Kinetic studies of the oxidative dimerization of methane on thin-film MgO and Li/MgO

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The oxidative dimerization of methane to ethane over thin-film MgO and Li/MgO catalysts prepared under well-controlled, ultrahigh vacuum (UHV) conditions has been studied using a combination UHV/reactor cell system that allows elevated pressure kinetic studies and surface science techniques to be employed. Reactions investigating temperature, pressure and pretreatment activation have been performed to determine ethane dependence on each reaction parameter. Agreement between turnover frequencies, activation energies and lithium promotional effects of the thin-film MgO and previously reported results for powdered MgO indicates that the thin-film catalyst is an excellent model catalyst for the oxidative coupling of methane.

Keywords: Methane coupling; magnesium oxide; lithium promotion; kinetic studies

1. Introduction

The use of methane as an alternative fuel source has developed into a major research interest over the past ten years. Abundant reserves of natural gas, of which methane is a principal component, are known throughout the world but difficulties in transportation of the gas to the consumer presently makes it an economically disadvantaged fuel source [1]. The discovery that methane can be converted to C_2H_6 and C_2H_4 in significant yields ($\approx 20\%$) by heterogeneous partial oxidation [2] has provided a favorable process for the utilization of this important resource.

The primary interest in the work on the oxidative dimerization of methane has been catalyst screening to achieve maximum C_2 yield. Some of the more successful catalysts are CaO [3], ZnO [4] and Sm_2O_3 [5] which are promoted with either sodium or lithium. The catalyst most frequently studied is lithium-promoted MgO [6] which provides an irreducible metal oxide with many of the

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properties necessary for a good oxidative coupling catalyst. The active sites are believed to be $[Li^+O^-]$ species which abstract a hydrogen from methane and generate methyl radicals that desorb and subsequently recombine in the gas phase [7]. However, a detailed characterization of the active site(s) for the key methane activation step has not been carried out.

Utilization of surface science techniques in the study of methane activation has been restricted due to the experimental difficulties presented by metal oxide catalysts. For example, most oxides are poor thermal conductors and will electrically charge when studied by the typical charged-particle probes used in ultrahigh vacuum (UHV) measurements. Many of these experimental difficulties have been recently circumvented by growing a thin oxide film onto a metal substrate. This approach has been used successfully for UHV studies on several oxide systems [8–10] but virtually no work has been carried out to connect the catalytic properties of these thin-film metal oxides to the catalytic properties of the more realistic catalysts.

In this letter we report the preliminary results from a kinetic investigation of the oxidative dimerization of methane over thin-film MgO and Li/MgO. Agreement in the turnover frequencies, activation energies and lithium promotional effects between the thin-film MgO presented here and the MgO powder catalyst reported by Lin et al. [11], indicate that the thin-film catalyst is an excellent model catalyst for the oxidative dimerization of methane.

2. Experimental

Experiments were carried out on a combined UHV/reactor cell system that allows the sample to be transferred from UHV conditions ($\approx 1.0 \times 10^{-10}$ Torr) to a reaction cell for kinetic studies at pressures up to 1000 Torr. The UHV chamber is equipped with Auger electron spectroscopy (AES), temperature programmed desorption (TPD) and dosing capabilities for both gases and metals. The reaction cell is a static cold wall reactor with a single inlet for reactant introduction and product removal.

The preparation of pure and Li-doped MgO films consisted of depositing Mg and Li onto a Pt(100) crystal in a controlled oxygen atmosphere. Magnesium was deposited by thermal evaporation of a high-purity ribbon tightly wrapped around a tungsten filament. Lithium deposition was performed via thermal evaporation from a SAES GETTERS source. The flux of Mg and Li evaporation was directly monitored by a mass spectrometer. The evaporation rate of each metal was determined by a combination of TPD and AES measurements which has been described in detail elsewhere [10].

