was only 6 mTorr in the VIEMS experiments. But considering the dilution factors, the CH3 radical partial pressures were about the same in the MIESR and the VIEMS systems. The data collection commenced 10 min after the reagents were introduced to the cell.

The VIEMS system was calibrated using gas mixtures similar to those employed under reaction conditions. Lieszkovsky *et*  $al.^{14}$  have reported, and we have confirmed, that a major component, Ar in our case, has a "matrix effect" on minor components in a gas mixture. That is, the sensitivity factors for the minor components are strongly influenced by the major component. The CH<sub>3</sub>• radical sensitivity factor at 15 amu and at a nominal electron-impact ionization energy of 15 eV was determined from the pressure of the gas mixture and the fact that 98% of the azomethane had decomposed. During calibration the leak was not in place, so there was no opportunity for radical coupling to occur.

## **Results and Discussion**

Determination of Sticking Coefficients of  $CH_3^{\circ}$  Radicals over Metal Oxides. The sticking coefficient is defined as the ratio of the number of  $CH_3^{\circ}$  radicals reacted on a metal oxide to the number of collisions between the  $CH_3^{\circ}$  radicals and the metal oxide. Here, we define sticking coefficient in a broad sense to include all surface reactions that result in the disappearance of  $CH_3^{\circ}$  radicals, whether they are stoichiometric or catalytic. With the catalyst in the Knudsen cell, the sticking coefficient is given by the relationship

$$S = \frac{A_{\rm h}}{(\mathrm{SA})W} \ln \frac{[\mathrm{CH}_3]_0}{[\mathrm{CH}_3]}$$
(2)

where  $A_h$  is the area of the exit aperture, in m<sup>2</sup>; SA is the surface area of the catalyst, in m<sup>2</sup> g<sup>-1</sup>; W is the amount of metal oxide



**Figure 2.** First-order relationship between CH<sub>3</sub><sup>•</sup> radical concentration and mass of Sr/La<sub>2</sub>O<sub>3</sub> catalyst: T = 650 °C,  $P(CH_3^•) = P(O_2) = 0.42$  mTorr,  $P_T = 14$  mTorr.



**Figure 3.** Sticking coefficients of CH<sub>3</sub> radicals on metal oxides at different partial pressures of O<sub>2</sub>:  $\nabla$ , ZnO (5 mg);  $\blacktriangle$ , CeO<sub>2</sub> (22 mg);  $\diamondsuit$ , Li/MgO (360 mg);  $\triangle$ , Sr/La<sub>2</sub>O<sub>3</sub> (40 mg);  $\blacklozenge$ , La<sub>2</sub>O<sub>3</sub> (120 mg);  $\bigcirc$ , La<sub>2</sub>O<sub>3</sub> (900) (40 mg).

used, in grams; and  $[CH_3^{\bullet}]_0/[CH_3^{\bullet}]$  is the ratio of methyl radical concentrations with and without the metal oxide present.

Implicit in the derivation of eq 2 is the assumption that the reaction rate is first order in the concentration of  $CH_3^{\circ}$  radicals. On the basis of this assumption, one can write an integrated rate equation

$$\ln \frac{[CH_3^*]_0}{[CH_3^*]} = k_s(SA)Wt_r$$
(3)

where  $k_s$  is the specific rate constant, in m<sup>-2</sup> s<sup>-1</sup>, and  $t_r$  is the residence time, in seconds. If the assumption of a first-order rate law in [CH<sub>3</sub><sup>•</sup>] is correct, a linear relationship should exist between ln [CH<sub>3</sub><sup>•</sup>]<sub>0</sub>/[CH<sub>3</sub><sup>•</sup>] and the amount of catalysts used. Figure 2 shows that a linear relationship was indeed observed over the 1 wt % Sr/La<sub>2</sub>O<sub>3</sub> catalyst. In blank experiments, it was demonstrated that about 15% of the CH<sub>3</sub><sup>•</sup> radicals coupled homogeneously or during pyrolysis and that the presence of the quartz wool, without the catalyst, had no effect on the radical concentration.

