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Oxidative Coupling of Methane

II. Formation of Active Sites by Lead and Tin Oxides on MgO

S. K. AGARWAL, R. A. MIGONE, AND G. MARCELIN[1]

Chemical and Petroleum Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

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The oxidative coupling of methane has been studied over Sn–Mg–O catalysts with varying amounts of Sn. The addition of small amounts of tin oxide to MgO increased both the rate of methane conversion and the C_2 selectivity. A maximum C_2 selectivity of 40% was obtained over 0.4 at.% Sn–Mg–O at 780°C at a methane conversion of 20%. The maximum in C_2 selectivity can be explained by considering an "isolated site" type mechanism in methane oxidation. According to this mechanism, an active and selective catalyst should have highly oxidizing sites isolated from each other by relatively inactive sites. Such an arrangement would allow a high methane conversion rate and the highest C_2 selectivity by limiting the total oxidation of intermediates on the catalyst. A simple kinetic model based on the isolated site mechanism, which explains most of the catalytic features of the Sn–Mg–O catalytic system, has been developed. The model predicts an optimum selectivity for C_2 hydrocarbons as a function of Sn content.

INTRODUCTION

Numerous studies on the oxidative coupling of methane have been reported using "promoted" MgO catalysts (*1–7*). Perhaps the best known example is the doping of magnesia with lithium ions which has been shown to increase both the activity and C_2 selectivity of the resulting catalyst when compared with pure MgO (*1*). Other magnesia-based catalysts have also been reported, including lead–magnesia (*8, 9*) and bismuth–magnesia (*10*). As with Li-doping, the addition of small amounts of these "reducible" oxides to magnesia resulted in a general increase in both the activity and the C_2 selectivity for oxidative coupling. A previous study of lead–magnesium mixed oxides has suggested that these mixed oxides act as selective coupling catalysts due to the dispersion of a highly active species on an inert matrix, i.e., PbO and MgO, respectively (*11*). If this view were correct, then other highly oxidizing species dispersed on an inert matrix should also be capable of acting as a selective coupling catalyst.

This paper reports a study of the oxidative coupling of methane over a series of Sn–Mg–O catalysts with varying Sn content and examines these results in light of previous studies on Pb–Mg–O catalysts. Tin was chosen because: (1) it is in the same periodic group as lead; (2) it is an active oxidation species (*12*); and (*3*) unlike PbO, tin oxide has a sufficiently high melting point to allow the pure material to be studied under coupling conditions.

Based on the experimental results a simple kinetic model has been developed which explains some of the catalytic features of both the Sn–Mg–O and the Pb–Mg–O systems.

EXPERIMENTAL

The catalysts were prepared starting with tin (II) acetate (95%) and MgO (99.5%) obtained from Alfa Products. Catalysts containing 0.2, 0.4, 0.8, and 2.6 at.% Sn were prepared by adding MgO to a $Sn(OAc)_2$ solution and evaporating to dryness. Pure tin

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[1] To whom correspondence should be addressed.

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oxide was prepared in the similar way starting solely with $Sn(OAc)_2$. The resulting materials were dried at 120°C and calcined in two steps, first at 500°C for 15 h, followed by 800°C for 4 h.

The BET surface areas of the catalysts were determined by N_2 physisorption at −196°C using a Micromeritics 2600 system. X-ray diffraction (XRD) measurements were taken with a General Electric XRD-5 diffractometer using Cu$K\alpha$ radiation.

The reaction was studied using a laboratory scale fixed-bed reactor system operating under atmospheric pressure. The reactor was a quartz tube of 5 mm inner diameter tapered to 1 mm after the catalyst zone. The complete reaction system has been described previously (*13*). The gases methane (99.97%), oxygen (99.6%), and helium (99.995%) were obtained from Matheson. These gases were further purified by passing through purifiers containing beds of indicating drierite and molecular sieves (5 Å).

