# Effect of temperature on methyl radical generation over $Sr/La_2O_3$ catalysts

Mingting Xu and Jack H. Lunsford

*Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.*

Received 4 September 1991; accepted 22 October 1991

The role of gas phase $CH_3\cdot$ radicals in the oxidative coupling of $CH_4$ over 1 wt% $Sr/La_2O_3$ is supported by the observations that (i) this is a very effective catalyst for the generation of $CH_3\cdot$ radicals and (ii) the concentration of $CH_3\cdot$ radicals increases with temperature over the range of 450 °C-800 °C.

**Keywords:** Methane oxidation; methyl radicals; strontium/lanthanum oxide; temperature effects

## 1. Introduction

It has been demonstrated that 1 wt% $Sr/La_2O_3$ is one of the most active and selective catalysts for the oxidative coupling of methane [1-3]. One would like to know, therefore, the mechanism by which the coupling reaction occurs on this important promoted metal oxide catalyst. Previous qualitative and quantitative studies on other effective oxidative coupling catalysts have shown that $CH_3\cdot$ radicals, formed at the surface of the metal oxide, emanate into the gas phase where they couple to produce $C_2H_6$ [4-7]. Gulcicek et al. [8] have used a resonance-enhanced multiphoton ionization (REMPI) time-of-flight mass spectrometer to detect $CH_3\cdot$ radicals that exit a 1 wt% $Sr/La_2O_3$ catalyst bed. They observed a maximum in $CH_3\cdot$ radical concentration at 590 °C for a fresh catalyst and at 660 °C for a catalyst that had been aged 6-8 hr under reaction conditions. At 850 °C almost no $CH_3\cdot$ radicals were detected at the exit of the catalyst bed. By contrast, Feng et al. [9] have recently used a photoionization mass spectrometer to detect $CH_3\cdot$ radicals produced over a 1 wt% $Sr/La_2O_3$ catalyst over the temperature range 709-865 °C. They found that the system exhibited normal Arrhenius type behavior and concluded that the activation energy for H-atom transfer from $CH_4$ to the active surface site was $21 \pm 5$ kcal $mole^{-1}$. In a conventional catalytic study by DeBoy and Hicks [1-3] it was shown that a 1 wt% Sr/$La_2O_3$ catalyst exhibits a maximum $C_2$ selectivity at 750 ° C [2]. Moreover, the $CH_4$ conversion increases in a normal manner with increasing temperature, giving an apparent activation energy of 39.4 kcal mole$^{-1}$ [3]. If the $CH_3\cdot$ radical concentrations detected by Gulcicek et al. represent the true rate of $CH_3\cdot$ radicals emanation into the gas phase, one may conclude, as they did, that the coupling reaction occurs on the surface of the catalyst, rather than in the gas phase.

In this study, we will show that the maxima in $CH_3\cdot$ radical concentration as a function of temperature are not a general phenomena over 1 wt% Sr/$La_2O_3$ catalysts. In fact, our results demonstrate that the radical concentration increases monotonically with temperature. Thus, over the temperature range from 450 ° C to 800 ° C the $CH_3\cdot$ radical production rate is consistent with the $CH_4$ conversion.

## 2. Experimental

Two 1 wt% Sr/$La_2O_3$ catalysts were used in these experiments. One of the catalysts, designated Sr/$La_2O_3$ (A) was made available to us [10], and the other was prepared in our laboratory. The sample designated Sr/$La_2O_3$ (*ex* $Sr(NO_3)_2$) was prepared by evaporating to dryness a slurry of $La_2O_3$ (Alpha, 99.99% purity) and $Sr(NO_3)_2$ (Johnson Matthey). The material was dried in air at 110 ° C for 12 hr, calcined at 600 ° C for 4 hr, sieved to 20–42 mesh and stored in a desiccator. Gulcicek et al. [8] did not indicate any pretreatment of their catalyst.

