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ABSTRACT

Recent interest in the partial oxidation of alkanes has focused attention on the role of surface-generated gas-phase radicals in catalysis. During the oxidative coupling of methane the importance of gas phase $CH_3\cdot$ radicals has been demonstrated using a matrix-isolation electron spin resonance (MIESR) system. This technique will be employed to study several important problems associated with the formation and reactions of hydrocarbon radicals. The production of gas phase propyl radicals over a V-MgO-O catalyst will be investigated to determine the intermediate that is responsible for the observed heterogeneous-homogeneous reaction. The nonoxidative formation of hydrocarbon radicals over supported CrO will be explored to establish whether radical reactions over this catalyst involve gas phase intermediates. In the proposed experiments the cross coupling of methyl radicals with benzyl, allyl, 1-methylallyl and 2-methylallyl radicals will be investigated, again to determine the role of surface-generated gas-phase radicals in these reactions. Secondary reactions of radicals with metal oxide surfaces often dictate product selectivity, therefore reactive sticking coefficients for methyl and allyl radicals colliding with metal oxides will be determined. Such quantitative information is essential for modeling complex heterogeneous-homogeneous reactions. A newly constructed laser-induced fluorescence (LIF) spectrometer will be used to complement the data obtained using the MIESR technique. An initial LIF investigation will focus on the $OH\cdot$ radical, which is a key intermediate in hydrocarbon oxidation reactions. The research will be extended to include CH and possibly CH_2 radicals. The proposed projects will provide conceptual information and quantitative data on an important class of catalytic reactions.

I. SUMMARY OF RECENT PROGRESS

Research in our laboratory supported by the Office of Basic Energy Sciences, Department of Energy, has been largely focused on surface-generated gas-phase methyl radicals and the secondary reactions that occur when these radicals collide with a metal oxide surface. The results of this study have been widely used to interpret results obtained on the oxidative dimerization of methane, which currently is one of the most active areas of catalytic research (1,2). Both qualitative and quantitative data provide convincing evidence that the coupling of gas phase methyl radicals is a significant step in the catalytic conversion of methane to ethane, with its subsequent dehydrogenation to ethylene (3-5).

The selectivity for C_2 hydrocarbons (ethane and ethylene) from CH_4 depends on a number of factors, but one of the most important is the occurrence of secondary reactions between $CH_3\cdot$ radicals and the metal oxide catalyst. For a catalyst to be selective in C_2 formation, these secondary reactions must be slow relative to the coupling reaction. A detailed study of several lanthanide oxide catalysts has provided information on the characteristics of the oxides that promote secondary reactions and the manner in which the oxides may be modified so as to minimize secondary reactions (6,7).

All of the results on the formation and reactions of methyl radicals have been obtained using a matrix-isolation electron spin resonance (MIESR) system that was developed under DOE sponsorship. More recently, a laser-induced fluorescence (LIF) spectrometer has been constructed to detect other gas phase radical species that could not readily be detected by ESR.

A. Quantitative Aspects of Radical Formation and Coupling

Because of the importance of quantitative experiments in demonstrating that the coupling of $CH_3\cdot$ radicals occurrs primarily in the gas phase, the study which began with Li^+/MgO was extended to include the catalysts Na^+/CaO and La_2O_3. The experiment involves the simultaneous determination of the rate of $CH_3\cdot$ radical formation and the rate of C_2 product formation over the same catalyst sample. By comparing the two rates, with the appropriate stoichiometric numbers, the percentage of C_2H_6 produced by the coupling of gas phase $CH_3\cdot$ radicals may be determined. This number is actually a minimum value as some of the $CH_3\cdot$ radicals may couple before they exit the catalyst bed. Previous results using Li^+/MgO as the catalyst showed that 40% of the C_2H_6 produced can be accounted for by the coupling of gas phase radicals (3). More recently values of 28% and 71% have been obtained for Na^+/CaO and La_2O_3, respectively (4,5). In the latter case the catalyst configuration was modified to improve the radical collection efficiency.

Although the importance of the gas phase coupling of $CH_3\cdot$ radicals over several closed-shell oxides was demonstrated by these results, Hatano and Otsuka (8) suggested from an analysis of their kinetic data that the reaction mechanism on the monophasic $LiNiO_2$ catalyst is primarily a surface phenomenon. A study was carried out using the MIESR system to determine whether the transition metal oxides, $LiNiO_2$ and $NaMnO_4/MgO$ are essentially different from other metal oxides with respect to the generation and coupling of gas phase $CH_3\cdot$ radicals (9). The results, described in more detail in Appendix A, demonstrate that the mechanism over these transition metal oxides is the same as found previously over Li^+/MgO; i.e., the gas phase coupling reaction is significant.

Another quantitative aspect of the reaction is the activation energy for $CH_3\cdot$ radical formation. Over a range of conditions we have observed over Li^+/MgO an apparent activation energy of 24-28 kcal/mol, based on the number of radicals collected. It is gratifying that using resonance-enhanced multiphoton ionization (REMPI) Lin and co-workers (10) have observed a very similar value of 23 kcal/mol over the same type of catalyst. If one considers that the measured $CH_3\cdot$ radical concentrations represent steady state values, then it may be shown that the actual activation energy is *ca.* 48-56 kcal/mol, which agrees well with the overall activation energy of 55 kcal/mol for CH_4 conversion (4,11).

