Gas-phase Coupling of Methyl Radicals during the Partial Oxidation of Methane over Transition Metal Oxide Catalysts

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At a CH_4/O_2 ratio of *ca.* 3 the $LiNiO_2$ and $NaMnO_4/MgO$ catalysts generate gas phase methyl radicals as effectively as a Li^+/MgO catalyst, which indicates that the mechanism for ethane formation over all three catalysts is the same and involves the coupling of these gas phase radicals.

The partial oxidation of methane to higher hydrocarbons, a process which has scientific and technological importance, occurs through the coupling of $Me^{\bullet}$ radicals.[1,2] Over a number of metal oxides, including Li^+/MgO, Na^+/CaO and La_2O_3, a matrix-isolation electron spin resonance (MIESR) technique has been employed to demonstrate, both qualitatively and quantitatively, that the gas-phase coupling of the $Me^{\bullet}$ radicals constitutes a major pathway for the formation of ethane, which subsequently is partially dehydrogenated to ethene.[3—5] By contrast, Hatano and Otsuka[6] have suggested from their kinetic data that the reaction mechanism on the monophasic $LiNiO_2$ catalyst is primarily a surface phenomenon. That is, C_2H_6 is produced by the coupling of $Me^{\bullet}$ radicals on the surface. The present study was carried out 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 methyl radicals. The catalyst $NaMnO_4/MgO$ was chosen as a second example of a transition metal oxide catalyst that is effective for the oxidative coupling reaction.[7]

The $LiNiO_2$, $NaMnO_4/MgO$, and Li^+/MgO catalysts were prepared and activated according to the methods described in the literature.[6—8] These materials exhibited the catalytic properties reported previously. Moreover, the $LiNiO_2$ and Mg_6MnO_8 phases in the respective catalysts were identified by their *X*-ray diffraction powder patterns. The MIESR apparatus, which has been described in detail elsewhere,[9] was modified to include a 10 mm i.d. conventional flow reactor. In order to determine more accurately the radical concentration in the catalytic zone, the leak into the high vacuum region was located within the catalyst bed, rather than at the exit of the catalyst bed. The reactor and the leak were constructed of fused quartz, which is inert under the conditions used here with respect to the formation or reaction of $Me^{\bullet}$ radicals. The reactor also was coupled to a gas chromatograph so that a total analysis could be made of the stable products. Approximately 0.5 ml (0.5—0.7 g) of a steady state catalyst was used in the reactor. The flow rates of the gases (at 298 K and 1 atm) were as follows: Ar, 78 ml min^{-1}; CH_4, 71 ml min^{-1}; O_2, 18 ml min^{-1} for $NaMnO_4/MgO$ and 30 ml min^{-1} for $LiNiO_2$ and Li^+/MgO. The pressure over the catalyst was 760 torr. Different CH_4 conversion levels and the corresponding $Me^{\bullet}$ radical concentrations could be achieved either by changing the temperature of the reaction or by varying the O_2 partial pressure. The former method was used to obtain the results reported here, although the latter method yielded the same type of data. The temperature ranges for the three catalysts were as follows: Li^+/MgO, 913—1002 K; $LiNiO_2$, 939—1024 K; $NaMnO_2/MgO$, 999—1088 K. Under these experimental conditions the CH_4 conversion was less than 10%.

In the previous MIESR experiments the amount of catalyst was *ca.* 0.1 g, and the O_2 partial pressure was typically small so as to avoid the formation of $MeO_2^{\bullet}$ radicals in the cooler regions of the system *via* reaction (1).[3—5] But under these unusual catalytic conditions it was observed that the surface-generated gas-phase $Me^{\bullet}$ radical concentration was anomalously small for the $LiNiO_2$ and $NaMnO_4/MgO$ catalysts. In the experiments reported here the O_2 partial pressure and the amount of catalyst substantially increased, and it was found that the radical concentration also increased for these two catalysts (see below). Likewise, the amount of O_2 exiting the catalyst bed increased so that under these more conventional catalytic conditions $MeO_2^{\bullet}$ was the major radical species observed by ESR. Less than 15% of the O_2 was converted during the reactions. (Typical spectra are shown in Figure 2 of ref. 10.) It is important to note that even though $MeO_2^{\bullet}$ radicals were formed downstream from the catalyst and were detected in the cold matrix, $Me^{\bullet}$ was the principal radical species in the hot catalyst zone as the equilibrium of reaction (1) is shifted far to the left at 900—1100 K.[11] Thus, the radical species reported here is $Me^{\bullet}$, not $MeO_2^{\bullet}$.

$$Me^{\bullet} + O_2 \leftrightharpoons MeO_2^{\bullet} \qquad (1)$$

It is evident from Figure 1(a) that for each of the three catalysts the (C_2^+ yield)$^{1/2}$ is linearly related to the concentration of gas phase $Me^{\bullet}$ radicals in the catalyst bed. Here, C_2^+ refers to ethane and ethene, plus a very small amount of higher hydrocarbons. The C_2^+ yield is the product of the CH_4 conversion times C_2^+ selectivity; thus it is a relative measure of C_2^+ productivity. The half power is expected because the formation of ethane involves the bimolecular reaction of $Me^{\bullet}$ radicals.