The $CH_3\cdot$ radicals were detected using a matrix isolation electron spin resonance (MIESR) system that has been described in detail previously [5,11]. Briefly, the reactant gases are passed through a heated catalyst bed in a fused-quartz reactor. Argon is used as a diluent. The effluent gases then pass through a leak into a low pressure collection region and are frozen in an Ar matrix 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 MIESR system was operated in a low pressure mode with the total gas pressure over the catalyst being ca. 1 Torr or in the high pressure mode with the total gas pressure being 760 Torr. The reactors used in the two modes are shown in fig. 1. In the low pressure mode 0.055 g of catalyst was held as a thin layer of powder between a fused-quartz frit and a layer of quartz wool. With this pressure and catalyst configuration the $CH_3\cdot$ radicals have a high probability of entering the leak without undergoing reactions either in the gas phase or with the catalyst bed. In the high pressure mode 0.045 g of catalyst was placed in a 3.0 mm i.d. tube. The bed length was 4.5 mm. The advantage of this configuration is that it more closely approximates a conventional catalytic reactor and the reactor used by Gulcicek et al. [8]; the disadvantage is that the radicals may undergo extensive reaction both in the gas phase and with the catalyst. At the flow rate employed the residence time in the catalyst bed was ca. 1.5 ms. The flow rates are given at 25 ° C and 760 Torr.

## 3. Results and discussion

The relative concentrations of $CH_3\cdot$ radicals observed as a function of temperature in the low pressure mode over the fresh and used $Sr/La_2O_3$ (A) catalysts are shown in fig. 2A. For the fresh catalyst the gas stream was passed over the catalyst at progressively greater temperatures, and the radical collection was made over a 25 min period. After obtaining the result at 800 ° C, the catalyst was left in the reagent stream for 9 hr at 800 ° C, and cooled to 500 ° C. The data for the used catalyst were then obtained. Clearly, no maximum was observed in the production rate of $CH_3\cdot$ radicals with respect to temperature. Apparent activation energies of 23 and 26 kcal $mole^{-1}$ were obtained for the fresh and used catalysts, respectively.

In fig. 2B analogous results are shown for the $Sr/La_2O_3$ (*ex* $Sr(NO_3)_2$) catalyst and a $Li^+/MgO$ catalyst that contained 5 wt% Li. Both catalysts had been pretreated in flowing $O_2$ for 0.5 hr at 500 ° C and then evacuated at the same temperature for 5 min. Again, neither set of data exhibits a maximum with respect to temperature, although the $CH_3\cdot$ radical concentration did not continue to increase exponentially at the higher temperatures. This deviation in radical concentration from the expected exponential increase may reflect an oxygen-limited reaction. The $CH_3\cdot$ radical production rate over the $Li^+/MgO$ catalyst was about 14% of that observed over the $Sr/La_2O_3$ (*ex* $Sr(NO_3)_2$) catalyst at 650 ° C, which is qualitatively consistent with the catalytic activities of the two materials.

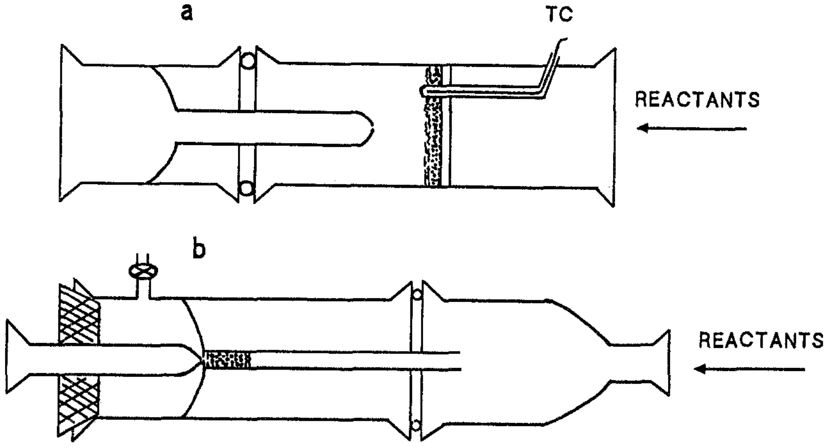

Fig. 1. Reactors used to detect $CH_3\cdot$ radicals: (a) low pressure mode, (b) high pressure mode.