B. Secondary Reactions of Methyl Radicals with Metal Oxides

The lanthanide oxides offer an excellent opportunity to study the relationship between the activity for methyl radical formation, secondary reactions of methyl radicals with an oxide, and overall catalytic properties as members of the series vary greatly with respect to each of these factors. A study has been completed on the radical forming ability of selected members of the series and the secondary reactions that occur among these oxides (6,12). The efficiency of the secondary reaction was determined by placing the oxide of interest between a radical source (CH_4 and O_2 over Sm_2O_3)

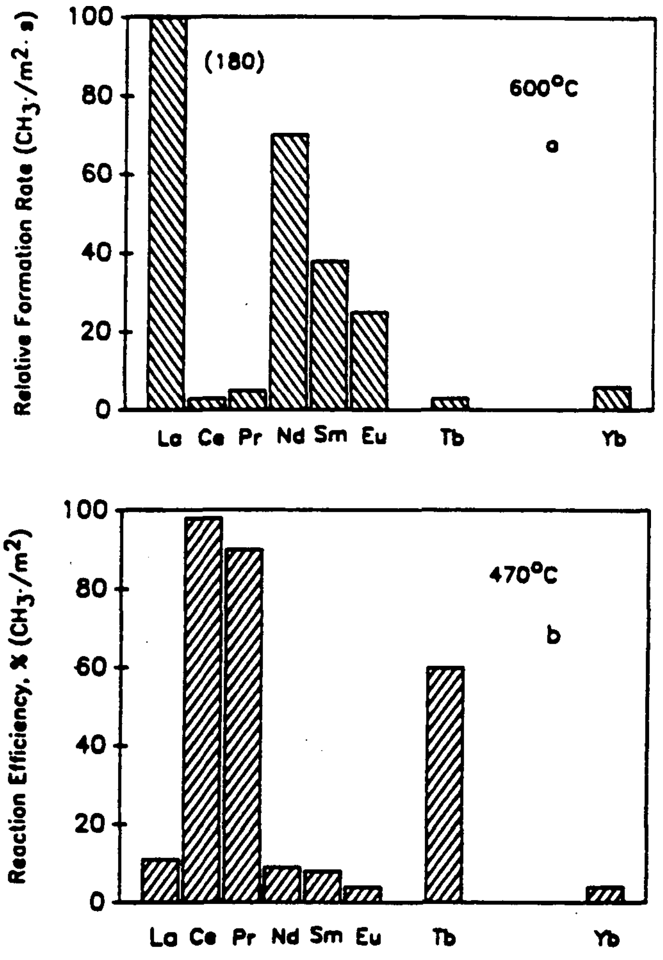


Figure 1. Comparison of (a) $CH_3\cdot$ formation rate and (b) rate of reaction with selected members of the lanthanide oxide series.

and the leak into the high-vacuum region of the MIESR system. The results are summarized in Fig. 1. First it should be noted that except for Yb_2O_3 there is an inverse relationship between radical formation ability and the efficiency for reaction with the radicals. The oxides fall into three categories with respect to radical formation/reaction: (i) the more basic sesquioxides are good radical formers, but they do not react extensively with the radicals; (ii) those oxides which exhibit multiple cationic oxidation states react extensively with the oxides; and (iii) Yb_2O_3 is neither a very good radical former nor a good radical scavenger. Those metal ions having multiple oxidation states are believed to react according to

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

where the methoxide ion would be an intermediate in the formation of CO_2.

Generally, in the pure form only the basic sesquioxides are good oxidative dimerization catalysts, which is consistent with their ability to produce, but not react with $CH_3\bullet$ radicals. But it is also known that certain of the oxides having multiple oxidation states can be transformed into selective catalysts by the addition of Na_2CO_3. Using CeO_2 as an example it has been shown (Fig. 2) that the addition of Na_2CO_3 decreases the $CH_3\bullet$ reaction efficiency, increases the rate of $CH_3\bullet$ radical formation and increases the C_2 selectivity. Thus, the catalyst was transformed from being totally nonselective to one which gave 60% C_2 selectivity (6).

This research has been extended recently by modifying with Na_2CO_3 three examples of the classes noted above. For the study, La_2O_3, CeO_2 and Yb_2O_3 were chosen (7). It was found by using ion scattering spectroscopy (ISS), that the surface of the CeO_2 catalyst promoted with Na_2CO_3 was completely covered with sodium-containing compounds, which suggests that a sodium oxide (e.g. Na_2O_2) was responsible for the oxidative dimerization activity, rather than a new oxide phase involving Na and Ce. All of the sodium-modified catalysts, and even pure Na_2CO_3, exhibited approximately the same specific activity for CH_4 conversion and C_2 selectivity. The Na^+/Yb_2O_3

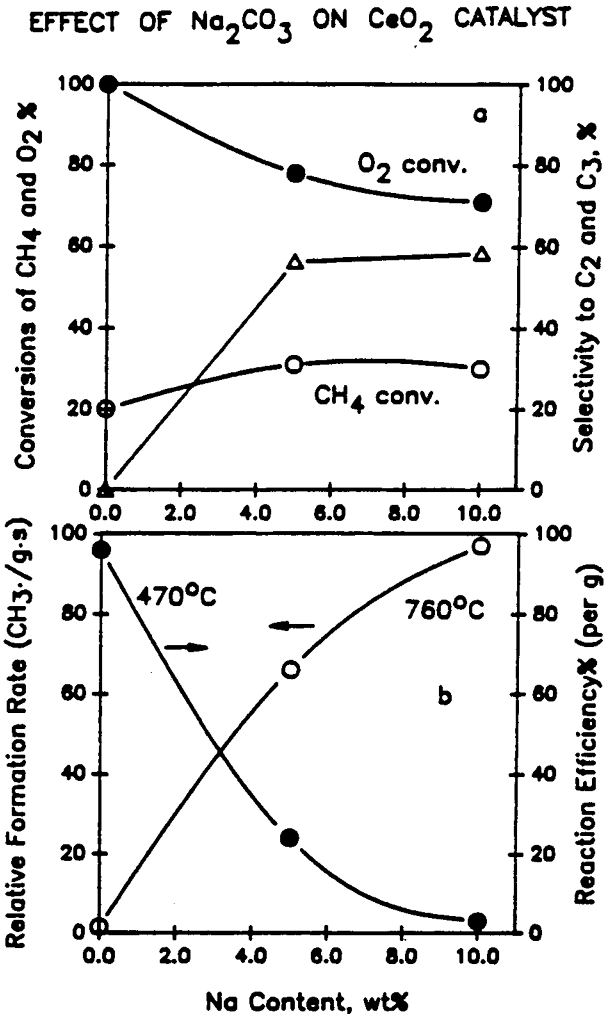


Figure 2. Effect of Na_2CO_3 addition to CeO_2 on (a) the catalytic oxidation of CH_4 and (b) the production of $CH_3\cdot$ radicals and their reaction with the catalyst: ○, CH_4 conversion; ●, O_2 conversion; △, combined C_2 and C_4 selectivity; ◇, relative formation rate of $CH_3\cdot$ radicals; ◆, reaction efficiency of $CH_3\cdot$ radicals with the catalysts. The catalytic reaction was carried out at 770°C, 1 atm, and a flow rate of 34 mL min^{-1}. The partial pressures of CH_4 and O_2 were 180 and 67 Torr, respectively. The $CH_3\cdot$ formation rates and the reaction efficiencies were determined with the catalysts at 760 and 470°C, respectively. The gas pressures were 1 and 1.5 Torr for the two cases.

