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A STUDY OF CATALYSTS AND MECHANISMS IN SYNTHESIS REACTIONS

Progress Report

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INTRODUCTION

It is becoming increasingly evident that surface-generated gas-phase radicals play an important role in the catalytic oxidation of hydrocarbons. The most notable example is the oxidative coupling of methane which is initiated by the formation of $CH_3\cdot$ radicals at the surfaces of metal oxides. The radicals emanate into the gas phase where they couple to form ethane.[1] These same catalysts are capable of generating $C_2H_5\cdot$ radicals from ethane, only in this case the reaction

$$C_2H_5\cdot + O_2 \rightarrow C_2H_4 + HO_2\cdot \qquad (1)$$

is predominant over the coupling reaction. Although the evidence is less direct, it appears that $OH\cdot$ radicals formed at Pt and Pd surfaces likewise enter the gas phase where they promote catalytic combustion reactions.[2-4]

During the earlier part of this study it was demonstrated quantitatively that these surface-generating $CH_3\cdot$ radicals could account for the ethane and ethylene that were formed during the oxidative coupling reaction.[5] More recently, emphasis has been placed on the secondary reactions that the radicals undergo when they react with a metal oxide surface.[6] These reactions may be important in determining product selectivity, as $CH_3\cdot$ radicals will collide with the surface many times before they react with another $CH_3\cdot$ radical. If secondary surfaces result in complete oxidation, then the selectivity for the oxidative coupling reaction would be severely diminished.

Another current aspect of the work is the emanation of $OH\cdot$ radicals from platinum and palladium metal surfaces. Hydroxyl radicals are known to be chain carriers during combustion reactions, and the metal surface may serve to introduce these radicals into the gas phase. Earlier studies showed that $OH\cdot$ radicals were formed during the catalytic oxidation of hydrogen over Pt,[2] but only recently has the oxidation of methane been considered.[4] The appearance of $OH\cdot$ in the gas phase is limited by the activation energy for desorption, which, in turn, is strongly affected by the oxygen on the surface or on the subsurface region. Surprisingly, OH· radicals also may be formed during the oxidation of methane over La_2O_3 surfaces.

Clearly, surface-generated radicals are observed during the high temperature oxidation of hydrocarbons over closed-shell metal oxides and certain metal surfaces. Our understanding of the importance of these radicals in selective and nonselective oxidative processes, however, is currently limited to only a few systems.

REACTIONS OF GAS-PHASE METHYL RADICALS WITH METAL OXIDES

A study was undertaken to determine the kinetics and the mechanism for the reaction of $CH_3\cdot$ radicals with six representative metal oxides; MoO_3 (or MoO_3/SiO_2)CeO_2, ZnO, NiO, MgO and Li^+/MgO. The first four metal oxides can be easily reduced, whereas MgO and Li^+/MgO cannot. Li^+/MgO is one of the more selective oxidative coupling catalysts. It is capable of generating gas phase $CH_3\cdot$ radicals, but previous work demonstrated that it does not react with $CH_3\cdot$ radicals nor does it promote the coupling of $CH_3\cdot$ radicals.[7] By contrast CeO_2 and ZnO are selective catalysts for the complete oxidation of CH_4.

The matrix-isolation electron spin resonance (MIESR) spectrometer, developed under DOE sponsorship, was used to determine the reactivities of the oxides of interest. Samarium oxide at 700° C was used as the $CH_3\cdot$ radical generator, and the radicals were allowed to react downstream with a second metal oxide at a lower temperature. By measuring the disappearance of the $CH_3\cdot$ radicals, the partial pressure of the radicals and the surface area of the catalyst it was possible to calculate the specific activities of the metal oxides and the reactive sticking coefficients.

The results are shown in Tables I and II, from which it is evident that the specific activitiess of the metal oxides differ by two orders of magnitude. These are believed to be the first quantitative data on the reaction rates of alkyl radicals with metal oxides. The activities help to explain the

Table 1. Relative Specific Reaction Rates.