The reaction conditions used were as follows: temperature = 780°C, total reaction gas flow = 260 cc/min, reaction gas composition: $CH_4/O_2/He = 8/3/7.6$. The catalyst was used in the form of 16/28 mesh pellets. In general, 35–150 mg of the catalyst, depending on its activity, were charged in the reactor. The effluent gases were analyzed by on-line GC equipped with TCD and FID in parallel. The hydrocarbon products, methane, ethane, ethylene, propane, and propylene were analyzed using a Porapak-Q column connected to the FID. The carbon oxides, oxygen, and water were analyzed using a Carbosphere column connected to the TCD.

The compositions of the catalysts are expressed in atomic percent in this paper. The methane conversion was calculated on the basis of total carbon balance, i.e., CH_4 conversion = (moles of C in products)/(moles of C in feed). Selectivity for C_2 is defined as the ratio of the yield of C_2 to the methane conversion, where yield of C_2 = (moles of C in C_2)/(total moles of C reacted). Some traces of C_3 hydrocarbons were observed but always with a selectivity of less than 2%, and hence they are not reported.

RESULTS AND DISCUSSION

The Sn–Mg–O catalysts were examined by BET and XRD, both before and after the reaction. The XRD patterns revealed the presence of crystalline MgO phase in all cases, as well as the presence of a crystalline SnO_2 phase for catalysts with high loadings of Sn (0.8% and above). As was the case for Pb–Mg–O (*11*) catalysts, no Sn–Mg–O compounds were identified even at 2.6% tin content. Additionally, the catalysts did not show any detectable change in the crystal structure after the reaction. The BET surface areas ranged from 36 m^2/g for pure MgO to ca. 9 m^2/g for pure tin oxide. A small decrease in the BET surface area was observed after the reaction.

The initial surface areas and catalytic properties of the Sn–Mg–O catalysts are tabulated in Table 1. The addition of tin oxide to MgO affected both the activity and the selectivity of the resulting catalysts. The overall rate of methane conversion increased on a unit surface area basis even for the lowest levels of tin addition. It should be noted that under our reaction conditions the contribution of the gas-phase reaction was negligible (*13*).

Pure Sn oxide was found to be 30 times more active on an areal basis than MgO. The very high activity of Sn oxide was also manifested in the drastic increase of CO_2/CO ratio with increasing amount of Sn. The one exception was the decrease in the CO_2/CO ratio observed for the pure tin oxide, which was probably due to the oxygen-deficient reaction condition as a result of the very high methane conversion and high CO_2 selectivity. Indeed, the high oxidizing ability of tin oxide is evident in the product distribution for pure tin oxide which produced over 95% CO_x. As was the case with the Pb–Mg–O catalysts (*11*), the C_2 selectivity exhibited a "volcano-type" pattern with increasing tin oxide content, with a

TABLE 1

Steady-State Catalytic Properties of Sn–Mg–O Catalysts at 780°C

Catalyst	Wt. (mg)	BET surface area (m^2/g)	% Methane conversion[a]	% Selectivities[a]		CO_2/CO	Pseudo specific rate[b] $\times 10^{17}$ molec/(sec m^2)
				C_2	CO_x		
MgO	150	36	9.4	25	75	0.7	8
0.2% Sn–Mg	80	36	14	31	69	1.2	22
0.4% Sn–Mg	80	36	20	40	59	5.5	32
0.8% Sn–Mg	80	33	24	31	68	20.6	42
2.6% Sn–Mg	80	27	22	26	73	22.1	47
SnO_2	35	9	16.5	4	96	8.1	240

[a] Values are reported after ca. 5 h of reaction.

[b] Based on initial surface area.

maximum C_2 selectivity observed for a 0.4% Sn catalyst. However, comparison of the Sn–Mg–O and Pb–Mg–O catalysts (*11*) showed the relative rate of methane conversion over Sn–Mg–O catalysts to be more than twice that for Pb–Mg–O catalysts for comparable amounts of Sn and Pb. The C_2 selectivity was lower in the case of Sn–Mg–O catalysts.