catalyst was somewhat more active than the others, which is consistent with the observation that sodium compounds did not cover the surface of Yb_2O_3 to the extent that it covered CeO_2 and La_2O_3. There was also a good correlation between the activity for CH_4 conversion and the rate of $CH_3\cdot$ formation. Thus, the lanthanide oxides mainly function as supports for the sodium carbonate/oxide phase, and in some cases they supply oxygen to this phase when molecular oxygen is not available (13). Additional details on this study are given in Appendix B.

The reactions of $CH_3\cdot$ radicals with other metal oxides and the first order rate constants for several of these oxides are shown in Fig. 3. The rate constants differ by more than two orders of magnitude, with ZnO and MoO_3 being the most active. The apparent activation energies are 2.6 and 5.7 kcal/mol for the reaction with ZnO and MgO, respectively. Currently we are attempting to determine for the first time the reactive sticking coefficient of $CH_3\cdot$ radicals reacting with metal oxides. As described in a subsequent section these studies will be the subject of continuing research.

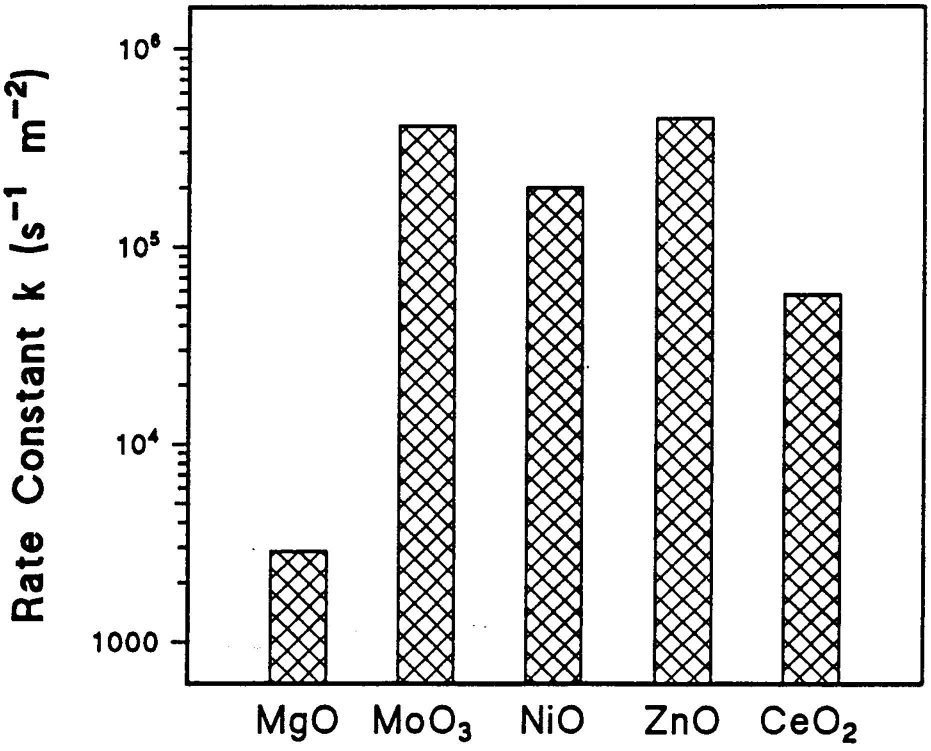


Figure 3. First order rate constants for the reactions of $CH_3\cdot$ radicals with metal oxides. The oxides were at °C.

C. Laser-Induced Fluorescence of Hydroxyl Radicals

As a complementary method to the MIESR technique for the study of reactive intermediates important in the conversion of methane to higher hydrocarbons, we are presently developing the LIF technique to probe gas-phase radicals near the catalyst surface. Initial work involves a study of the OH• radicals. These radicals may either be directly generated by the catalyst or generated by subsequent chain-branching reactions involving $CH_3\cdot$ radicals in the gas phase. There are two main reasons for choosing the OH• radical for the initial study: first, the importance of OH• in the combustion reactions of hydrocarbons is well known, and, second, the spectroscopy of this radical has been thoroughly investigated, perhaps more than any other radical.

The system that has been constructed produces tunable UV laser pulses (with sub-wave number resolution) by frequency doubling the output of a tunable dye laser which is pumped by a Q-switched Nd:YAG laser at 10 Hz. Excitation spectra are normally obtained by collecting the fluorescence signal induced by 500 laser shots per point. The spectrum of OH• radicals produced in a flame is shown in Fig. 4, and preliminary results have been obtained during CH_4 oxidation at 680°C over a La_2O_3 catalyst.