Oxide	Amt.,g	Surf. Area, m^2g^{-1}	Relative specific rate [a] ($CH_3 \cdot m^{-2}s^{-1}$)
ZnO	0.050	0.03	150
MoO_3	0.15	0.58	129
NiO	0.050	1.2	63
CeO_2	0.050	2.4	18
MgO	0.15	14.9	0.9
Li^+/MgO	0.20	2.7	1.1

[a] Temperature 470° C

Table II. Rate Constants, Activation Energies and Sticking Coefficients

Oxides	$k^a(s^{-1}m^{-2})$	E_a(kcal mol^{-1}	S^a
MgO	3.0×10^2	5.7	1.2×10^{-7}
CeO_2	3.1×10^3		2.1×10^{-6}
NiO	2.1×10^4		
MoO_3	4.3×10^4		
ZnO[b]	4.4×10^4	2.6	1.8×10^{-5}

[a] T = 482° C. [b] The surface area of this ZnO was 5.2 m^2g^{-1}; those of the other oxides were the same as listed in Table I.

observed selectivities for C_2 compounds or CO_x compounds that have been observed over these catalysts. The sticking coefficients are surprisingly small, even for the more reactive oxides, but they are consistent with the fact that a $CH_3\cdot$ radical would collide with a surface *ca.* 10^5 times before it reacted with another $CH_3\cdot$ radical.

It was previously suggested that the reaction of $CH_3\cdot$ radicals with a metal oxide may occur through electron transfer to the metal ion with the concomitant formation of a methoxide ion:

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

To determine whether the oxidation states of the metal cations decreased as a result of reactions with $CH_3\cdot$ radicals the paramagnetic properties of two of the most reactive materials, 2% MoO_3/SiO_2 and CeO_2, were investigated with the use of ESR spectroscopy. The spectra of Fig. 1 show that $CH_3\cdot$ radicals indeed promote the reduction of Mo^{6+} to Mo^{5+}, which is characterized by the spectrum with $g_\perp = 1.934$ and $g_\parallel = 1.881$. In the case of CeO_2 the reduced metal transferred its electron to O_2, forming O_2^- ions that were detected by ESR. An infrared study of a CeO_2 sample, after reaction with $CH_3\cdot$ radicals indicated the presence of methoxide ions, as predicted by reaction 2.

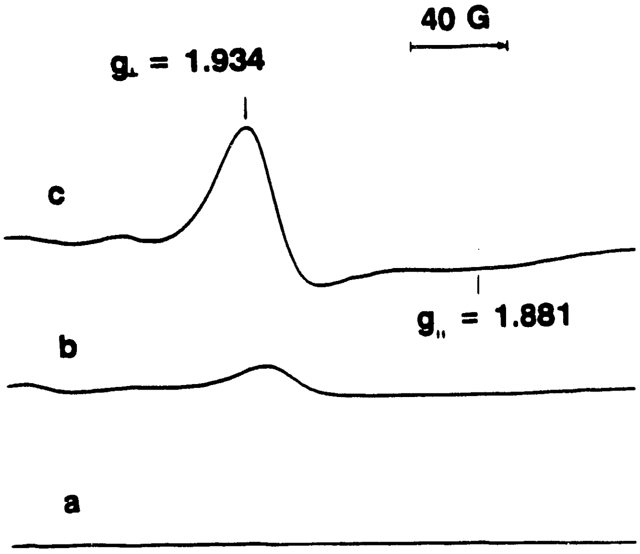

Figure 1. ESR spectra of 2% MoO_3/SiO_2; (a) untreated; (b) after exposure to flowing CH_4 and O_2 plus a small concentration of $CH_3\cdot$ radicals at 25%°C for 90 min; (c) after exposure to the reactants containing a high concentration of methyl radicals at 25°C for 90 min.

Curiously, the reactions of $CH_3\cdot$ radicals with metal oxides were characterized by both small activation energies and small sticking coefficients. Two alternative mechanisms have been proposed to interpret these observations. In one of the mechanisms, the electrons on weakly absorbed $CH_3\cdot$ radicals tunnel through the oxide ions and reduces the metal ions in the proximity of the surface. According to the other mechanism, a $CH_3\cdot$ radical is initially adsorbed on a metal cation with a partial electron transfer. The adsorbed $CH_3\cdot$ species then moves to a neighboring oxide ion as a result of a coulombic interaction.