Sticking Coefficients in the Absence and Presence of an Oxidant. The effect of  $O_2$  on the sticking coefficients of CH<sub>3</sub><sup>•</sup> radicals with several metal oxides is shown in Figure 3. In the absence of  $O_2$ , the sticking coefficients ranged from  $6 \times 10^{-8}$  over La<sub>2</sub>O<sub>3</sub> pretreated at 900 °C to  $3 \times 10^{-5}$  over ZnO. With the exception of ZnO, all of the results were obtained at 650 °C. Since oxygen was lost from ZnO at 650 °C, as indicated by the formation of a zinc film, the sticking coefficient over

this oxide was determined at 500 °C. As will be discussed below, the effect of temperature on the sticking coefficients is rather small. Previously, using Sm<sub>2</sub>O<sub>3</sub> to generate the CH<sub>3</sub>• radicals, a sticking coefficient of  $2 \times 10^{-5}$  was observed for ZnO at 482 °C,<sup>5</sup> which may be compared with a value of  $3 \times 10^{-5}$  in this study. The agreement for CeO<sub>2</sub> was not quite as good, with a value of  $5 \times 10^{-6}$  for this study, compared to a value of  $2 \times 10^{-6}$  from the previous study,<sup>5</sup> with both values being reported at 480 °C. The magnitude of the sticking coefficients is qualitatively consistent with the selectivities of the oxides for the oxidative coupling reaction.

As shown in Figure 3, the addition of even 0.1 mTorr of  $O_2$  to the reagent stream caused a marked increase in the sticking coefficients for the La<sub>2</sub>O<sub>3</sub>, Li/MgO, and Sr/La<sub>2</sub>O<sub>3</sub> catalysts. The sticking coefficient for the La<sub>2</sub>O<sub>3</sub>(900) catalyst increased by a factor of 50. With additional increases in the O<sub>2</sub> pressure, the sticking coefficients for the La<sub>2</sub>O<sub>3</sub>(900) and Sr/La<sub>2</sub>O<sub>3</sub> catalysts increased further, whereas the sticking coefficients over the ZnO and CeO<sub>2</sub> catalysts decreased a modest amount. For the CeO<sub>2</sub> sample the decrease was within experimental error. Interestingly, in the presence of  $\geq 0.4$  mTorr of O<sub>2</sub> the sticking coefficients of La<sub>2</sub>O<sub>3</sub>(900) and CeO<sub>2</sub> were essentially the same.

At least three explanations have been given for the negative effect that  $O_2$  has on  $C_2$  selectivity during the oxidative coupling reaction. First, the secondary products, particularly ethylene, may be oxidized both homogeneously and heterogeneously.<sup>15</sup> Second, a reactive, but nonselective, oxygen species such as  $O_3^-$  may be formed.<sup>16</sup> Third,  $CH_3O_2^*$  radicals formed in the presence of  $O_2$  react with the surface to produce  $CO_x$ .<sup>17</sup> Since the effects noted in Figure 3 occurred at very low  $O_2$  pressures, it seems unlikely that homogeneous reactions would have been important. Moreover, the extent of these homogeneous reactions should have increased with  $O_2$  pressure. This is particularly true for the formation of  $CH_3O_2^*$ , which would be in equilibrium with  $CH_3^*$  and  $O_2$ .

The effect that small amounts of  $O_2$  have on the CH<sub>3</sub><sup>•</sup> radical sticking coefficients may be more reasonably ascribed to electron transfer reactions that occur on the oxides. Ito and co-workers<sup>18</sup> have observed that the coadsorption of CH<sub>4</sub> and  $O_2$  on MgO at 50 °C resulted in the formation of  $O_2^-$  ions. The analogous reaction did not occur at this temperature with N<sub>2</sub>O as the oxidant. Previously, we showed that CH<sub>3</sub><sup>•</sup> radicals reacted on CeO<sub>2</sub> at 25 °C to produce superoxide ions, and in this case, a small amount of O<sub>2</sub> was present in the reagent gases. Thus, we propose that the reaction

$$CH_3 + O_2 + O_s^{2-} \xrightarrow{MO} CH_3 O_s^{-} + O_{2s}^{-}$$
(4)

may account for the increased sticking coefficients in the presence of  $O_2$ . This would be the dominant reaction for the nonreducible oxides, but over the other oxides reaction 1 would prevail, at least at the low  $O_2$  pressures and high temperatures of this experiment.