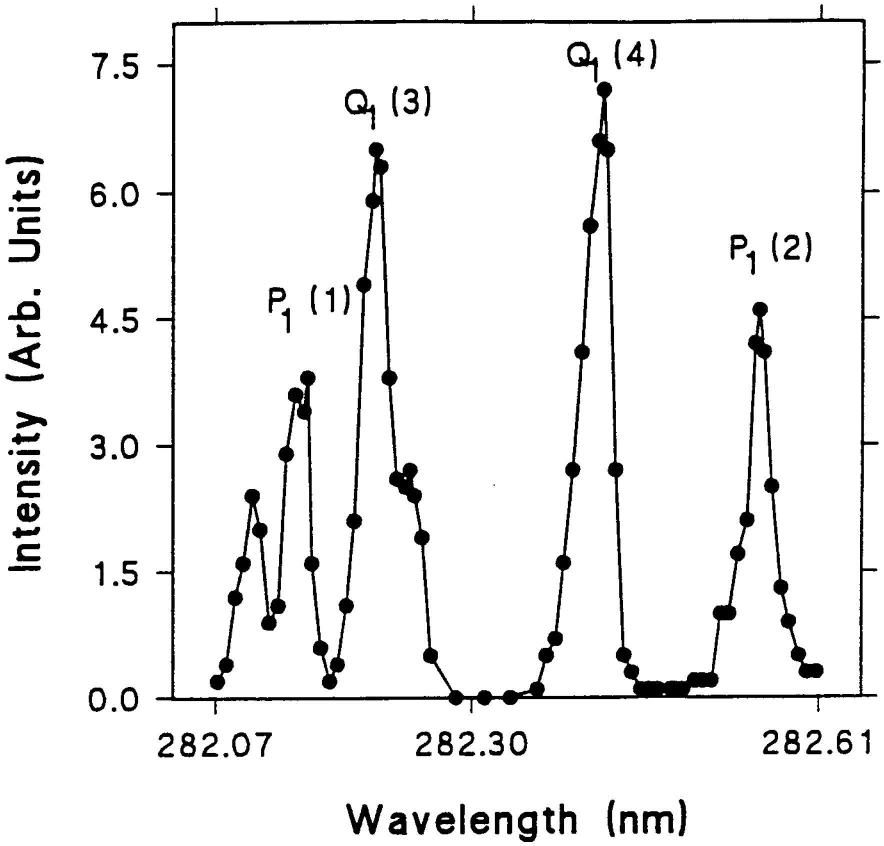


Figure 4. Excitation spectrum of OH• radical in a methane/air flame at atmospheric pressure. The fluorescence was detected near 309.0 nm with an instrument bandwidth of 1.5 nm. The four major peaks have been tentatively assigned as noted.

D. Papers Published or Submitted

1. "Gas-Phase Coupling of Methyl Radicals during the Catalytic Partial Oxidation of Methane," K.D. Campbell, E. Morales and J.H. Lunsford, J. Am. Chem. Soc., 109, 7900-7901 (1987).
2. "Methane Activation by the Lanthanide Oxides," K.D. Campbell, H. Zhang and J.H. Lunsford, J. Phys. Chem., 92, 750-753 (1988).
3. "Contribution of Gas-Phase Radical Coupling in the Catalytic Oxidation of Methane," K.D. Campbell and J.H. Lunsford, J. Phys. Chem., 92, 5792-5796 (1988).
4. "The Role of Surface-Generated Gas-Phase Radicals in Catalysis," J.H. Lunsford, Langmuir, 5, 12-16 (1989).
5. "Secondary Reactions of Methyl Radicals with Lanthanide Oxides: Their Role in the Selective Oxidation of Methane," Y.-D. Tong, M.P. Rosynek and J.H. Lunsford, J. Phys. Chem., 93, 2896-2898 (1989).

6. "Gas-Phase Coupling of Methyl Radicals during the Partial Oxidation of Methane over Transition Metal Oxide Catalysts," Y. Tong and J.H. Lunsford, J. Chem. Soc., Chem. Commun., in press.

7. "The Role of Sodium Carbonate and Oxides Supported on Lanthanide Oxides in the Oxidative Dimerization of Methane," Y. Tong, M.P. Rosynek and J.H. Lunsford, submitted to J. Catal.

II. SCOPE OF PROPOSED INVESTIGATION

Research carried out in our laboratory using the MIESR system has largely established the role of surface-generated gas-phase $CH_3\cdot$ radicals during the oxidative coupling of CH_4. Secondary reactions of $CH_3\cdot$ radicals with metal oxides have been studied for the first time. The reactions may significantly influence the selectivities that are achieved during the partial oxidation of CH_4. In future studies both the qualitative and quantitative aspects of these secondary reactions will be investigated in more detail. Moreover, the scope of the work will be expanded to include more complex hydrocarbon systems and reactions that are not necessarily oxidative. In addition to the more conventional temperatures of 600-800°C, reactions will be carried out at temperatures up to 1000°C. Laser-induced fluorescence (LIF) spectroscopy will continue to be developed as a complementary method to detect other gas-phase intermediates in the oxidation reactions.

A. Reactions of Methyl Radicals with Metal Oxides

In a conventional catalyst bed methyl radicals that emanate into the gas phase undergo many secondary collisions with the surface before they react with another methyl radical. If these surface collisions result in a reaction, then the selectivity of the overall oxidation reaction will be changed. As described in the previous section, the addition of sodium carbonate to cerium oxide markedly altered the selectivity in CH_4 oxidation from CO_2 to C_2H_4 and C_2H_6 (6). This change in selectivity was largely a result of a modification in the catalyst so that it became less reactive with $CH_3\cdot$ radicals. Although in this particular case the reactions of the methyl radicals with the metal oxide catalyst resulted in the formation of CO_2, at lower temperatures and on other oxides one might expect that the alkoxide intermediates could further react to yield methanol and formaldehyde.

We are now interested in determining the more quantitative aspects of these surface reactions and the surface species that are formed. As far as we are aware the reactive sticking coefficient of a simple alkyl radical with a metal oxide has not been determined. Such information is crucial for the development of realistic models to describe, for example, the partial oxidation of CH_4 over a Li^+/MgO catalyst.

With the MIESR system it is possible to determine quantitatively the number of $CH_3\bullet$ radicals that have been removed from a gas stream. We are now developing a Knudsen cell that will replace the scavenger bed used to obtain the results of Figs. 1-3. The Knudsen cell will function as a batch reactor in which the $CH_3\bullet$ radical will both couple and react with a metal oxide catalyst. At low pressures (e.g. 10^{-3} torr) the coupling reaction will be negligible relative to the collisions with the oxide surface. The oxide will either be coated on the inner walls of the reactor or will be dispersed in quartz wool which will partially fill the reactor. A blank experiment without the oxide will provide information on the number of radicals lost through the coupling reaction. We have already show that methyl radicals do not extensively react with fused quartz. By controlling the size of the exit from the cell it will be possible to control the residence time of the radicals in the cell. The one remaining parameter that needs to be determined is the pressure in the cell. Initially this will be done by calculating the conductance in and out of the cell, but ultimately a thermal conductivity detector or an ion gauge detector will be constructed in a replica of the actual cell. It would not be possible to have the gauge in a working cell because the metal components could react extensively with the radicals. Once the cell is developed the reactive sticking coefficient of $CH_3\bullet$ radicals with ZnO, CeO_2 and MgO will be determined. These oxides were chosen because the qualitative results indicate that they exhibit a wide range of reactivities with respect to $CH_3\bullet$ radicals.

