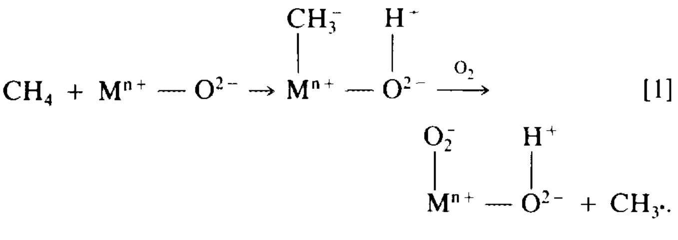
JOURNAL OF CATALYSIS **146**, 613–615 (1994)

NOTE

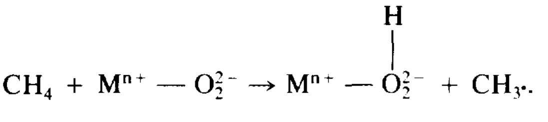
Site Differentiation in Homolytic vs. Heterolytic Activation of Methane Over Ba/MgO Catalysts

It has become generally accepted that the initial step in the selective oxidation of methane to C_2 hydrocarbon products over alkali/alkaline earth and other "basic" oxide catalysts involves hydrogen abstraction on the catalyst surface to produce methyl radicals, which then emanate into the gas phase and undergo coupling (1–3). Disagreement remains, however, regarding the identity of the surface sites on which hydrogen abstraction occurs and the nature of the C–H bond breaking that is involved in methyl radical formation. In one view, C–H bond cleavage occurs heterolytically on coordinatively unsaturated metal–oxygen pair sites to produce methyl carbanions, which then subsequently react with oxygen to release methyl radicals (4–7):



$$CH_4 + M^{n+}-O^{2-} \rightarrow \overset{CH_3^-}{\overset{|}{M^{n+}}}-\overset{H^+}{\overset{|}{O^{2-}}} \xrightarrow{O_2} \overset{O_2^-}{\overset{|}{M^{n+}}}-\overset{H^+}{\overset{|}{O^{2-}}} + CH_3\cdot \qquad [1]$$

The resulting superoxide species (O_2^-) presumably react in a sequence of subsequent reaction steps to produce H_2O. The methyl radicals resulting from Reaction [1] are thus generated by an indirect process. An alternative theory is that C–H bond breaking in methane occurs homolytically *via* H abstraction by a partially reduced surface oxygen species, such as O_2^-, O^-, or O_2^{2-}, to produce methyl radicals directly (8–11), e.g.,



$$CH_4 + M^{n+}-O_2^{2-} \rightarrow M^{n+}-\overset{H}{\overset{|}{O_2^{2-}}} + CH_3\cdot \qquad [2]$$

Because of the very weakly acidic nature of the C–H bonds in alkanes, sites that are able to heterolytically activate methane must be much more strongly basic than those capable only of promoting homolytic C–H bond breaking. Such strongly basic sites would presumably also be more susceptible to poisoning by the CO_2 by-product that is generated during methane oxidation. Hence, even if both types of sites are initially present on a freshly pretreated oxide catalyst, those capable of heterolytically activating methane may quickly become deactivated by irreversibly adsorbed CO_2 and play no sustained role in the steady-state reaction.

Since H–D isotopic exchange reactions among alkanes are known to occur over metal oxide catalysts *via* heterolytic dissociation of C–H and C–D bonds (7, 12–15), the reaction involving redistribution of H and D between CH_4 and CD_4 can be used to independently probe the behavior of such sites. In a previous investigation, Lapszewicz and Jiang used the isotopic exchange reaction between D_2 and CH_4 to study the oxidative coupling activities and surface basicities of Sm_2O_3, MgO, and γ-Al_2O_3 and concluded that no direct correlation exists between C–H bond activation and methane conversion (12). Nelson *et al.* observed that oxidative coupling of CH_4/CD_4 mixtures occurs over Li/MgO without H–D exchange (2).

The present study was performed to obtain additional information about the relative importance of the two modes of methane activation on a series of previously characterized Ba/MgO catalysts that are very active and selective for oxidative coupling (16). The comparative poisoning effects of CO_2 added to the separate reactant streams were used to differentiate the behaviors of the two types of methane-activating sites. The results demonstrate that although C–H bond breaking in methane may, in principle, occur heterolytically on certain sites under oxidative coupling conditions, such strongly basic sites are much more susceptible to deactivation by even trace amounts of CO_2 than are the sites responsible for homolytic activation.