Oxygen vacancies at the surface may mediate the electron transfer process of reaction 4. Such vacancies could be introduced by the thermal treatment of the La<sub>2</sub>O<sub>3</sub> at 900 °C, which removes the residual carbonate and hydroxide ions, leaving oxygen vacancies. The large CH<sub>3</sub>• radical sticking coefficient observed for La<sub>2</sub>O<sub>3</sub>(900) in the presence of O<sub>2</sub> is consistent with the catalytic properties of this material during the oxidative coupling reaction. LeVan *et al.*<sup>20</sup> observed that, with  $P(CH_4) = 60$  Torr and  $P(O_2) = 15$  Torr, the C<sub>2</sub> (ethane plus ethylene) selectivity was only 30% at a conversion level of 10% over La<sub>2</sub>O<sub>3</sub>(900) catalyst; however, at the same level of CH<sub>4</sub> conversion, the selectivity reached 70% over a La<sub>2</sub>O<sub>3</sub> catalyst pretreated at 650 °C.



**Figure 4.** Arrhenius plots for CH<sub>3</sub> radicals reacting with metal oxides:  $\blacktriangle$ , CeO<sub>2</sub>,  $E_a = 3$  kcal/mol;  $\bigcirc$ , La<sub>2</sub>O<sub>3</sub>(900),  $E_a = 8$  kcal/mol;  $\triangle$ , Sr/La<sub>2</sub>O<sub>3</sub>,  $E_a = 4$  kcal/mol;  $\diamondsuit$ , Li/MgO,  $E_a = 4$  kcal/mol.  $P(O_2) = 0.42$  mTorr.

Nitrous oxide had no effect on the reactivity of CH<sub>3</sub> radicals with a Li/MgO catalyst, even at N<sub>2</sub>O pressures up to 8 mTorr. The sticking coefficient remained constant at a value of  $3 \times 10^{-7}$ . Since N<sub>2</sub>O has a lower electron affinity than O<sub>2</sub>, the electron transfer process, analogous to reaction 4, may not occur. The smaller sticking coefficient is in agreement with the larger C<sub>2</sub> selectivity that was found with N<sub>2</sub>O as the oxidant. For example, at a conversion of *ca*. 3% the C<sub>2+</sub> selectivities with N<sub>2</sub>O and O<sub>2</sub> as oxidants were 92% and 35%, respectively.<sup>16</sup>

From the Arrhenius plots of Figure 4 the activation energies of the sticking coefficients were determined. The sequence of measurements was from high temperature to low temperature in order to minimize the effect of carbonates on the surface. As noted below, the presence of carbonates can significantly decrease the sticking coefficient. For CeO<sub>2</sub>, Sr/La<sub>2</sub>O<sub>3</sub>, and Li/ MgO the activation energies were 3-4 kcal/mol, whereas for La<sub>2</sub>O<sub>3</sub>(900) it was 8 kcal/mol. In view of these small activation energies it is surprising that the sticking coefficients were so small. The reason for this apparent anomaly has been discussed previously and is related to the rapid desorption of CH<sub>3</sub><sup>•</sup> radicals relative to electron transfer and formation of methoxide ions.<sup>5</sup> The situation is analogous to the dissociative adsorption of nitrogen molecules on Fe surfaces.<sup>21</sup>