The second part of the problem involves the nature of the surface species that are formed when $CH_3\bullet$ radicals react with the metal oxides. We previously suggested that a reductive addition reaction occurs in which the metal ion is reduced and a methoxide species is formed on the surface (reaction 1). Currently ESR and IR experiments are being carried out to determine whether this type of reaction indeed occurs. The MIESR system has been modified so that metal oxides after exposure to $CH_3\cdot$ radicals may be transferred to an ESR or an IR spectrometer. Preliminary results tend to confirm our expectation. For example, with MoO_3/SiO_2 as the reactive oxide the characteristic ESR spectrum of Mo(V) is much more intense after exposure to a gas stream containing methyl radicals, as shown in Fig. 5. Moreover, with CeO_2 as the reactive oxide infrared bands at *ca.* 2840 cm^{-1} and at 1095 cm^{-1} confirm the presence of methoxide ions.

As a result of collaboration with Prof. Peter Stair at Northwestern University the PI has been introduced to an alternate technique for producing $CH_3\cdot$ radicals that involves the thermal decomposition of azomethane. For the purpose of studying the species that are formed on the surface this method has an advantage as no oxygen is required. Therefore, there are no oxygenated

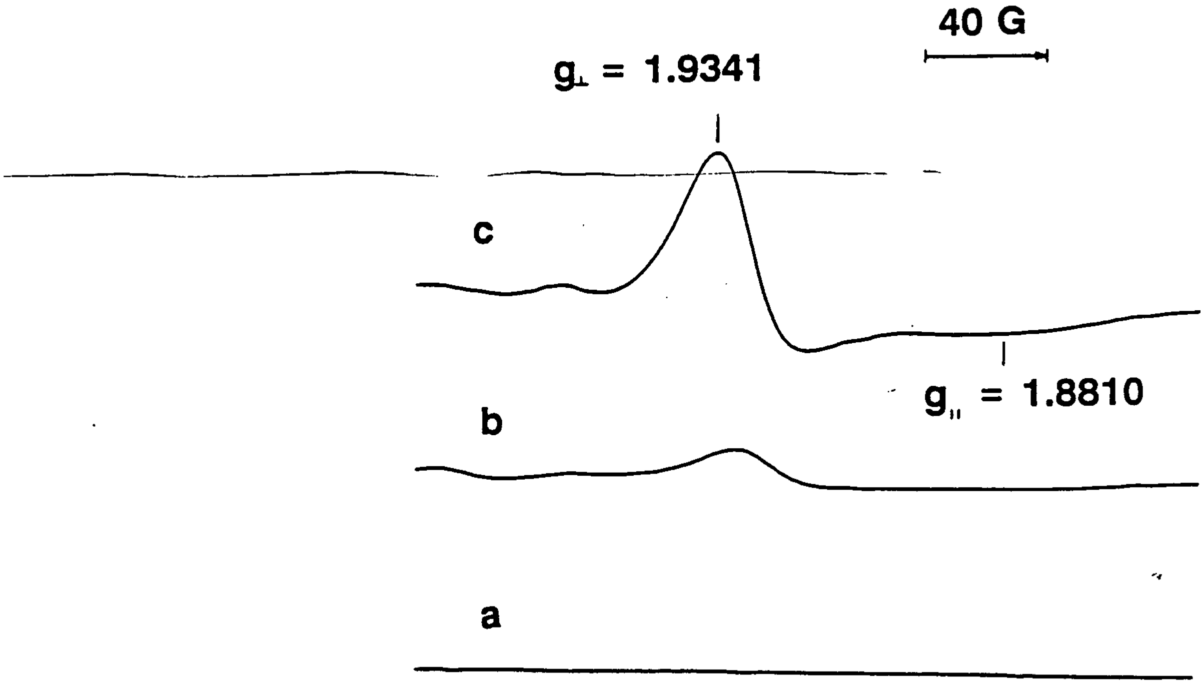


Figure 5. ESR spectra of 2% Mo/SiO_2: (a) in oxidized form, (b) after exposure to flowing CH_4, (c) after exposure to flowing $CH_3\cdot$ and CH_4. The 2% Mo/SiO_2 was at 25°C.

gas phase products to complicate the interpretation surface infrared spectra. Infrared experiments designed to identify the surface species will be carried out using the thermal decomposition of azomethane, as well as the reaction of CH_4 and O_2 over Sm_2O_3, for the production of $CH_3\cdot$ radicals. In some experiments CD_4 will be used instead of CH_4 to aid in the interpretation of the IR bands.

Finally, it should be noted that other reactions between gas phase hydrocarbon radicals and metal oxides are of interest in systems that are characterized by heterogeneous-homogeneous reactions. Keulks and co-workers (14) have proposed that allyl radicals formed from propylene react with bismuth molybdate to produce acrolein. Our earlier work with the MIESR system indicate that allyl radicals react with MoO_3 (15). We now plan to extend these studies to obtain more quantitative data on the reactions of allyl radicals for comparison with the reactions of methyl radicals.

B. Alternate Radical Coupling Reactions

Most of the research up to this point has focused mainly on the coupling of $CH_3\cdot$ radicals to form C_2H_6; however, recently studies by two groups (16,17) have demonstrated that it also is possible to form the cross coupling product, ethyl benzene, by oxidatively reacting methane and toluene over a modified Li^+/MgO catalyst. This reaction presumably involves the coupling of methyl and benzyl radicals. Combined styrene and ethylbenzene selectivities of 37% have been achieved at a toluene conversion of 27%. We briefly looked for the formation of benzyl radicals from toluene over a Bi_2O_3 and MgO catalysts and observed a broad line centered at $g \simeq 2.00$ (18). Although no hyperfine structure was detected, the spectrum is consistent with an unresolved benzyl radical spectrum. The benzyl radical spectrum in solution is characterized by four different types of protons having a_H values of 1.75, 5.14, 6.14 and 16.35 G. For the π radicals trapped in an Ar matrix one might expect anisotropy both in the g and the hyperfine tensor, thus the observation of the broad unresolved spectrum is not surprising. The presence of benzyl radicals in the gas phase suggests that the coupling with methyl radicals occurs there, which is unexpected considering the fact that no dibenzyl or stilbene was detected (17). Apparently the coupling of benzyl radicals with methyl radicals is much more rapid than the coupling of benzyl radicals with each other.