The three Ba/MgO catalysts, containing 0.5, 2.0, and 8.0 mol% Ba, were identical to those described previously (16) and were prepared by impregnation of MgO (ACS certified grade, 99.9%) with aqueous solutions of $Ba(NO_3)_2$ (ACS certified grade, 99.3%), followed by drying and calcination for 16 h at 800°C. Neither reagent contained detectable amounts of noble metal impurities that could contribute to the observed H/D exchange levels. All catalytic experiments were performed at a reaction

0021-9517/94 $6.00

temperature of 850°C using a downflow tubular quartz reactor having an internal diameter of 2.85 mm. The catalyst particles were secured in the reactor between quartz wool plugs, and a 5.0-cm layer of quartz chips, located on top of the catalyst bed, served as the preheating zone. Measurements of the activity of the various catalysts for methane oxidation were performed under nearly differential conditions, in which oxygen and methane conversions were typically less than 20 and 10%, respectively. These conditions were achieved by using small amounts (5 mg) of catalyst and high reactant/diluent flow rates ($CH_4:O_2:He = 5:1:194$ cm^3/min and $CH_4:CD_4:He = 2.5:2.5:195$ cm^3/min), corresponding to linear space velocities of ~2 × 10^6 hr^{-1}. Methane (99.99%) from Matheson Co., and oxygen (99.9%), helium (99.995%), and carbon dioxide (99.9%) from Airco were used without further purification. Methane-d_4 was from Isotec, Inc. and was 99.4% D.

The comparative effects of CO_2 poisoning were studied for the oxidative coupling ($CH_4 + O_2$) and H–D exchange ($CH_4 + CD_4$) reactions in separate experiments because, as will be shown below, CO_2 partial pressures generated by the coupling reaction, even at low CH_4 conversions, were sufficient to cause virtually complete poisoning of the exchange reaction. The desired partial pressures of CO_2 during the separate reactions were maintained by introducing measured amounts of a 10% CO_2/He mixture into the 5 : 1 $CH_4:O_2$ and 1 : 1 $CH_4:CD_4$ reactant streams. Reaction gas mixtures were separated and analyzed using a Hewlett–Packard model 5890 gas chromatograph equipped with a model 5971 mass sensitive detector. Extents of CH_4/CD_4 exchange are expressed as the average number of H or D atoms exchanged per molecule of methane, i.e.

$$\text{H (D) Exchanged/Molecule} = \frac{X[CH_3D] + 2 \cdot X[CH_2D_2] + X[CHD_3]}{4}, \quad [3]$$

where $X(i)$ is the mole fraction of species i among all methane species. The form of Equation [3] implies that the species CH_3D and CHD_3 have undergone only one exchange step, rather than three, which is a valid assumption at the small extents of exchange observed in this study.

The comparative effects of CO_2 on both the oxidative coupling and CH_4/CD_4 exchange reactions at 850°C over the three Ba/MgO catalysts studied are presented in Figs. 1–3. (In each figure, the first data point shown for the oxidation reaction was that obtained with no added CO_2, and thus corresponds to the lowest attainable CO_2 partial pressure under the reaction conditions employed.) In the case of the H–D exchange reaction, even very low partial pressures of added CO_2 (<0.1 Torr) were sufficient to cause extensive poisoning of the reaction over all three of the catalysts. At CO_2 pressures >~2 Torr (Fig. 1), the extent of exchange approach that measured under the same conditions for the purely homogeneous gas-phase CH_4/CD_4 reaction in a reactor containing only quartz chips, *viz.*, ~0.003 H or D atoms exchanged per methane molecule.

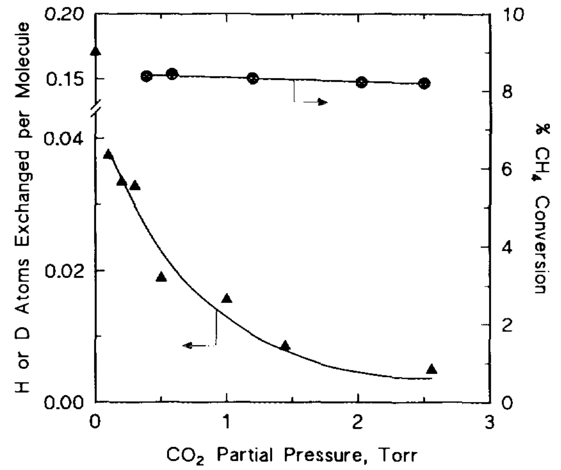


FIG. 1. Effect of CO_2 partial pressure on CH_4/CD_4 exchange (▲) and CH_4/O_2 oxidation reaction (●) at 850°C over 0.5 mol% Ba/MgO.