EFFECT OF TEMPERATURE ON METHYL RADICAL GENERATION OVER Sr/La_2O_3 CATALYSTS

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.[8] The same mechanism is expected over this catalyst as has been found for other selective catalysts; however, Gulcicek et al.[9], using a resonance-enhanced multiphoton ionization (REMPI) technique, have recently reported 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, a 1 wt% Sr/La_2O_3 catalyst exhibits a maximum C_2 selectivity in the oxidative coupling reaction at 750°C.[8] If the $CH_3\cdot$ radical concentrations detected by Gulcicek *et al.*[9] represent the true rate of $CH_3\cdot$ radical emanation into the gas phase, one may conclude that the coupling reaction occurs on the surface of the catalyst, rather than in the gas phase. We undertook a brief study, using the MIESR system, to determine whether the radical concentrate indeed went through a maximum with respect to temperature. Several reactor configurations were employed, including one that was similar to that used by Gulcicek *et al.*[9]

The results depicted in Fig. 2 show that over the temperature range from 450°C to 800°C

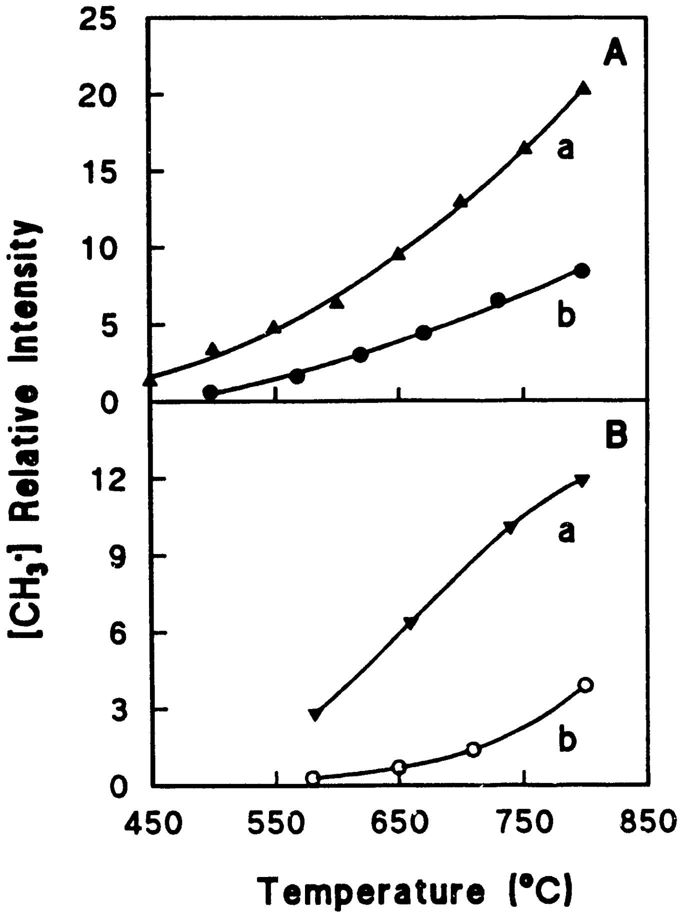

Figure 2. Relative concentrations of $CH_3\cdot$ radicals obtained in the low pressure mode: (A) with the (a) fresh and (b) used Sr/La_2O_3 (A) catalyst; (B) with the (a) Sr/La_2O_3 ($ex Sr(NO_3)_2$) catalyst and (b) Li^+/MgO catalyst. 0.055 g Sr/La_2O_3 (A) was used with flow rates of Ar = 3.8, CH_4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

there was no maximum in the rate of $CH_3\cdot$ radical formation. These results were obtained at a total pressure of *ca.* 1 Torr so as to avoid secondary gas phase reactions. The Sr/La_2O_3(A) catalyst is believed to be from the same batch as that used by Gulcicek *et al.* In the high pressure mode, under conditions similar to those used by Gulcicek *et al.* no maximum was observed. Thus, by analogy with quantitative results obtained with Li^+/MgO, we conclude that the coupling of $CH_3\cdot$ radicals occurs primarily in the gas phase over the Sr/La_2O_3 catalyst. The origin of the maximum observed by Gulcicek *et al.* with the used catalyst is likely a result of the fact that the reaction was severely oxygen limited at the exit of the catalyst bed. This explanation, however, does not appear to apply for their fresh catalyst.

As a secondary issue, we noted that the activity of the Sr/La_2O_3 catalyst for $CH_3\cdot$ radical formation was much greater than that of a Li^+/MgO catalyst. These relative activities for $CH_3\cdot$ radical formation are in agreement with the relative activities for CH_4 conversion over the two catalysts.