In a previous publication it was speculated that a catalyst containing highly active oxides dispersed on an inert support, like MgO, should give a maximum in C_2 selectivity because the isolation of highly active sites limites the total oxidation on the catalyst while increasing the total rate of methyl radical generation (*11*). From this concept a simple kinetic model for such an "isolated site" mechanism in methane oxidation can be developed and its predictions compared with the experimental results. This model is based on an Eley–Rideal-type mechanism (*14*) involving the reaction of gas-phase methane molecules with a surface site. Oxidative coupling of methane is reported to take place by abstraction of a hydrogen atom from methane giving a $CH_3\cdot$ radical which can desorb to the gas phase and combine with another $CH_3\cdot$ to give ethane (*1*, *15*). For the sake of simplicity, only three reactions are considered in this model: (1) abstraction of a H atom from methane forming a methyl ($CH_3\cdot$) radical; (2) total oxidation of the $CH_3\cdot$ radical on the catalyst to CO_x; and (3) recombination of the $CH_3\cdot$ radicals in the gas phase to form C_2; that is

$$CH_4 + \theta_1 \xrightarrow{k_1'} CH_3\cdot \tag{1}$$

$$CH_4 + \theta_2 \xrightarrow{k_2'} CH_3\cdot \tag{2}$$

$$CH_3\cdot + \theta_1 \xrightarrow{k_3'} CO_x \tag{3}$$

$$CH_3\cdot + \theta_2 \xrightarrow{k_4'} CO_x \tag{4}$$

$$2\,CH_3\cdot \xrightarrow{k_5} C_2. \tag{5}$$

In Sn–Mg–O, two different active sites can be considered to be involved in methane oxidation. These can be identified as an active site associated with the highly oxidizing sites on tin oxide (or a Sn species) and a relatively inactive site associated with MgO. The relative concentrations of these two sites are represented by (θ_1) and (θ_2), respectively. The initial H-abstraction from methane, which can occur on both sites, results in the formation of $CH_3\cdot$ radicals and the number of radicals generated depends on both the relative activities and the relative concentrations of these sites on the catalyst. If the number of "active" sites is high, more radicals will be generated. The radicals can desorb to the gas phase and, in this simple model, recombine to form ethane. Alternatively, the radicals can remain or readsorb on the surface and oxidize to CO_x.

When pure MgO is used as the catalyst the number of radicals generated is low, due to its relative inactivity, and in turn total methane conversion is low. As noted in Table 1, the oxidizing power of tin oxide is much higher than that of MgO. As a result, the addition of tin oxide to MgO, in small amounts, can result in the formation or dispersion of highly active sites over the MgO matrix, enhancing the rate of hydrogen abstraction and thus methyl radical generation. However, because the active sites are isolated the $CH_3\cdot$ radical has little likelihood of being further oxidized by a neighboring strong site and can desorb into the gas phase where it can couple with other $CH_3\cdot$ to form ethane. Since the gas-phase coupling of $CH_3\cdot$ is second order while the formation of CO_x is first order with respect to $[CH_3\cdot]$, the overall C_2 selectivity, that is, $\mathrm{Rate}_{C_2}/(\mathrm{Rate}_{C_2} + \mathrm{Rate}_{CO_x})$, increases. This increase in methane conversion and C_2 selectivity with increasing tin content continues until a high enough tin oxide level is reached such that the active sites become contiguous, thus resulting in the further oxidation of $CH_3\cdot$ to CO_x on the catalyst and decreasing the selectivity for partial oxidation products. Thus, it appears that one possible requirement for a highly selective methane coupling catalyst is the presence of strong oxidizing sites isolated on an inert matrix. Such an arrangement will allow maximum methyl radical generation while controlling the total oxidation due to further oxidation of the radical intermediates. Tin oxide is more easily reduced than MgO (*16*), and at these high temperatures the oxidation of methyl radicals would be expected to proceed rapidly leading to the formation of CO_x. In addition, at the levels of conversion used in this work, the presence of a large number of highly active sites can lead to the combustion of any intermediate partial oxidation products. The preceding argument may apply for any highly oxidizing species diluted in an inert matrix. Indeed, similar selectivity patterns have been reported for Pb–Mg–O and supported Bi_2O_3 (*8, 10, 11*), while Callahan and Grasselli have similarly suggested that for selective allylic oxidation the oxygen must be distributed on the catalyst surface in an arrangement which provides for limitation of the number of active oxygen atoms in various isolated groups (*17*).