Effect of CO<sub>2</sub> on Sticking Coefficients. It has been demonstrated previously that CO<sub>2</sub> at pressures of 0.26-2.1 Torr had a strong inhibiting effect on the reaction of CH<sub>3</sub> radicals with a Li/MgO catalyst.<sup>8</sup> Moreover, CO<sub>2</sub> is a reversible poison for the formation of CH3 radicals and for the catalytic conversion of CH<sub>4</sub>.<sup>2,8</sup> The results of Figure 5 are consistent with those previously reported for Li/MgO in that the reactive sticking coefficient decreased by a factor of 3 as the CO<sub>2</sub> pressure was increased to 7.7 mTorr. Here it should be noted that the  $O_2$  pressure was 0.42 mTorr; thus, the amount of  $CO_2$ formed by CH<sub>3</sub><sup>•</sup> radical oxidation was small. The La<sub>2</sub>O<sub>3</sub>(900) catalyst was similarly poisoned by CO<sub>2</sub>, only in this case the effect was much more dramatic at lower pressures of CO<sub>2</sub>, which implies a larger heat of adsorption of  $CO_2$  on the surface. (Here, we do not distinguish between heat of adsorption and heat of carbonate formation.) After the La<sub>2</sub>O<sub>3</sub>(900) sample had been exposed to progressively higher pressures of CO<sub>2</sub>, up to 7.7 mTorr, the sticking coefficient was determined in the absence of any added CO<sub>2</sub>. The strong adsorption of CO<sub>2</sub> was confirmed by the fact that La<sub>2</sub>O<sub>3</sub>(900) did not recover its original activity at 650 °C.

The effect of added  $CO_2$  on the  $CH_3^{\bullet}$  radical sticking coefficients was much less with  $Sr/La_2O_3$ , which is surprising since this is also a strongly basic mixed-metal oxide. Appar-



**Figure 5.** Sticking coefficients of CH<sub>3</sub><sup>•</sup> radicals on:  $\bigcirc$ , La<sub>2</sub>O<sub>3</sub>(900); **.**, La<sub>2</sub>O<sub>3</sub>(900) after exposure to 7.6 mTorr of CO<sub>2</sub> at 655 °C;  $\triangle$ , Sr/La<sub>2</sub>O<sub>3</sub>;  $\diamond$ , Li/MgO.

TABLE 2: Effect of CH<sub>4</sub> on the Sticking Coefficient<sup>a</sup>

press. of	CH <sub>3</sub> • rad (relativ	sticking		
O <sub>2</sub> /CH <sub>4</sub> /CH <sub>3</sub> ·	quartz wool	1 wt % Sr/La2O3	coefficient	
0.4/0/0.4	49	29	$5.5 \times 10^{-7}$	
0.4/0.8/0.4	65	45	$5.6 \times 10^{-7}$	
0.4/4/0.4	102	105	$7.9 \times 10^{-7}$	
0.4/0.8/0		7		
0.4/4/0	2	58		
a <b>T</b> (50.00 F				

<sup>*a*</sup>  $T_2 = 650 \,^{\circ}\text{C}, P_T = 14 \,\text{mTorr.}$ 

ently, a pretreatment temperature of 700 °C was inadequate to remove all of the carbonates on the  $Sr/La_2O_3$ , as was the case for  $La_2O_3$ ; therefore, the addition of a small amount of  $CO_2$  did not significantly affect the activity of the surface with respect to  $CH_3^{\bullet}$  radicals.

Effect of CH<sub>4</sub> on Sticking Coefficients. It was of interest to determine whether CH<sub>4</sub> competes with CH<sub>3</sub> radicals for centers of activity on the catalyst surface. If so, then the sticking coefficients determined in the absence of CH<sub>4</sub> may not be relevant to the catalytic reactions that are carried out in an excess of CH<sub>4</sub>. The results of experiments to determine the effects of CH<sub>4</sub> on the reactive sticking coefficients over Sr/La<sub>2</sub>O<sub>3</sub> are given in Table 2. Since CH<sub>4</sub> also was a *source* for CH<sub>3</sub><sup>•</sup> radicals under the reaction conditions, it was necessary to correct for those radicals that were produced over the catalyst. The relative numbers of radicals produced from CH4 were obtained in blank experiments, i.e., experiments in which no CH3<sup>•</sup> radicals were introduced from azomethane. The results show that the presence of 0.8 mTorr of CH<sub>4</sub> had no effect on the reactive sticking coefficient. The apparent increase in sticking coefficient at 4 mTorr of CH<sub>4</sub> may well be due to the error introduced by the relatively large production of CH3 radicals from CH4. It is difficult to rationalize how CH4 would cause an increase in the sticking coefficient. At least within the pressure range of these experiments, we conclude that CH<sub>4</sub> and CH<sub>3</sub> radicals do not compete for the same active centers on the surface.