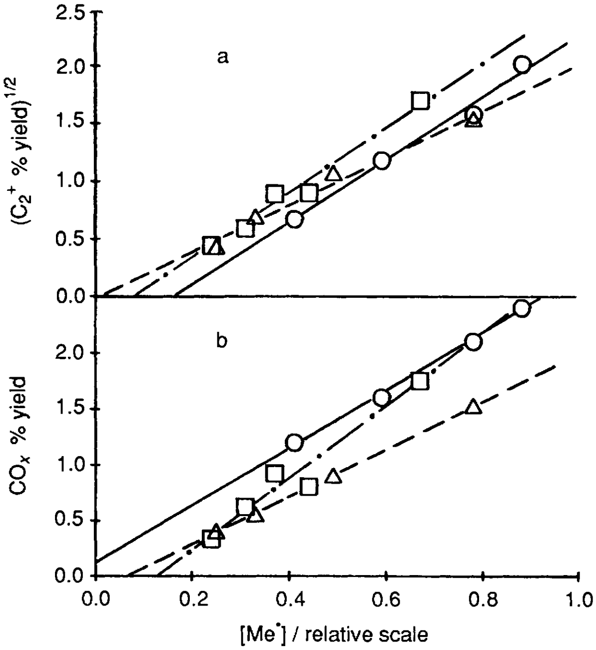

Figure 1. Relationship between $Me^{\bullet}$ radical concentration in the gas-phase above the catalyst and (a) C_2^+ yield or (b) CO_x yield: ○, $LiNiO_2$; △, $NaMnO_4/MgO$; □, Li/MgO. For each of the three catalysts the same relative scale was used for the $Me^{\bullet}$ radical concentration.

Although separate lines have been drawn to fit the data for the three catalysts, a single line would fit all of the data reasonably well, considering the experimental error associated with each point. These results indicate that all three catalysts behave similarly with respect to the formation of ethane *via* the coupling of gas phase Me$^{\bullet}$ radicals. This is particularly significant as the importance of gas phase Me$^{\bullet}$ radicals in the formation of C_2 products has been demonstrated quantitatively for Li^+/MgO.[3] If the mechanism were exclusively a surface phenomenon, one would expect a positive intercept on the ordinate; *i.e.*, $C_2{}^+$ products would be formed without there being any gas phase Me$^{\bullet}$ radicals. In fact, the ordinate intercept was either zero or negative.

In a similar manner the CO_x yield (the combined yields of CO and CO_2) is linearly related to the Me$^{\bullet}$ radical concentration, as shown in Figure 1(b). In this case it is more difficult to fit the data for the three catalysts by a single straight line. The linear relationship is consistent with the formation of CO_x *via* gas phase Me$^{\bullet}$ radicals, either through secondary reactions with the surface or through gas phase chain branching reactions. The results, however, do not exclude the formation of CO_x from $C_2{}^+$ products, particularly at high levels of conversion.

The inability of the $LiNiO_2$ catalyst to generate gas phase Me$^{\bullet}$ radicals at high CH_4/O_2 ratios may in part result from a change in composition. Thomas and co-workers[12] observed that a $Li_{0.46}Ni_{0.54}O$ catalyst, after exposure to a gas mixture containing 19.7% CH_4 and 3% O_2 for *ca.* 3 h, was transformed to NiO and presumably Li_2O with a concomitant loss in C_2 selectivity. Further reaction resulted in the formation of Ni metal. We have confirmed the loss in selectivity at comparable CH_4/O_2 ratios, but at a CH_4/O_2 ratio of 2 we observed that the catalyst was stable, in agreement with the results of Hatano and Otsuka.[13] Nickel oxide would not be expected to generate gas phase Me$^{\bullet}$ radicals as this material undergoes extensive secondary reaction with these radicals. The inability of the $NaMnO_4/MgO$ catalyst to generate Me$^{\bullet}$ radicals in the conventional mode (*i.e.*, with the leak at the exit of a small catalyst bed) appears to be related more to the size of the catalyst sample than to the CH_4/O_2 ratio. For reasons that are not presently clear we have observed that small amounts of this catalyst result in the nonselective oxidation of CH_4.

In summary, at CH_4/O_2 ratios of *ca.* 3 the transition metal oxide catalysts $LiNiO_2$ and $NaMnO_4/MgO$ behave in a manner similar to Li^+/MgO with respect to the generation of gas phase Me$^{\bullet}$ radicals as well as the formation of $C_2{}^+$ hydrocarbons and CO_x products. Since the formation of ethane over Li^+/MgO is known to occur *via* the coupling of gas phase Me$^{\bullet}$ radicals, we conclude that a similar mechanism occurs over the transition metal oxides. A parallel reaction in which Me$^{\bullet}$ radicals couple on the surface cannot be excluded, but such a reaction clearly is not a dominant channel.

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