Based on this idea a selectivity expression can be developed based on Eqs. (1–5) and the following assumptions: (i) the concentrations of the active and inactive sites are only a function of the mole fraction of the two components. Thus $\theta_1 = k'x_1$ and $\theta_2 = k''x_2 = k''(1 - x_1)$, where x_1 and x_2 are the mole fractions of Sn and Mg, respectively, and k' and k'' are constants of proportionality; (ii) the catalyst is continuously replenished with the gas-phase oxygen, such that the active site concentration is at steady state; (iii) all secondary reactions from C_2 to CO_x are neglected.

On the basis of these assumptions, the rate of CO_x production can be expressed as

$$\begin{aligned} R_{CO_x} &= (k_3'\theta_1 + k_4'\theta_2)[CH_3\cdot] \\ &= [k_3x_1 + k_4(1 - x_1)][CH_3\cdot], \end{aligned} \tag{6}$$

where $k_3 = k_3'k'$ and $k_4 = k_4'k''$, the rate for C_2 production is expressed as

$$R_{C_2} = k_5[CH_3\cdot]^2, \tag{7}$$

and the rate of methane consumption can be expressed as

$$\begin{aligned} -R_{CH_4} &= (k_1'\theta_1 + k_2'\theta_2)[CH_4] \\ &= [k_1x_1 + k_2(1 - x_1)][CH_4], \end{aligned} \tag{8}$$

where $k_1 = k_1'k'$ and $k_2 = k_2'k''$. Thus, the C_2 selectivity is given by

$$\begin{aligned} S_{C_2} &= \frac{R_{C_2}}{R_{CO_x} + R_{C_2}} \\ &= \frac{k_5[CH_3\cdot]^2}{k_5[CH_3\cdot]^2 + [k_3x_1 + k_4(1 - x_1)][CH_3\cdot]}, \end{aligned} \tag{9}$$

and at steady state

$$\begin{aligned}\frac{d[\mathrm{CH_3\cdot}]}{dt} &= [k_1x_1 + k_2(1 - x_1)][\mathrm{CH_4}] \\ &\quad - (k_3x_1 + k_4(1 - x_1))[\mathrm{CH_3\cdot}] \\ &\quad - 2k_5[\mathrm{CH_3\cdot}]^2 = 0. \qquad (10)\end{aligned}$$

For a binary system the relative rate of Eq. (1) can be represented as $k_1 = mk_2$; that is, the rate of hydrogen abstraction occurring on site 1 is m-times faster than the similar process occurring on site 2. Similarly the rate of Eq. (3) can be expressed as $k_3 = nk_4$. Thus, m and n are characteristic constants for a given mixed oxide system. Substituting for $[\mathrm{CH_3\cdot}]$ from Eq. (10) into Eq. (9) and simplyfing it, results in Eq. (11) describing the C_2 selectivity as a function of concentration for a highly dispersed mixed oxide:

$$S_{C_2} = \frac{1}{1+\dfrac{4}{-1+\sqrt{1+8k_5[\mathrm{CH_4}]\dfrac{[(m-1)x_1+1]k_2}{[(n-1)x_1+1]^2k_4^2}}}}. \qquad (11)$$

The rate constant k_5 for the recombination of $\mathrm{CH_3\cdot}$ radicals in the gas phase has been measured and is reported to be 1.5×10^{15} cm^3/mol/min (*18*). The concentration of methane, $[\mathrm{CH_4}]$, in this work was maintained at 1.8×10^{-5} gmol/cm^3. The unknowns m, n, k_2, and k_4 can be estimated by solving the selectivity equation at the two extremes, i.e., for pure MgO and for pure tin oxide. For MgO, the experimental C_2 selectivity was determined to be 25%, i.e., $S_{C_2} = 0.25$ (see Table 1), and k_2/k_4^2 is calculated as 2.1×10^{-11} min. This value of k_2/k_4^2 can be assumed to be constant for all the MgO-based mixed oxide catalysts under these experimental conditions. For tin oxide, the experimental C_2 selectivity was 4%, i.e., $S = 0.04$, resulting in a value for m/n^2 of 0.08. Thus, for Sn–Mg–O catalysts, the C_2 selectivity is given by

$$S_{\mathrm{Sn\text{–}Mg\text{–}O}} = \frac{1}{1+\dfrac{4}{-1+\sqrt{1+4.54\dfrac{[(0.08n^2-1)x_1+1]}{[(n-1)x_1+1]^2}}}}. \qquad (12)$$