**Reactions of CH<sub>3</sub>** • **Radicals in Porous Materials.** Although it is now generally accepted that the coupling of CH<sub>3</sub> • radicals occurs primarily in the gas phase, rather than on the surface of the catalyst, all of the selective catalysts have surface areas less than 10 m<sup>2</sup>/g. One might expect that the coupling of CH<sub>3</sub> • radicals would occur with a higher efficiency in porous, high surface area (>100 m<sup>2</sup>/g) catalysts, where the radicals confined in small pores or channels would have a higher probability of coupling. Thus, the reactions of CH<sub>3</sub> • radicals in several silica gels and Y-type zeolites have been investigated.

TABLE 3: Reactions of CH<sub>3</sub> Radicals in Porous Materials<sup>a</sup>

	surface area (m²/g)	Fe content (wt %)	CH <sub>3</sub> • radicals reacted (%)	
			MIESR	VIEMS
Na-Y (LZ-Y52)	987		74	_
H-Y (LZ-Y62)	890		90	87
Cab-O-Sil	270	0.0003	36	
SiO <sub>2</sub> (57)	283	0.007	56	58
SiO <sub>2</sub> (03)	625	0.006	45	

<sup>*a*</sup> T = 200 °C,  $P_T = 14$  mTorr in the MIESR system and 6 mTorr in the VIEMS system, and no O<sub>2</sub> was added to the reagents.

The five porous oxides tested, the surface areas of these materials, and percentage of CH3 radicals reacted in these solids are listed in Table 3. The percentage of CH<sub>3</sub> radicals reacted is based on the amount of CH3 radicals that escape the Knudsen cell when only quartz wool was present. For the Cab-O-Sil silica the reaction of 36% of the CH<sub>3</sub> radicals, in the absence of O<sub>2</sub>, corresponds to a sticking coefficient of  $1 \times 10^{-8}$ , which is less than any of the values reported in Figure 3. Because the sticking coefficient is so small, the use of eq 2 is justified, even for this highly porous material. If the sticking coefficient were not small, one would be concerned about the loss of a large fraction of the radicals near the pore mouth, leaving only a small fraction to react in the pores. While all of these materials promote the loss of CH3\* radicals, there is no correlation with pore structure or surface area. The two Y-type zeolites have the same internal pore structure and impurity level, yet the H-Yzeolite was more effective in removing CH<sub>3</sub> radicals. Similarly,  $SiO_2(03)$  had a higher surface area than  $SiO_2(57)$ , yet the former was less effective in removing CH3<sup>•</sup> radicals than the latter. Since Cab-O-Sil is the purest silica and the least effective in promoting CH3<sup>•</sup> radical reactions, one might expect that transition metal impurities, especially iron, would play a role. Zeolites are known to contain up to 0.1 wt % Fe; therefore, a stoichiometric reaction involving Fe cannot be ruled out for these materials. It seems unlikely, however, that impurity ions would be involved in the reaction of CH3• radicals with Cab-O-Sil.

The observation that the H-Y zeolite was more effective than Na-Y in removing  $CH_3^*$  radicals suggested that acidic hydroxyl groups might be involved, perhaps by a reaction such as

$$CH_3^{\bullet} + OH_s^{-} \rightarrow CH_4O_s^{-}$$
(5)

After allowing  $CH_3^{\bullet}$  radicals to flow over the H-Y zeolite, an ESR spectrum was obtained for the sample. There was no evidence for a  $CH_4O_s^{-1}$  radical, although such a species may have been present as a transient intermediate.

In order to further investigate the reactions of  $CH_3^*$  radicals over porous solids, the VIEMS system was used to determine whether the loss of radicals corresponded to the formation of the coupling products  $C_2H_6$ . With the VIEMS system, it was possible to detect  $CH_3^*$  radicals, as well as any stable products that might be present. Comparisons are made between the reactions of  $CH_3^*$  radicals over quartz wool, as a background, and those that occurred over the H-Y zeolite, silica(57), and cerium oxide. The  $CeO_2$  was chosen for comparison because this material is known to be a total oxidation catalyst with respect to methane.

