Pretreatment effects on the active site for methane activation in the oxidative coupling of methane over MgO and Li/MgO

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Received 13 March 1995; accepted 30 June 1995

The effects of high temperature pretreatments on the activity of MgO and Li/MgO catalysts for the oxidative coupling of methane have been studied. The MgO powder catalyst exhibited a turnover frequency of 3.0×10^{-3} molecules/site s, at 990 K, whereas the Li/MgO catalyst showed a turnover frequency of 7.0×10^{-2} molecules/site s, under the same reaction conditions. The initial C_2 formation rate was observed to increase with pretreatment temperature over the MgO catalyst, supporting our previous proposal that F-type defects are responsible for methane activation.

Keywords: oxidative methane coupling; methane activation; MgO; Li/MgO

1. Introduction

The thermodynamic stability and relative inertness of methane make its conversion to higher hydrocarbons one of the more intriguing problems in heterogeneous catalysis. Among the various proposals for converting methane into more useful and manageable hydrocarbons, direct oxidative coupling over heterogeneous catalysts has received considerable attention [1]. Since the pioneering work of Keller and Bhasin [2], a wide variety of catalysts has been studied. One of the more promising catalyst materials was found to be Li-promoted MgO [3]. In their early work on the oxidative coupling reaction over Li/MgO, Lunsford and coworkers [1] established many of the generally accepted principles concerning the reaction mechanism and the nature of the active site. In Lunsford's proposed reaction scheme the active sites for CH_4 activation are assumed to be surface O^- species

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which generate CH_3 radicals upon interaction with methane. The CH_3 radicals desorb and combine in the gas phase to form C_2H_6. The O^- species is believed to be present in the form of a $[Li^+O^-]$ defect in the near surface region of the catalyst [4].

Recently, Goodman and coworkers [5] studied defect sites that were present in a thin-film, Li/MgO/Mo(100) model catalyst. As the Li/MgO catalyst was annealed to high temperatures (~ 1300 K), defect centers were observed to form in the band gap. A feature corresponding to a $[Li^+O^-]$ center was identified following an anneal to 1000 K and observed to maintain a relatively constant intensity for higher anneal temperatures. On the other hand, features representative of F-type defects (oxygen vacancies with two electrons) were found to increase with temperature up to 1300 K. The concentration of F-type defects could be correlated with the formation of ethane, suggesting that these sites are responsible, either directly or indirectly, for the important hydrogen abstraction step in the oxidative coupling reaction [6,7].

Additional support for F-centers as the active sites is the thermal stability and maximum density of F-type defects relative to $[Li^+O^-]$ defects. The stability of F-type defects has been found to increase with temperature in the 1000–1200 K range [8] whereas the $[Li^+O^-]$ defects are highly unstable at these high temperatures [9]. The concentration of F-centers in MgO was found to saturate at a level of $\sim 10^{19}\ \mathrm{cm^{-3}}$ [10]. In contrast, the maximum density of $[Li^+O^-]$ centers is reported to be on the order of 10^{16}–$10^{17}\ \mathrm{cm^{-3}}$ [11].

The promotional effect of lithium on MgO as an oxidative coupling catalyst is proposed, using the F-center argument, to be a result of an increase in the number of surface F-center sites upon the addition of lithium to MgO. According to the model of Abraham and coworkers [12], lithium impurities in MgO crystals are considered to concentrate primarily as Li_2O precipitates. Recent thermal desorption studies [8] have shown that Li_2O begins to desorb at ~1000 K with a desorption peak maximum at ~1250 K. The increase in the production of defects of F-type at high temperature is likely a consequence of the desorption of Li_2O that leads to the generation of oxygen vacancies in the MgO.

In this paper, we present the results of a study on the effects of thermal pretreatment on the nature of the active site for methane activation in the oxidative methane coupling reaction over high surface area MgO and Li-promoted MgO. Results on the formation, lifetime, and loss of active sites at the surface are presented. The findings of this study support our previous proposal that F-centers are responsible for methane activation in the oxidative methane dimerization reaction.