Following preparation and characterization of the film in the UHV chamber, the model catalyst was transferred in situ into the reaction cell via a double-stage differentially pumped teflon sliding seal. Catalytic experiments were run in a

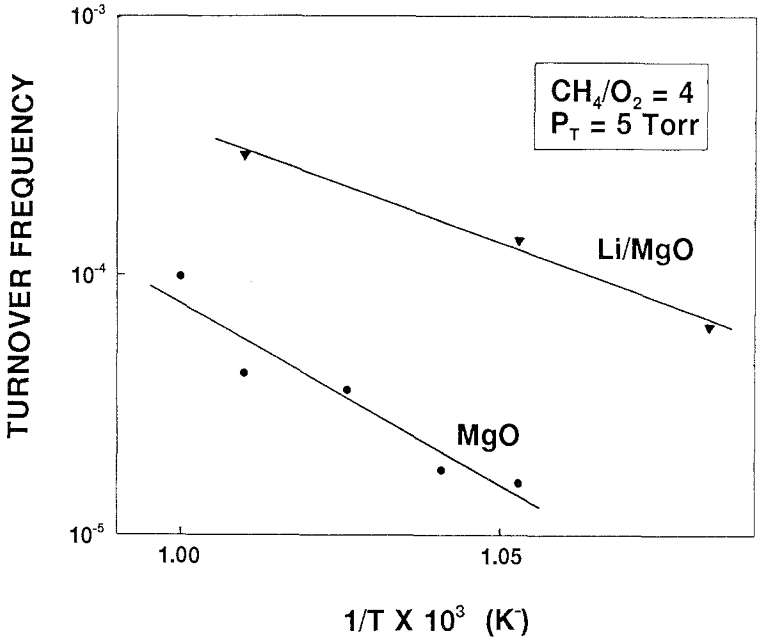

Fig. 1. Arrhenius plots of ethane formation rates versus reciprocal temperature. The apparent activation energies for pure and Li promoted MgO films are 60 and 50 kcal/mol, respectively.

temperature range of 950–1000 K and a pressure range of 1–25 Torr. The CH_4 to O_2 ratio was varied from 0.2:1 to 20:1 for the pressure dependent studies while the temperature dependent studies were carried out at a $CH_4:O_2$ ratio of 4:1 with a total pressure of 5 Torr. After a 5 min reaction, the product gas mixture was analyzed with gas chromatography (GC) utilizing a flame ionization detector.

3. Results and discussion

The activity of the thin film for the oxidative coupling of methane was studied at methane conversions of $< 1\%$ with ethane, CO and CO_2 being the major products. Activities expressed as turnover frequencies (TOF) for ethane formation for both the pure and the Li-promoted MgO are shown in Arrhenius form in fig. 1. The MgO catalyst shows a TOF of 4.0×10^{-5} molecules/site s at 990 K and an apparent activation energy of 60 kcal/mol for ethane production. The Li/MgO model catalyst exhibits a TOF of 3.0×10^{-4} molecules/site s at 990 K and an apparent activation energy of 50 kcal/mol. The tenfold increase in the TOF and the relative activation energies over the MgO and Li/MgO film agree well with the powdered MgO results of Lin et al. [11]. Extrapolating the TOF for the Li/MgO film to the pressures used for the MgO powdered catalyst shows