A similar argument can be used for developing selectivity equations for other mixed oxide systems. Using previously reported data, summarized in Table 2 (*11*), the Pb–Mg–O system can also be examined. This also results in a value of 2.1×10^{-11} min for k_2/k_4^2. Unfortunately, the reaction could not be conducted over pure PbO catalyst due to the vaporization of lead species blocking the reactor by condensing on the colder regions of the reactor exit. However, an estimate of the C_2 selectivity over pure PbO can be obtained by noting that a catalyst with high lead content (7.3% Pb) exhibited a C_2 selectivity of 20%. Thus the C_2 selectivity over pure PbO should be less than 20%. Additionally, since the C_2 selectivity for Sn–Mg–O catalysts was lower than that for Pb–Mg–O, for comparable amounts of Sn and Pb, the C_2 selectivity over pure PbO would be expected to be greater than that of pure tin oxide, i.e., 4%. Thus, a C_2 selectivity of about 10% can be reasonably estimated for the conversion of methane over PbO under our reaction conditions, resulting in a value of $m/n^2 = 0.21$.

TABLE 2

Catalytic Properties of Pb–Mg–O Catalysts at 780°C[a]

Catalyst	Space velocity (cc/(min gm))	% Methane conversion[a]	% Selectivities[a]		CO_2/CO[a]	Pseudo specific rate $\times 10^{17}$ molec/(sec m^2)
			C_2	CO_x		
MgO	1513	8.7	27.2	72.8	0.7	8.2
0.2% Pb–Mg	1513	12.8	42.6	56.4	0.9	14.4
0.4% Pb–Mg	1513	13.1	51.0	47.6	2.4	15.8
0.8% Pb–Mg	1200	13.9	46.0	51.3	9.3	16.3
2.6% Pb–Mg	1200	10.8	38.0	60.0	11.7	20.7
4.4% Pb–Mg	1200	10.4	20.0	78.8	26.3	25.4
7.3% Pb–Mg	1200	10.5	20.0	78.8	55.2	25.6

Note. Catalyst weight = 150 mg.

[a] Taken from Ref. (*11*).

[b] Steady-state measurements were conducted after ca. 5 h on stream.

Equation (12) thus has two variables: x_1, the atomic fraction of Sn (or Pb); and n, a parameter which is constant for a given oxide system and relates the activity of tin oxide (or PbO) relative to MgO, for the formation of CO_x from the methyl radicals. From the relative rates of CO_x formation for the pure oxides, i.e., MgO and tin oxide, a value of 39 is obtained for n for the Sn–Mg–O system. However, since the reaction over tin oxide took place under an oxygen-limiting condition, the actual value of n is likely to be higher. An alternative approach to estimating the value of n is to calculate a corresponding value of n using Eq. (12) for each of the Sn–Mg–O catalysts and to extrapolate these values to pure tin oxide. This results in a value of n for the Sn–Mg–O system of 100 and for the Pb–Mg–O system of 56. Although the validity of this approach is questionable since the reaction was not measured under differential conditions, the resulting numbers can be used for comparison with the kinetic equation. In any case, n could always be considered simply an adjustable parameter which can be fitted to the experimental data.

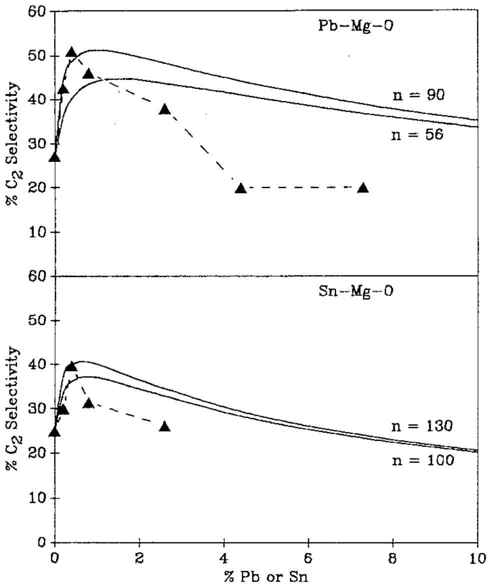

FIG. 1. Comparison of experimental and predicted C_2 selectivities for Pb–Mg–O and Sn–Mg–O catalysts. Symbols represent the experimental data. The predicted selectivities for the indicated values of n are shown by curves without symbols.