In marked contrast to the behavior exhibited by the CH_4/CD_4 exchange reaction, the oxidative coupling process was influenced much less by the presence of comparable additions of CO_2. In the case of 0.5 mol% Ba/MgO (Fig. 1), in fact, CO_2 partial pressures of <3 Torr had virtually no poisoning effect on the oxidation reaction. With increasing barium content in the catalyst (Figs. 2 and 3), the coupling reaction was increasingly susceptible to poisoning by CO_2. However, even for the 8 mol% Ba/MgO catalyst, the exchange reaction was affected to a much greater extent by low CO_2 concentrations than was the oxidation reaction. At a CO_2 partial pressure of 2.4

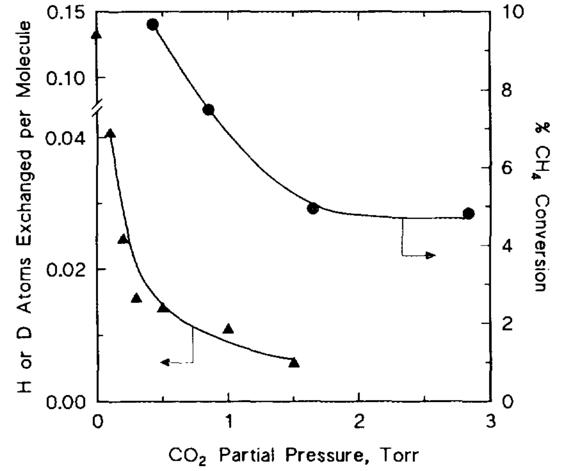


FIG. 2. Effect of CO_2 partial pressure on CH_4/CD_4 exchange (▲) and CH_4/O_2 oxidation reaction (●) at 850°C over 2 mol% Ba/MgO.

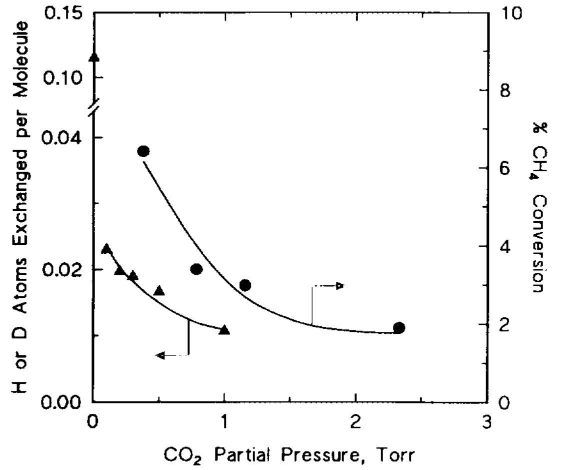


FIG. 3. Effect of CO_2 partial pressure on CH_4/CD_4 exchange (▲) and CH_4/O_2 oxidation reaction (●) at 850°C over 8 mol% Ba/MgO.

Torr, for example, the extent of CH_4 conversion over this catalyst was still ~30% of that observed in the absence of added CO_2, whereas >90% of the H–D exchange reaction was poisoned by as little as 1.0 Torr of added CO_2. For both the H–D exchange and CH_4 oxidation reactions, the poisoning effect of CO_2 was reversible over each of the three catalysts; i.e., removal of added CO_2 from the reactant streams caused the CH_4 conversion and extent of H–D exchange to return to their original unpoisoned levels.

These results demonstrate that the C–H bond in methane can be activated on at least two distinguishable kinds of surface sites on each of these catalysts. One type of site is sufficiently strongly basic to promote heterolytic C–H bond cleavage in methane, allowing exchange of H-atoms among CH_4 molecules. The fact that these sites become almost completely deactivated in the presence of even very low partial pressures of CO_2, which is reversibly adsorbed, suggests that they are very sparsely distributed on the surfaces of all three of the Ba/MgO catalysts. If such sites were available during the CH_4/O_2 reaction, they could, in principle, contribute to the observed level of oxidative coupling by indirectly producing methyl radicals. However, because of their low population, strong basicity, and consequently high susceptibility to poisoning by CO_2, these sites almost certainly play no significant sustained role during the steady-state oxidation reaction. The partial pressures of CO_2 that are typically generated during oxidation, even at low methane conversions and high C_2 selectivities, would be sufficient to cause complete deactivation of these sites.

The other type of site, much more numerous and presumably less basic, is capable of catalyzing only homolytic C–H bond cleavage in methane, directly producing $CH_3\cdot$ radicals which then emanate into the gas phase and undergo coupling. With increasing Ba content in the catalyst, these sites become increasingly susceptible to poisoning by the CO_2 that is produced during the oxidation reaction. This behavior has been reported previously and correlates with the increasing surface basicity of these materials, as measured by their tendency to form a stable surface carbonate upon exposure to approximately equal concentrations of CO_2 (16). In the latter study, XPS characterization of each catalyst after exposure to a CH_4/O_2 reaction mixture at 800°C and subsequent cooling in O_2 revealed no observable surface CO_3^{2-} species on 0.5 mol% Ba/MgO. On the 2 mol% Ba/MgO catalyst, a small amount of reaction-generated carbonate was observed, while over 8 mol% Ba/MgO, a substantial surface $BaCO_3$ phase was produced during methane oxidation.

ACKNOWLEDGMENT

The authors gratefully acknowledge financial support of this research by the National Science Foundation under Grant CHE-9005808.

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Received September 10, 1993; revised November 10, 1993

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