2. Experimental

The catalytic experiments were carried out in a fixed bed reactor operated at 1 atm. The catalysts were high purity MgO (Johnson-Matthey grade 1) and Li/MgO (Li/MgO = 0.33). The Li-promoted MgO was prepared by adding Li_2CO_3 to the MgO using established preparation procedures [4]. The powder samples were pressed into disks then crushed and sieved. A 300 mg sample of catalyst was placed in a ceramic tube flow reactor with a chromel–alumel thermocouple located in the center of the catalyst bed. The reactor volume above the catalyst bed was filled up with ceramic chips in order to preheat the reactant gas mixture. The activity of the ceramic chip-loaded reactor was tested and found to be negligible in comparison with the catalyst-loaded reactor (less than 5% of the lowest catalyst activity). The methane (99.99%), oxygen (99.99%), and helium (99.99%) were obtained from Matheson Gas and used as received. The reactant and product gases were analyzed by a gas chromatograph (GC) equipped with a flame ionization detector.

The samples were pretreated in the reactor at 1200 K in flowing helium for 60 min. For the reactions run in the absence of O_2, an additional pretreatment procedure at high temperature in flowing oxygen was carried out for 60 min. Following the high temperature pretreatment the catalyst was cooled to the desired reaction temperature and the reactant gas mixture introduced. Oxidative coupling reactions, using a $CH_4/O_2/He$ gas mixture with a partial pressure of 77, 23 and 660 Torr, respectively, were carried out over the catalyst at a total flow rate of 64 cm^3/min. For the MgO and Li/MgO catalysts, ethane was the primary product, with small amounts of ethylene being produced by the further dehydrogenation of ethane.

3. Results and discussion

The ethane and ethylene production as a function of time on stream over the Li/MgO catalyst are shown in fig. 1. A sharp decrease is observed for both the ethane and ethylene production during the first 50 min of reaction. After 90 min on stream, the catalyst reaches its steady-state activity. A maximum conversion of 2.5% is observed initially with the conversion decreasing to $< 0.5\%$ at steady-state. This initial decrease in activity is attributed to the formation of lithium carbonate at the surface of the catalyst [13]. Initially, during the high temperature (1200 K) anneal, essentially all of the Li_2CO_3 is decomposed and the catalytic activity is high. With increasing reaction time the CO_2, produced by the complete oxidation of hydrocarbons, reacts with the surface Li_2O to form Li_2CO_3. A steady-state activity is reached at a given temperature as an equilibrium is established between the formation and decomposition of lithium carbonate ($Li_2CO_3 \rightleftharpoons Li_2O + CO_2$) [13].

The specific activities for ethane production at steady-state for the MgO and Li/MgO powder catalysts are plotted in Arrhenius form in fig. 2. The turnover frequencies (TOF) were calculated using the surface areas of MgO and Li/MgO of 50 and 0.75 m^2/g, respectively, and assuming a saturation concentration of active surface sites. The MgO powder exhibits a TOF of 3.0×10^{-3} molecules/site s at

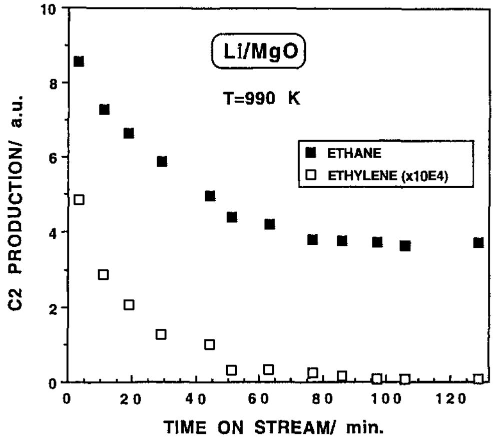

Fig. 1. Ethane/ethylene production as a function of time on stream over Li/MgO. The catalyst was annealed to 1200 K followed by exposure to a CH_4 (77 Torr)/O_2 (23 Torr)/He (660 Torr) gas mixture. Total flow rate was 64 cm^3/min.

990 K and an apparent activation energy of 268 kJ/mol. The Li/MgO exhibits a TOF of 7.0×10^{-2} molecules/site s at 990 K and an apparent activation energy of 213 kJ/mol. The apparent activation energies and the tenfold increase in activity of the Li-promoted catalyst agree well with previous results obtained from thin-film MgO and Li/MgO model catalysts [7]. Any discrepancies in the absolute reaction rates can be attributed to the uncertainty in the specific number of active sites at the surface of the catalyst. The excellent agreement between the catalytic properties of the powdered MgO and Li/MgO and the model thin-film catalysts provides a basis for direct comparison of the observed catalytic changes with surface modification.