In the proposed experiments we first plan to analyze the ESR spectrum in more detail to confirm that it indeed is characteristic of benzyl radicals. For purposes of comparing spectra, benzyl radicals also will be prepared at low temperatures by irradiation of toluene in the Ar matrix. Once we are confident that benzyl radicals are being formed in the MIESR system, the conditions will be optimized in order to obtain the maximum gas phase concentration of this intermediate. Under these same conditions the gas phase will be analyzed by gas chromatography for dibenzyl and stilbene. Different catalysts will be used to determine the one that is best for conversion and selectivity.

After the single hydrocarbon component has been studied mixtures of methane and toluene will be introduced into the MIESR system. The sharp, four-line spectrum of the $CH_3\cdot$ radicals should be easy to resolve from the broad line that we currently attribute to the benzyl radical. Thus it should be possible to simultaneously follow the concentrations of both radical species. Likewise, the stable products will be analyzed in the same reactor system, as well as in a separate catalytic system that may be more suitable for obtaining higher yields of ethylbenzene and styrene. It is conceivable that the coupling of methyl radicals and benzyl radicals would be so rapid in the gas phase, or even on the surface, as to prevent the detection of gas phase benzyl radicals. We have the ability to place the sampling leak into the high vacuum region of the MIESR system at various distances from the exit of the catalyst bed and to determine the rate of disappearance of the respective radicals from the gas phase. Such a method was previously used to determine the rate constant for $CH_3\cdot$ radical coupling, which compared well with literature values (3,4).

Numerous other cross coupling studies could be carried out in a similar manner. Because of our previous work in obtaining allyl, 1-methylallyl and 2-methylallyl radicals from propylene, 1-butene and isobutylene, respectively (19), we are interested in coupling these radicals with methyl radicals.

The allyl radicals have the advantage of being relatively stable, and in addition, their spectra are well characterized. We have previously shown that Li^+/MgO catalysts are effective in generating methyl radicals from methane and allyl radicals from propylene under comparable conditions (20). It would be of interest to compare the cross coupling in these systems with that in the methane/toluene system.

C. Other Heterogeneous-Homogeneous Oxidation Reactions.

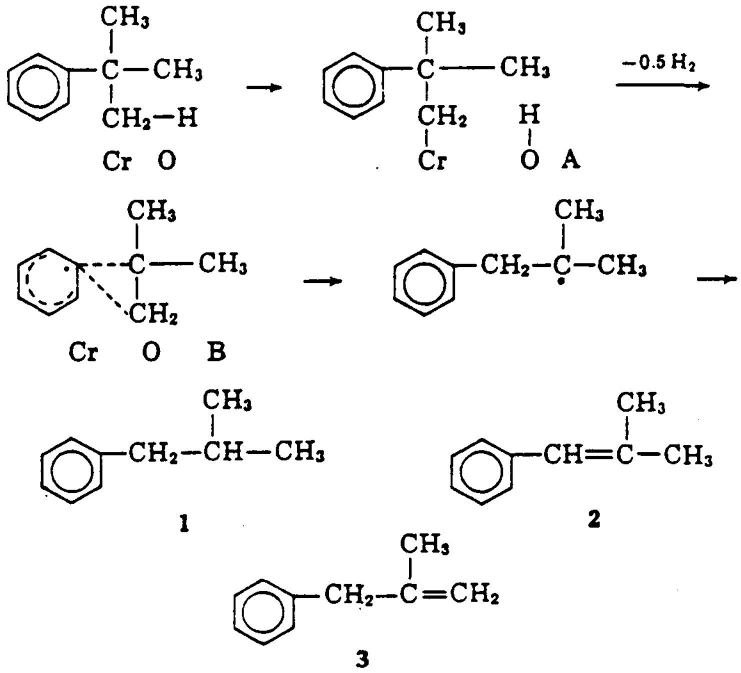
Nguyen and Kung (21) have recently demonstrated that the oxidative dehydrogenation of propane over a V-MgO-O catalyst is one example of a heterogeneous-homogeneous reaction in which surface-generated intermediates promote reactions in the gas phase. The reactive species are believed to be either propyl or hydroxyl radicals, and modeling studies suggest that the propyl radicals may be the most important (22). It is estimated that the rate of desorption of propyl radicals may be as great as 23% of the rate of reaction of propane on the catalyst surface at 570°C.

In collaboration with Professor Kung, we plan to investigate the emanation of propyl and allyl radicals from the surface of V-Mg-O and related catalysts using our MIESR system. Hydroxyl radicals will be observed with the LIF system (see below). The radical-forming properties of selective oxidation catalysts will be compared with ZnO, which is not selective for the partial oxidation of propane.

Still another system that deserves further attention is the possible generation of vinyl radicals from ethylene. The oxidation of ethylene is a crucial factor in the oxidative dimerization of methane because it places a limit on the C_2 (ethane plus ethylene) yield. Earlier work in our laboratory indicated that vinyl radicals were not released into the gas phase, but this study was carried out at only 475°C (20). The experiments will be extended to the much higher temperatures of 700-900°C, at which the oxidative dimerization reactions are normally carried out.