The results of Figure 6 indicate that, with quartz wool present in the reactor, part of the  $CH_3^{\bullet}$  radicals couple to form  $C_2H_6$ . This coupling occurs homogeneously and even in the pyrolysis region.<sup>12</sup> The small amount of  $CH_4$  probably was formed in



**Figure 6.** Comparison of product distribution after reaction of CH<sub>3</sub><sup>•</sup> radicals with metal oxides at the indicated reaction temperatures.

the mass spectrometer. A large decrease in the  $CH_3^{\bullet}$  radical concentration was detected when the H-Y zeolite was introduced into the reactor. The  $C_2H_6$  concentration actually decreased, which means that the zeolite did not promote the coupling reaction. Rather, the zeolite inhibited  $C_2H_6$  formation by removing  $CH_3^{\bullet}$  radicals. On the basis of the decrease in  $CH_3^{\bullet}$  radicals, it is surprising that the  $CH_4$  concentration increased slightly. Apparently,  $CH_4$  was formed by a type of hydrogen transfer reaction in the zeolite. The small amount of  $CO_2$  may have resulted from variations in the background.

The results obtained with the silica gel were qualitatively similar, although the removal of CH<sub>3</sub>• radicals was not as extensive, and consequently, the C<sub>2</sub>H<sub>6</sub> concentration did not decrease as much. The observation that a relatively inert material of high surface area did not promote the formation of C<sub>2</sub>H<sub>6</sub> confirms that surfaces do not function as an effective "third body" in the coupling reaction. Certainly, the coupling induced by the surface is small compared to the reaction of CH<sub>3</sub>• radicals with the surface.

The results obtained over CeO<sub>2</sub> were significantly different in that the CH<sub>3</sub><sup>•</sup> radicals were totally removed, and CO<sub>2</sub> was the major product. Previously, we reported that CH<sub>3</sub><sup>•</sup> radicals initially reacted with CeO<sub>2</sub> to form methoxide ions, and at 100 °C these are transformed into formate ions.<sup>5</sup> The formate ions decompose by 300 °C, presumably to form the CO<sub>2</sub> that was found in the present experiment. Again, the loss of CH<sub>3</sub><sup>•</sup> radicals to the surface inhibits the coupling reaction. There was an increase in the amount of H<sub>2</sub>O formed, and hydrogen transfer reactions, perhaps between surface methoxide ions and methyl radicals, may have resulted in the formation of additional methane. The origin of the CH<sub>4</sub>, however, is speculative.

The distribution of products depicted in Figure 6 was obtained after exposure of the CeO<sub>2</sub> to CH<sub>3</sub> radicals for 12 min. In contrast to the constant product distribution obtained over the porous solids, the distribution over the CeO<sub>2</sub> changed with time, *i.e.*, as more oxygen was removed from the lattice. After 220 min of exposure, the amount of CO<sub>2</sub> decreased to one-third the original value, the amount of CH<sub>4</sub> doubled, and the amount of C<sub>2</sub>H<sub>6</sub> increased slightly.

### Conclusions

The intrinsic probability of a CH<sub>3</sub> radical reacting with a metal oxide upon collision depends very much on the nature of the oxide, with the easily reducible oxides being the most reactive. For the nonreducible oxides, the presence of even limited amounts of O<sub>2</sub> significantly enhances the sticking coefficient, presumably via electron transfer to the molecular oxygen. Nevertheless, the sticking coefficients are sufficiently small ( $< 10^{-6}$ ) for coupling to occur during the partial oxidation of CH<sub>4</sub> at high pressures. On the strongly basic oxide,  $La_2O_3$ , the defects introduced by the loss of carbonate ions appear to facilitate the electron transfer reaction. The loss of carbonate ions may be partially reversed by the addition of  $CO_2$  to the reagent gas. The presence of CH<sub>4</sub> does not inhibit the reactions between CH<sub>3</sub><sup>•</sup> radicals and a nonreducible oxide. Although high surface area silicates and aluminosilicates react with CH3<sup>•</sup> radicals, the intrinsic sticking coefficients are actually quite small. Moreover, the coupling of  $CH_3$  radicals to form  $C_2H_6$ is not a major pathway for the loss of radicals in these porous materials.

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