HYDROXYL RADICAL FORMATION DURING METHANE OXIDATION

The hydroxyl radical is one of the most important radicals involved in combustion processes, as it is a major chain carrier. We have developed a laser-induced fluorescence (LIR) spectroscopy system to study the formation and desorption of this reactive intermediate during the methane oxidation, both on metal and metal oxide surfaces. In complementary experiments the oxidation of H_2 also is being explored. The initial problem was to determine the effect of oxygen on the emission

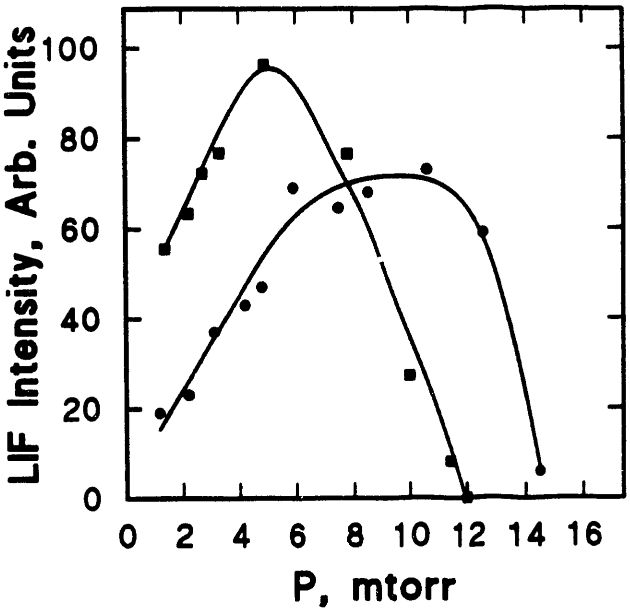

Figure 3. Gas-phase hydroxyl radical LIF signal as a function of CH_4 and H_2 pressure near a polycrystalline Pt wire at T = 900°C; ●, CH_4 with $P(O_2)$ = 4.8 mtorr; ■, H_2, $P(O_2)$ = 5.3 mtorr. The total pressure was 60 mtorr with the balance as He.

OH· radicals from a Pt surface. As indicated by the results of Fig. 3 the pressure of H_2 or H_4 had a profound effect on the generation of OH· radicals at 900°C. It was subsequently demonstrated that this phenomenon is related (i) the competitive removal of surface OH by reactions such as

$$OH_s + H_s \rightarrow H_2O_s \quad (3)$$

and (ii) the effect that surface oxygen has on the activation energy for hydroxyl radical desorption. The E_a values vary from ~ 30 kcal/mol for Pt with high oxygen coverage to ~ 60 kcal/mol on Pt under oxygen-depleted conditions. Thus, as the CH_4 partial pressure is increased, the activation energy for OH· radical desorption increases and the rate of OH· radical emission decreases as shown in Fig. 3.

The study currently is being extended to the reaction of H_2 and O_2 over Pd. This system is characterized by a distinct discontinuity in the activation energy for OH· radical emission at *ca* 950°C for O_2:H_2 ratios greater than 4. The E_a abruptly decreases from 48 kcal/mol at lower temperatures to 20 kcal/mol at greater temperatures. This change in activation energy may result from a variation in surface structure or the composition, such as the formation of a PdO phase.

PLANS FOR THE COMING YEAR

Research on the reactivity of CH_3· radicals with surfaces will be extended to include both metals and metal oxides in various states. The work on metals will begin with gold and will be extended to zinc films which contain overlayers of zinc oxide. The state of the surfaces will be determined using XPS and ISS techniques. In addition to determining rates of reactions with CH_3· radicals, the reactivities of allyl radicals also will be explored. Allyl radicals are stable in the gas phase and they can be readily formed from propylene over certain metal oxide surfaces.[10]

Preliminary studies have begun on the generation of OH· radicals over metal oxide surfaces. Hydroxyl radicals have indeed been detected over La_2O_3 during the partial oxidation of methane.

Although the laser beam is about one mean-free-path away from the surface, it remains to be determined whether the radicals are desorbed from the surface, or whether they are formed in the gas phase by reactions such as

$$CH_3\cdot + O_2 \rightarrow CH_2O + OH\cdot \tag{4}$$

In order to distinguish between these two possibilities, information on the absolute numbers of OH· radicals is needed. Experiments will soon begin to determine these concentrations. Assuming that the OH· radicals indeed come from the surface, a study will be undertaken to explore the mechanism by which they are formed on a metal oxide. It will be of particular interest to determine whether the formation of OH· radicals on the surface is directly related to the formation of $CH_3\cdot$ radicals. The formation of OH· radicals over metal oxides at high temperatures has not been previously reported, therefore it is an important area of research that is relevant to catalytic combustion and the partial oxidation of hydrocarbons.

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