D. Nonoxidative Radical Formation

It has been demonstrated by Pines and co-worker (23,24) that a number of skeletal rearrangement reactions occur over supported chromia via a radical reaction. One such example is the conversion of t-butylbenzene to the products isobutylbenzene (**1**), β, β-dimethyl-styrene (**2**) and isobutenylbenzene (**3**), according to the scheme:



An even simpler reaction that occurs over the same catalyst is the dehydrogenation of C_2H_6 to C_2H_4 and H_2. We have shown that this reaction takes place at temperatures of about 500°C over CrO derived either from α-Cr_2O_3 or supported chromia (25). It is of interest to determine whether gas phase radicals are produced during these and related reactions. In the case of ethyl radicals the competing reaction

$$C_2H_5\bullet \rightarrow C_2H_4 + H\bullet \qquad (2)$$

is rapid and may occur before desorption of the ethyl radical, but with other molecules the sequence of events may be reversed.

The production of gas phase $CH_3\cdot$ radicals over CrO also will be investigated. Although the reaction

$$2CH_4 \rightarrow C_2H_6 + H_2 \tag{3}$$

is thermodynamically unfavorable at temperatures below 1,000°C, it may be possible to detect methyl radicals in small concentrations by passing CH_4 over supported CrO at considerably lower temperatures.

Supported CrO may be particularly suitable for these radical-forming reactions because it is difficult to reduce chromium below Cr(II), thus reactions of alkyl radicals with the oxide are minimized. Instead, rearrangement reactions, loss of another hydrogen atom or desorption of the radical into the gas phase may occur. As noted by Pines (24), it is necessary to poison with Na^+ any acid sites on the alumina support in order to avoid acid-catalyzed reactions.

In the proposed study hydrocarbons such as methane, ethane and t-butylbenze would be passed over a reduced Cr_2O_3/Al_2O_3 catalyst, and the gas phase radicals, if present, would be identified using the MIESR system. The temperature of the catalyst would be varied from 300 to 1,100°C, depending on the hydrocarbon. Blank experiments would, of course, be needed to determine the thermal (i.e. noncatalytic) contribution to the observed product. The formation of $CH_3\cdot$ radicals from CH_4 would complement other studies in our laboratory which are addressing reactions at higher temperatures than those normally used in oxidation coupling reactions. Because of the purely thermal reactions at these high temperatures the reactor part of the MIESR system will have to be modified so that the residence time in the heated zone will be only a few milliseconds.

E. Laser-Induced Fluorescence Spectroscopy

Our recently constructed LIF spectrometer will initially be used to study the role of $OH\cdot$ radicals in the partial oxidation of alkanes. When CH_4 and O_2 are simultaneously passed over a catalyst, the surface-generated $CH_3\cdot$ radicals may enter into chain-branching gas-phase reactions of the type

$$CH_3\cdot + O_2 \rightarrow CH_3O\cdot + O \tag{4}$$

$$CH_4 + CH_3O\cdot \rightarrow CH_3\cdot + CH_3OH \tag{5}$$

$$CH_4 + O \rightarrow CH_3\cdot + OH\cdot \tag{6}$$

$$CH_4 + OH\cdot \rightarrow CH_3\cdot + H_2O \tag{7}$$

These gas phase reactions, which are a source of additional $CH_3\cdot$ radicals, may actually consume more methane than is reacted on the surface. The $OH\cdot$ radical is believed to be a major chain carrier in these reactions, thus it is an important intermediate to follow.

The possible role of $OH\cdot$ radicals during the oxidation of propane over V-Mg-O catalysts was noted previously. The detection of $OH\cdot$ radicals using the LIF system will complement the detection of propyl and allyl radicals using the MIESR system.

One goal of the research on the catalytic hydrocarbon oxidation reactions will be to determine the extent to which the observed $OH\cdot$ radicals are produced on the surface versus the gas phase. This problem will be addressed by varying the hydrocarbon and oxygen partial pressures, the flow rates of the reactants and by substituting N_2O for O_2 as the oxidant. The extent of the chain reactions depends on the reaction time and the presence of O_2. The experimental results will be interpreted in terms of gas phase reaction models that are currently being used in our laboratory. It is important to note that both the emanation of $OH\cdot$ radicals from the surface and their formation through chain-branching gas phase reactions is of interest in understanding these partial oxidation reactions.

It should also be possible to generate $OH\cdot$ radicals by reacting O_2 and H_2O over a Li^+/MgO catalyst that contains $[Li^+O^-]$ centers (26). The $OH\cdot$ intermediate should be formed by the reaction

$$O_s^- + H_2O \rightarrow OH^- + OH\cdot. \tag{8}$$

The overall reaction is thermally neutral as the final products, O_2 and H_2O, are the same as the reactants.

In addition to the OH• radicals, the CH_2 and CH radicals also are of interest as they may be formed during the high temperature reactions of hydrocarbons. Detection of the methylene radical, CH_2, is a problem in that its triplet ground state is not amenable to observation by LIF spectroscopy. The lowest lying $^1A_1$ singlet state has been studied by LIF spectroscopy, but it is 8 kcal/mol above the ground state (27), and even at 1000°C only about 2% of the molecules would be in the singlet state at equilibrium. In reality the concentration would be less as the singlet state is highly reactive. Nevertheless we shall attempt to detect CH_2 by LIF. The CH radical has been observed in flames using LIF spectroscopy (28), and it will be studied in the catalytic systems.

At sufficiently low pressures so that multiple collisions can be avoided, it is possible to determine by LIF the internal energies of radicals emitted from a surface. Lin and co-workers (29) measured the internal energy distribution of OH• radicals which desorbed from polycrystalline and single crystal Pt surfaces at 860°C. By using planar metal oxide films and low pressures we should be able to obtain analogous data on OH• radicals in our system. The problem of determining absolute concentrations of radicals by LIF has recently been addressed, and it now appears possible to make such measurements with an estimated accuracy of ±30% (29).

III. SIGNIFICANCE OF THE PROPOSED WORK

Natural gas constitutes a vast hydrocarbon resource; however, the utilization of this resource has not been fully realized because of the difficulties in converting alkanes into more useful chemicals and liquid fuels. The conversion of simple alkanes (e.g., methane) often requires severe catalytic conditions that result in heterogeneous-homogeneous reactions. Surface-generated gas-phase radicals, which are the subject of the proposed study, play a major role in the homogeneous component through the coupling of hydrocarbon radicals and if oxygen is present, through chain branching reactions. The former usually results in the desired product and the latter in the complete oxidation. The research described here will provide information on the classes of catalysts that form these radicals, the conditions under which they are formed, and their subsequent reactions in a catalytic system. This research also may find application in the emerging field of catalytic combustion, which has the potential for reducing air pollution.