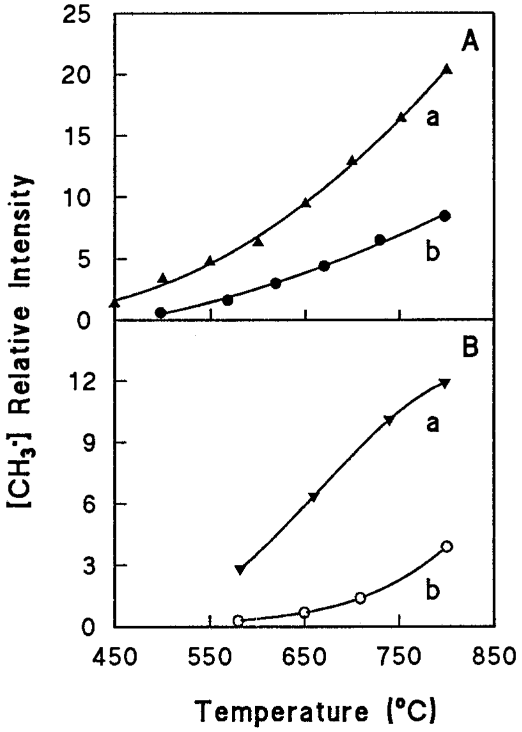

Fig. 2. Relative concentrations of $CH_3\cdot$ radicals obtained in the low pressure mode: (A) with the (a) fresh and (b) used Sr/$La_2O_3$ (A) catalyst; (B) with the (a) Sr/$La_2O_3$ (*ex* $Sr(NO_3)_2$) catalyst and (b) $Li^+$/MgO catalyst. 0.055 g Sr/$La_2O_3$ (A) was used with flow rates of Ar = 3.8, $CH_4 = 1.1$ and $O_2 = 0.10$ mL $min^{-1}$; 0.055 g Sr/$La_2O_3$ (*ex* $Sr(NO_3)_2$) and $Li^+$/MgO was used with flow rates of Ar = 3.8, $CH_4 = 1.1$ and $O_2 = 0.025$ mL $min^{-1}$.

The results obtained in the high pressure mode are similarly compared in fig. 3. Maxima were not observed for either the fresh or the used catalysts. Again, the catalyst was aged by keeping it at 800 °C for 9 hr. The apparent activation energy 17 kcal $mole^{-1}$ for $CH_3\cdot$ radical production over the fresh catalyst. This decrease in activation energy, relative to that obtained in the low pressure mode, may reflect oxygen limitations or secondary reactions involving $CH_3\cdot$ radicals. These same factors may be responsible for the fact that the deactivation was not as great in the high pressure mode as it was in the low pressure mode. That is, in the former mode the observed changes in $CH_3\cdot$ radical concentration do not accurately reflect changes in catalytic activity.

The secondary reactions of $CH_3\cdot$ radicals with catalysts have recently been studied, and it was found that the probability for reaction varies by orders of magnitude, depending on the type of metal oxide [12]. Lithium-promoted MgO is one of the least reactive catalysts with $CH_3\cdot$ radicals. The relative reactivities of $CH_3\cdot$ radicals over fused-quartz, $Li^+$/MgO and Sr/$La_2O_3$ (*ex* $Sr(NO_3)_2$) are compared in table 1. In the experiment, which has been described previously

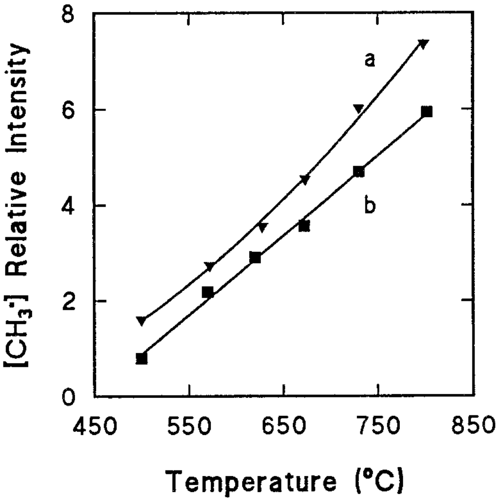

Fig. 3. Relative concentrations of $CH_3\cdot$ radicals obtained in the high pressure mode (a) fresh and (b) used Sr/$La_2O_3$ (A). 0.045 g catalyst was used with flow rates of Ar = 225, $CH_4$ = 70, $O_2$ = 6.6 mL $min^{-1}$.