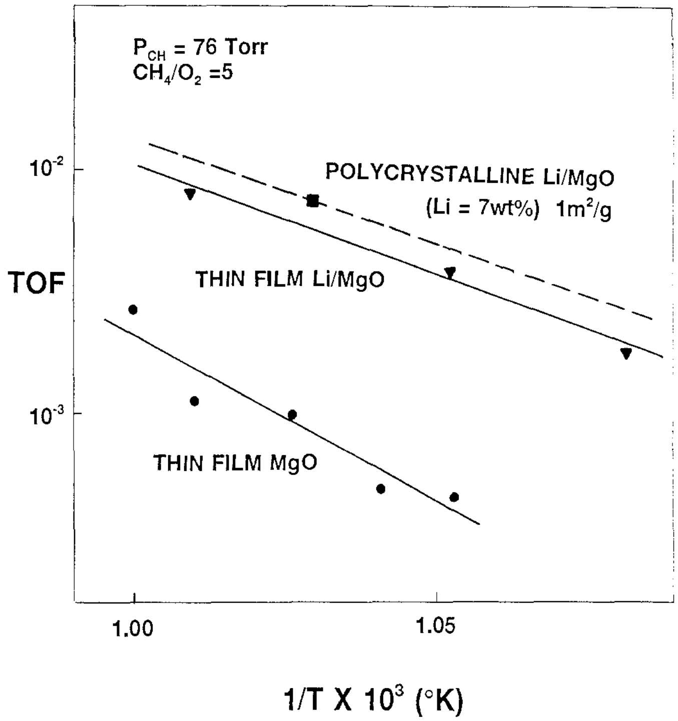

Fig. 2. A comparison of results for the Li/MgO thin-film catalyst and data for a powdered Li/MgO catalyst [12]. The results for the MgO and Li/MgO film were adjusted to the conditions employed in the powdered Li/MgO work using the measured CH_4 and O_2 pressure dependencies of 1.8 and −0.8, respectively.

that the TOF of the Li/MgO film (9.0×10^{-3} molecules/site s) and the powdered Li/MgO (1.0×10^{-2} molecules/site s) [12] at 990 K are essentially identical (fig. 2). Agreement in the TOFs, activation energies and lithium promotional effects between the model thin-film catalyst and the powdered MgO catalyst clearly shows that the MgO thin film is an excellent model for the more realistic catalyst.

Lithium promoted MgO contains defects whose concentrations were found to increase when exposed to increasing temperatures in an oxygen background [13–15]. To investigate the dependence of the C_2 production on the concentration of certain types of defects, the model Li/MgO was pretreated by heating in oxygen to various temperatures (800–1250 K) prior to reaction at 990 K. Fig. 3 presents the pretreatment temperature versus the C_2 formation rate and shows a tenfold increase in the ethane yield as the pretreatment temperature of the catalyst was increased from 1000 to 1250 K. This increase in the ethane formation rate changes in concert with an increase in the concentration of F-type defects in the catalyst as measured with high resolution electron energy loss spectroscopy [15]. This behavior is contrary to the widely accepted belief

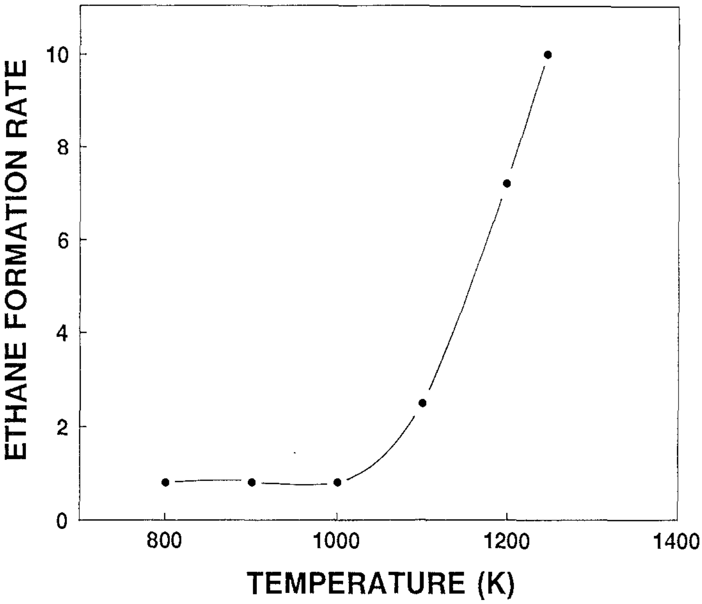

Fig. 3. Ethane formation rate versus the sample pretreatment temperature. The reaction was carried out at a sample temperature of 990 K for 5 min at a partial pressure of CH_4 and O_2 of 5 and 1 Torr, respectively.

that [Li^+O^-] centers play a direct role in the methane activation step. A detailed argument for the F center as the active site in methane activation can be found elsewhere [16].

These preliminary results, which show an excellent correlation between the kinetic results obtained over the thin-film MgO and those obtained over a powdered MgO catalyst, indicate that thin MgO films can serve as excellent models for methane coupling studies. The thin films have been shown to be very amenable to study by the charged particle techniques of surface science. Further kinetic and surface spectroscopic experiments are under way to investigate specific reaction mechanisms and surface intermediates for this potentially important technological reaction.

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