At a more fundamental level the reactions of radicals with metal oxide surfaces has not been previously addressed except in a very cursory manner. In order to fully understand the complicated network of reactions that occur in heterogeneous-homogeneous systems it is essential that data be obtained on one of the more important elementary steps; namely, the specific reaction rate of the hydrocarbon radicals with oxides that are important in catalysis. Moreover, the surface species that are formed will largely dictate the effect of these surface reactions on product selectivity.

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V. CURRENT SUPPORT AND PENDING PROPOSALS

A. Summary of Current Support

1. "Gas-Solid Interactions at Semiconductor Surfaces," National Science Foundation (CHE-8617436), $262,000, starting date - June 1, 1987, 3 year grant.
2. "A Study of Catalysts and Mechanisms in Synthesis Reactions," Department of Energy (DE-AS05-76ER05220), $353,415, starting date - January 1, 1989, 3 year grant.
3. "New Directions for the Catalytic Conversion of Methane: Use of Alkali Salt Melts and Li-MgO Solid Solutions," Gas Research Institute, $350,000, starting date - November 1, 1988, 3 year grant.
4. "Synthesis and Characterization of Zeolites Having Superacidity," Texas Advanced Technology Program, $212,000, starting date - January 1, 1990, 2 year grant, with Dr. Rayford Anthony.
5. "Surface-Catalyzed Conversion of Methane to Acetylene and Aromatic Hydrocarbons," Texas Advanced Research Program, $80,000, starting date - January 1, 1990, 2 year grant, with Dr. Michael Rosynek.
6. "Acid Catalysis over Molecular Sieves and Zeolites," Dow Chemical Co., $56,746, starting date - November 15, 1989, 1 year grant.

B. Pending Proposal

1. "Gas-Solid Interactions at Semiconductor Surfaces," National Science Foundation, $352,257, 3 years.

BIOGRAPHICAL DATA

NAME AND ADDRESS

Dr. Jack H. Lunsford
Department of Chemistry
Texas A&M University

PRESENT POSITION

Professor of Chemistry

PLACE OF BIRTH AND DATE

Houston, Texas - February 6, 1936

EDUCATION

B.S., Texas A&M University, 1957
Ph.D., Rice University, 1962

POSITIONS HELD

1961-1962, Assistant Professor, University of Idaho
1962-1965, 1st Lieutenant, U.S. Air Force
1965-1966, Assistant Professor, Sam Houston State College
1966-1968, Assistant Professor, Texas A&M University
1968-1971, Associate Professor, Texas A&M University
1971-1980, Professor and Administrative Officer, Texas A&M University
1980-Present, Professor, Texas A&M University

PROFESSIONAL APPOINTMENTS

- Editorial Board, **Journal of Catalysis** (1976-1984, 1988-present)
- Editorial Board, **Langmuir** (1990)
- Editorial Board, **Zeolites** (1981-1988)
- Chairman, Gordon Conference on Catalysis, 1976
- ACS Committee on Professional Training (1977-1980)
- Gordon Research Conferences Council (1979-1982)
- Executive Council Committee, Division of Colloid and Surface Chemistry (1978-1983)
- Board of Directors, Catalysis Society
- Chairman, Catalysis Society Meeting, 1985

AWARDS AND HONORS

- Paul H. Emmett Award in Fundamental Catalysis, 1975
- Distinguished Faculty Achievement Award, 1982
- American Chemical Society, Southwest Regional Award, 1983
- The Catalysis Society of Metropolitan New York Award for Excellence in Catalysis, 1986
- Guggenheim Fellow, 1985-1986
- Langmuir Lecture, Division of Colloid and Surface Chemistry, 1988
- Burwell Lectures, North American Catalysis Society, 1989
- Cherry Emerson Lecturer, Emory University, 1989
- V.N. Ipatieff Lecturer, Northwestern University, 1990

PRINCIPAL AREAS OF INTEREST

Physical Chemistry: Surface chemistry and catalysis, using modern spectroscopic techniques.

CONSULTING

Dow Chemical Co. (1979-1981)
Phillips Petroleum Co. (1981-1988)
Oxy USA, Inc. (1989-   )

PUBLICATIONS

(Since 1980)

93. "Spectroscopic Characterization of Tetrakis-(pyridine)copper(II) Complexes in Zeolite Y," P.-S.E. Dai and J.H. Lunsford, **Inorg. Chem.**, 19, 262-264 (1980).

94. "A Study of Ruthenium in Zeolite-Y by X-Ray Photoelectron Spectroscopy," L.A. Pedersen and J.H. Lunsford, **J. Catal.**, 61, 39-47 (1980).

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151. "Determination of Framework Aluminium Content in Dealuminated Y-type Zeolites: A Comparison Based on Unit Cell Size and Wavenumber of i.r. Bands," J.R. Sohn, S.J. DeCanio, D.J. O'Donnell and J.H. Lunsford, **Zeolites**, 6, 225-228 (1986).

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155. "Acid Catalysis by Dealuminated Zeolite-Y. 2. The Roles of Aluminum," J.R. Sohn, S.J. DeCanio, P.O. Fritz and J.H. Lunsford, **J. Phys. Chem.**, 90, 4847-4851 (1986).

156. "Characterization of $[Li^+O^-]$ Centers in Lithium-Doped MgO Catalysts," J.-X. Wang and J.H. Lunsford, **J. Phys. Chem.**, 90, 5883-5887 (1986).

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158. "A Solid-State NMR Study of Acid Sites in Zeolite Y Using Ammonia and Trimethylamine as Probe Molecules," W.L. Earl, P.O. Fritz, A.A.V. Gibson, and J.H. Lunsford, **J. Phys. Chem.**, 91, 2091-2095 (1987).

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161. "Formation of Gas-Phase Methylally Radicals during the Oxidation of 1-Butene and Isobutylene over Bismuth Oxide," D.J. Driscoll, W. Martir, and J.H. Lunsford, **J. Phys. Chem.**, 91, 3585-3588 (1987).

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