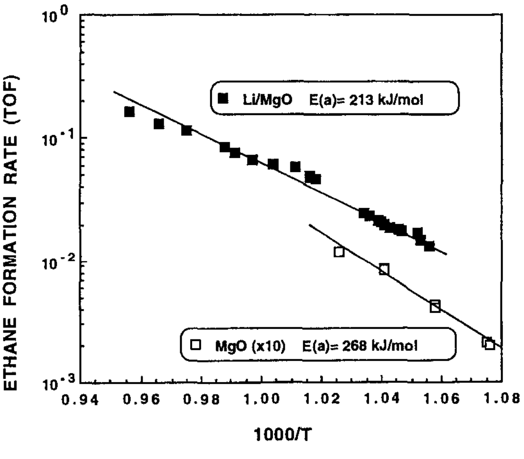

Fig. 2. Temperature dependence of the ethane formation rates for MgO and Li/MgO.

The dependence of ethane production on the concentration of thermally generated surface defects was investigated by treating a pure MgO powder catalyst at high temperatures in flowing oxygen. As previously discussed, a similar pretreatment of thin-film MgO samples produced an excellent correlation between the concentration of F-type defects and catalytic activity [5,6]. Fig. 3 shows the effect of pretreatment temperature on the ethane formation rate for a pure MgO powder. The catalytic activity increased with increasing pretreatment temperatures as the anneal temperature was raised from 1200 to 1350 K. However, no further increase in catalytic activity was observed as the pretreatment temperature was increased to 1400 K. These findings for the MgO powder catalyst parallel the results observed for the thin-film Li/MgO [6] catalyst, and thus, are consistent with an F-type defect being the active site for methane activation. The decrease in activity with time is due to the initial loss of active sites at the catalyst surface as the active site concentration adjusts to its lower steady-state value at the lower reaction temperatures. Extended reaction periods at a given reaction temperature yielded steady-state rates, independent of the activation temperature.

After having established the dependence of the active site concentration for methane activation on the pretreatment temperature over the MgO catalyst, reactions were carried out in the absence of oxygen. The catalyst was activated at 1200 K in flowing O_2 for 60 min and then purged with He to exclude any gas phase O_2. These reactions were carried out to investigate the surface reaction between CH_4 molecules and the active centers formed by the pretreatment in oxygen at 1 atm. Running the reaction in the absence of gas phase O_2 eliminates any possibility of gas phase reaction between oxygen and the C_2 products formed in the coupling reaction. Furthermore, elimination of CO_2 product excludes its subsequent reaction with the active sites. The ethane production as a function of reaction time for

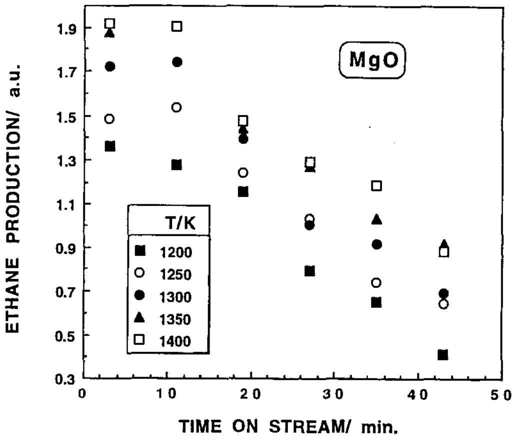

Fig. 3. Ethane production as a function of time on stream over MgO. The catalyst was pretreated in flowing O_2 at the temperatures indicated followed by reaction at 990 K.

the oxygen activated MgO powder is displayed in fig. 4. The decrease in the catalytic activity with time for each reaction temperature studied can be attributed to the initial loss of active sites at the surface. The absence of oxygen in the reactant gas mixture eliminates the regeneration of the active sites responsible for methane activation. The higher the reaction temperature, the sharper the decline in the ethane production rate with time on stream. At high temperatures, the diffusion of the defect sites from the bulk to the surface is rapid therefore the catalyst exhibits high activity. However, the concentration of bulk defect sites decreases much faster at the high temperatures which results in the relatively sharp initial rate decrease. The activity of the catalyst at low reaction temperature remains essentially constant since the diffusion of defect sites to the surface is relatively slow.