Figure 1 compares the experimental C_2 selectivities with those calculated based on Eq. (12) using both the values of n derived from the extrapolation procedure as well as values of n adjusted to best fit the initial experimental points. The model predicts a volcano-type behavior for C_2 selectivity with increasing Pb or Sn content. Additionally, the model predicts a lower maximum C_2 selectivity for Sn–Mg–O than for Pb–Mg–O, in agreement with experimental findings. It is also worth noting that the comparison which gives the maximum C_2 selectivity is predicted reasonably well and that this composition does not depend highly on the exact value of *n* used in the equation. The main discrepancy between the model and the experimental results lies in the fast drop in C_2 selectivity observed experimentally and not predicted by the kinetic model. The cause for this discrepancy is not known but could be due to either the formation of agglomerates of the active species with increasing loadings, such as was reported for the Pb–Mg–O system (*11*) or perhaps the role that secondary reactions play in influencing selectivity at high conversions.

It is worth commenting on the limit of maximum selectivity that can be achieved based on this model. It is clear, from the selectivity expression, that the relative activity and selectivity of the active oxide strongly influence the overall C_2 selectivity. Figure 2 shows the effect of the C_2 selectivities for the pure oxides on the predicted behavior of the resulting mixed oxide systems. Figure 2A shows that a slight increase in C_2 selectivity for the pure active oxide significantly increases the overall C_2 selectivity. However, as shown in Figure 2B a similar change in C_2 selectivity for the inactive oxide does not result in an appreciable change in the overall C_2 selectivity. Thus, this suggests that it is possible to achieve very high C_2 selectivities over a catalytic system of the type *A*–Mg–O, where *A* is an active oxide, provided the pure oxide *A* has high activity and high selectivity for partial oxidation products. However, most single oxides which are highly active for oxidation reactions tend to be less selective for partial oxidation products thereby limiting the overall maximum selectivity over *A*–Mg–O catalysts.

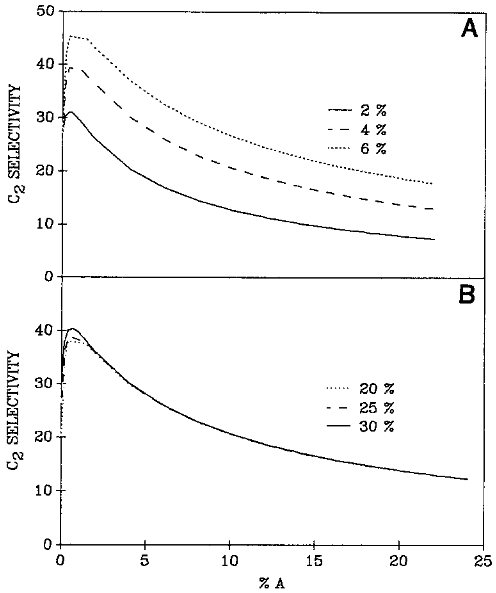

FIG. 2. Effect of C_2 selectivity of the pure oxides on the overall predicted selectivities of an *A*–Mg–O system. (A) Effect of varying the "active" oxide selectivity; (B) effect of varying the "inert" oxide selectivity.

In conclusion, catalytic systems of the type *A*–Mg–O, where *A* is an "active" oxide for methane oxidation, exhibit a maximum in C_2 selectivity as a function of the active oxide content. The increase in the activity and selectivity upon addition of small amounts of an active oxide to MgO is believed to be due to the formation of highly oxidizing sites "isolated" from each other which increase the overall rate of methyl radical generation resulting in higher C_2 selectivity. A kinetic model based on the isolated site mechanism explains most of the catalytic features of the title reaction.

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