[13], $CH_3\cdot$ radicals are generated over one type of metal oxide, e.g. $Sm_2O_3$, and they are allowed to react with a second metal oxide, known as the scavenger. The temperature of the scavenger must be sufficiently low so that it does not serve as a source of $CH_3\cdot$ radicals. Because of the activity of Sr/$La_2O_3$ in generating $CH_3\cdot$ radicals it was necessary to keep the scavenger at 240 ° C. Hence, the scavenger was placed 2.3 cm downstream from the $Sm_2O_3$, which was at 650 ° C. At the low pressure in this region ($< 1$ Torr) the radical coupling reaction was relatively inefficient; the $CH_3\cdot$ radical concentration decreased by about 50% before reaching the scavenger.

The data of table 1 confirm that Sr/$La_2O_3$ is about as ineffective as fused-quartz and $Li^+$/MgO in removing $CH_3\cdot$ radicals. These results suggest that $CH_3\cdot$ radicals neither react with the Sr/$La_2O_3$ catalyst nor do they couple extensively on the surface at the relatively low temperature of this experiment. It seems unlikely that $CH_3\cdot$ radical coupling on the surface would increase with temperature as the entropy factor would favor desorption.

Table 1
Relative reactivities of metal oxides with $CH_3\cdot$ radicals [a]

| Metal oxide | Rel. reactivity |
|---|---|
| $Li^+$/MgO | 1 |
| Sr/$La_2O_3$ | 0.8 |
| Quartz | 0.8 |

[a] $Sm_2O_3$ at 650 ° C was used to generate the $CH_3\cdot$ radicals. The mass of scavenger was 0.15 g.

## 4. Conclusions

It is evident that over the temperature range from 450 °C–800 °C the concentration of $CH_3\cdot$ radicals exiting the catalyst bed did not go through a maximum. Thus, the increase in $CH_3\cdot$ radical concentration with respect to temperature agrees qualitatively with the increase in $CH_4$ conversion obtained during the oxidative coupling reaction. The differences in the activation energies of 23-26 kcal mole$^{-1}$ for $CH_3\cdot$ radical generation and the value of 39.4 kcal mole$^{-1}$ for the $CH_4$ conversion may reflect $CH_3\cdot$ radical coupling prior to detection [6] or, more likely, the greater activation energy for $CH_4$ conversion is a result of $CO_2$ poisoning, which becomes less effective as the temperature is increased. The origin of the maxima in $CH_3\cdot$ radical production rate, as reported by Gulcicek et al. [8], is not apparent; however, it is not inherent to the REMPI method as Lee (et al.) [14], using the same technique, found that the formation rate of $CH_3\cdot$ radicals over a $Li^+/MgO$ catalyst increased up to 675 °C and remained essentially constant at higher temperatures.

## Acknowledgment

We acknowledge financial support of this work by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.

## References

[1] J.M. DeBoy and R.F. Hicks, J. Chem. Soc., Chem. Commun. (1988) 982.
[2] J.M. DeBoy and R.F. Hicks, Ind. Eng. Chem. Res. 27 (1988) 1577.
[3] J.M. DeBoy and R.F. Hicks, J. Catal. 113 (1988) 517.
[4] K.D. Campbell, E. Morales and J.H. Lunsford, J. Am. Chem. Soc. 109 (1987) 7900.
[5] D.J. Driscoll, K.D. Campbell and J.H. Lunsford, Adv. Catal. 35 (1987) 139.
[6] K.D. Campbell and J.H. Lunsford, J. Phys. Chem. 92 (1988) 5792.
[7] J.H. Lunsford, Langmuir 5 (1989) 12.
[8] E.E. Gulcicek, S.D. Colson and L.D. Pfefferle, J. Phys. Chem. 94 (1990) 7069.
[9] Y. Feng, J. Niiranen and D. Gutman, J. Phys. Chem. 95 (1991) 6558; J. Phys. Chem. 95 (1991) 6564.
[10] We are indebted to Dr. Mark Barr of AMOCO Oil Company for providing us with a sample of 1 wt% Sr/La$_2$O$_3$.
[11] W. Martir and J.H. Lunsford, J. Am. Chem. Soc. 103 (1981) 3728.
[12] Y. Tong and J.H. Lunsford, J. Am. Chem. Soc. 113 (1991) 4741.
[13] Y. Tong, M.P. Rosynek and J.H. Lunsford, J. Catal. 126 (1990) 291.
[14] S.-P Lee, T. Yu and M.C. Lin, Intl. J. Chem. Kinet. 22 (1990) 975.