From the plots of fig. 4, the initial activities can be determined by extrapolation of the rates to $t = 0$. The initial rates for ethane production are plotted as a function of reaction temperature in fig. 5 in Arrhenius form. The apparent activation energy deduced from the slope of this plot is identical, within experimental error, to that obtained from the plot in fig. 2 for the CH_4/O_2 reactant gas mixture. The agreement between the two activation energies for ethane formation over MgO suggests that the same rate-determining step is operative in the presence and absence of oxygen.

The catalytic activity for ethane production as a function of time on stream for a Li/MgO sample, pretreated using a similar procedure as described for the MgO catalysts, is shown in fig. 6. As seen for the MgO catalyst, the catalytic activity decreases with reaction time over the Li/MgO catalysts. The initial rates of ethane production as a function of reaction temperature are plotted in Arrhenius form in fig. 7. The slope of this plot gives an apparent activation energy of 167 kJ/mol for the production of ethane which is considerably less than the activation energy of 213 kJ/mol observed for the CH_4/O_2 reactant gas mixture. Such differences in activation energies for methane coupling in the presence and absence of oxygen over

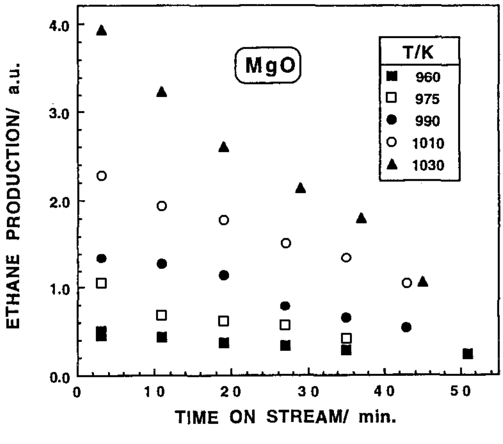

Fig. 4. Ethane production in the absence of O_2 as a function of reaction time over thermally pretreated MgO.

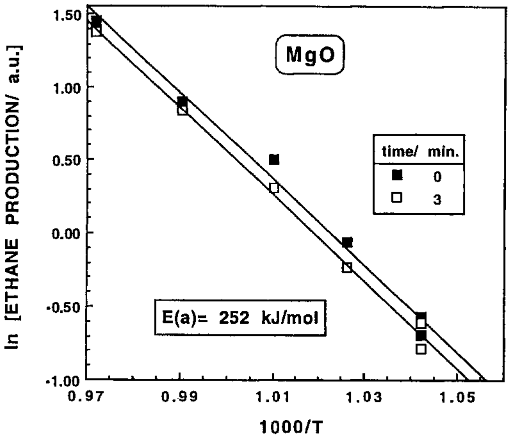

Fig. 5. Ethane production as a function of temperatures in the absence of O_2 over MgO.

Li/MgO have been observed previously over thin-film, Li/MgO catalysts [13]. It has been reported [13,14] that CO_2 dramatically alters the rate laws describing methyl radical production in the oxidative coupling reaction. The effect of carbon dioxide on the Li/MgO catalysts has been proposed to be two-fold [7]. First, the lithium promoter is stabilized by the formation of Li_2CO_3. At temperatures where the methane coupling reactions are carried out, the highly volatile Li_2O would desorb in the absence of gas phase CO_2. The loss of Li from the Li/MgO catalysts during methane coupling is well documented [7]. The activity of the Li/MgO catalyst, in spite of the significant extent of Li loss, remains essentially constant as long as a critical amount of Li is present at the catalyst surface. As the Li concentration falls below a certain value, the activity decreases rapidly. This critical Li con-

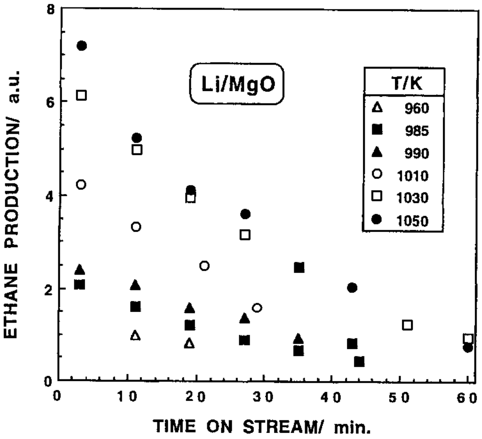

Fig. 6. Ethane production in the absence of O_2 as a function of time on stream over Li/MgO. The catalyst was pretreated in O_2 at 1200 K for 60 min.

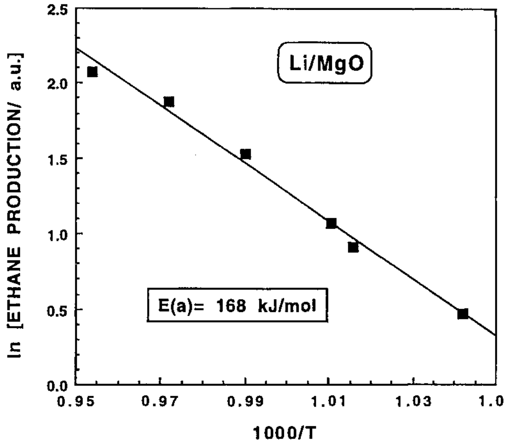

Fig. 7. Temperature dependence of ethane production in the absence of O_2 over Li/MgO.

centration is much lower than the amount of Li generally used in Li/MgO catalysts. With respect to Li loss, the presence of CO_2 is advantageous in that it prevents the rapid loss of Li from the Li/MgO catalyst.

The second effect of carbon dioxide is that CO_2 in the form of a carbonate or a carbonate-like species of Li inhibits the reaction. A good correspondence has been found between the activation energy of CO_2 desorption from Li/MgO and the apparent activation energy for the dimerization reaction in the presence of high concentrations of CO_2 for both high surface area catalysts [14] and for thin-film Li/MgO [7]. The results found in this study for the oxygen-free reactions over Li/MgO support this proposed CO_2 inhibition. Formation of the Li_2CO_3 species on the catalyst surface is minimized in the coupling reaction that is carried out in the absence of O_2. The 167 kJ/mol activation energy determined for ethane formation in the absence of O_2 over the Li/MgO catalyst is essentially identical to that required to produce two CH_3 radicals. This suggests that the rate-determining step for CH_4 activation over Li/MgO in the absence of O_2 is H abstraction from CH_4. Over the Li/MgO catalyst, in contrast to pure MgO, the formation of the active F-type defects sites is likely not rate-determining. In the presence of O_2 in the reactant gas mixture, the surface carbonate found by the reaction with CO_2, originating from the complete oxidation of hydrocarbons, has to decompose to provide active sites (F-centers) for the H abstraction. Since the majority of surface Li is present in the form of carbonate, its decomposition rate will determine the rate of active site formation, thus the rate of H abstraction. This carbonate decomposition process is characterized by an activation energy of 213 kJ/mol.

The observation of a drop in activation energy for the reactions run in the absence of oxygen can be informative in terms of increasing the C_2 yield of the oxidative coupling reaction. For the reaction with oxygen, the concentration of CO_2 increases with an increase in the methane conversion, thus shifting the rate-determining step from C–H bond cleavage to CO_2 desorption. Removal of gas phase oxygen clearly improves the selectivity of the dimerization reaction, suggesting that cycling the catalyst in oxygen at high temperatures to generate active sites followed by a second step in which the pretreated catalyst is reacted with methane, should maximize the C_2 yield.

4. Conclusions

The dependence of C_2 formation on pretreatment temperatures of MgO catalysts for the oxidative coupling reaction indicates that the active site for methane activation is most likely an F-type defect in agreement with results obtained from model thin-film catalysts. The formation of these active sites is the rate-determining step in the oxidative coupling reaction over MgO. For the Li/MgO catalyst the rate-determining step is dependent upon the reactant gas mixture used to carry out the reaction, i.e., whether O_2 is present or not. Since Li promotes the formation of the catalytically active F-type defect sites, the rate-determining step for CH_4 activation over Li/MgO is different compared to pure MgO. In the presence of oxygen the rate-determining step over Li/MgO is the decomposition of lithium carbonate which is characterized by an activation energy of 219 kJ/mol. On the other hand, in the absence of O_2 the formation of a surface carbonate is inhibited and the ethane formation rate is determined by the hydrogen abstraction from CH_4 which occurs with an activation energy of 167 kJ/mol.

Acknowledgement

We acknowledge with pleasure the support of this work by the Gas Research Institute and the Department of Energy, the Office of Basic Sciences, the Division of Chemical Sciences. We also thank Professor Lunsford for providing the MgO and Li/MgO catalysts used in this study.

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