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Selective oxidation of methane over MoO_x/SiO_2: isolation of the kinetics of reactions occurring in the gas phase and on the surfaces of SiO_2 and MoO_x

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Abstract

The selective oxidation of methane to formaldehyde over MoO_x/SiO_2 was investigated to identify the contributions of methane and formaldehyde reactions occurring in the gas phase and on the surfaces of SiO_2 and dispersed MoO_x to the overall observed reaction rate. Experiments were conducted with 4.5 wt% MoO_3/SiO_2 at a nominal surface concentration of 0.44 $\mathrm{Mo\,nm^{-2}}$. Data were acquired for CH_4/O_2 ratios from 2 to 34 and temperatures from 848 to 923 K. Homogeneous oxidation of methane was negligible, and the homogeneous oxidation of formaldehyde contributed only to a small degree. The formation of formaldehyde was found to occur largely over MoO_x and only to a limited degree over SiO_2. By contrast, the rates of formaldehyde consumption over MoO_x and SiO_2 were comparable. For SiO_2 the only process occurring was CH_2O decomposition, which was independent of the CH_4/O_2 ratio, whereas in the case of MoO_x, CH_2O decomposition was accompanied by combustion of the H_2 formed and by direct CH_2O combustion principally to CO. A comprehensive model of the overall reaction kinetics was assembled from the kinetics determined for the reactions of methane and formaldehyde in the gas phase and on the surfaces of SiO_2 and MoO_x. This model describes the observed rates of methane conversion and the formaldehyde selectivity measured experimentally as functions of temperature and CH_4/O_2 ratio. This model is then used to determine the maximum single-pass yield of CH_2O for a given temperature and CH_4/O_2 ratio. It is predicted that the maximum single-pass yield increases with reaction temperature and decreasing CH_4/O_2 ratio.

Keywords: Methane; Formaldehyde; Methane oxidation; Formaldehyde oxidation; MoO_3/SiO_2; Molybdena; Silica

1. Introduction

The selective oxidation of methane to formaldehyde in a single step is a challenging problem of great practical importance [1]. Silica-supported oxides are among the best-performing heterogeneous catalysts for the selective oxidation of methane, especially the supported oxides of Mo, V, and Fe [2–4]. Silica has emerged as the preferred support because other refractory supports, such as TiO_2 and Al_2O_3, burn formaldehyde very rapidly at temperatures well below those required for the activation of methane [5]. Although SiO_2 is inert to CH_2O relative to other supports, it still decomposes CH_2O rapidly at temperatures and contact times relevant to methane oxidation [6]. Since the optimum metal loading needed to achieve maximum formaldehyde yield is well below monolayer coverage [2,7], most of the exposed surface area is SiO_2. The loss of CH_2O via homogeneous reaction is also known to occur [8,9] and has been implicated as a primary factor limiting CH_2O yield during CH_4 oxidation over MoO_x/SiO_2 [7]. However, previous studies modeling the kinetics of CH_4 oxidation over bare SiO_2 and MoO_x/SiO_2 have ignored the gas-phase contribution to the CH_2O reaction rate [10–13]. Therefore the question arises, how much of a role do the silica support and the gas phase play in determining the product distribution during methane oxidation over silica-supported oxides?

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The selective oxidation of methane to formaldehyde may be reduced to two processes, the formation and consumption of the product formaldehyde. The kinetics of formaldehyde consumption (i.e., decomposition and oxidation) have typically been studied indirectly by analysis of rate data for methane oxidation. However, we can obtain a better understanding of the kinetics of CH_2O decomposition and oxidation by studying these secondary processes independently of CH_4 oxidation.

This study focuses on decoupling the rates of reaction occurring over MoO_x/SiO_2. The rates of CH_4 oxidation and CH_2O consumption occurring in the gas phase, on the SiO_2 support, and on the MoO_x sites are decoupled through kinetic analysis of CH_4 oxidation and CH_2O reaction data obtained over a wide range of feed compositions and over a range of temperatures relevant to methane activation (> 848 K). The reaction network and rate laws utilized are justified by kinetic analysis. The individually measured kinetics are assembled to describe the relevant processes occurring during CH_4 oxidation over MoO_x/SiO_2. The model is used to describe the effects of operating conditions on catalyst performance and to define the contributions of the gas phase, exposed support, and supported MoO_x to the overall rates of methane oxidation and formaldehyde consumption.

2. Experimental

A MoO_x/SiO_2 catalyst was prepared by aqueous impregnation of Silicycle 60-Å silica gel with ammonium heptamolybdate (AHM) tetrahydrate (Aldrich 99.98% pure). The bare silica gel was washed in 9 M HNO_3 at 333 K, rinsed thoroughly with deionized water, and calcined in flowing air for 3 h at 973 K to remove alkaline earth impurities [14,15]. This treatment reduced the silica surface area from 500 to 460 $m^2\,g^{-1}$, as measured by five-point BET analysis of N_2 adsorption isotherms. AHM (0.067 g) was dissolved in 2.1 g of deionized water (150% of the pore-filling amount) for each gram of silica gel to be prepared. The silica and solution were mixed to dryness in a bath heated at 333 K, oven-dried at 383 K overnight, and calcined under flowing air at 873 K for 3 h before use. After loading with molybdena, the catalyst surface area was 426 $m^2\,g^{-1}$. Elemental analysis (Galbraith Laboratories) determined the Mo weight fraction to be 3.0% (4.5 wt% as MoO_3), so that the nominal surface coverage of MoO_x was 0.44 $Mo\,nm^{-2}$. The diameter of the catalyst particles was 200–500 µm, which was sufficiently small to ensure that the reactions were not limited by mass transfer according to the Weisz–Prater criterion [16]. The catalyst was used without adjustment of the size distribution or dilution.

The catalyst properties are summarized in Table 1. The parameter ζ describes the ratio of the exposed SiO_2 area per unit bed volume of the MoO_x/SiO_2 catalyst to that of the bare SiO_2, and is calculated as

$$\zeta = \frac{a_m \rho_b}{a_m^0 \rho_b^0}\left(1 - \frac{c_m}{c_m^{mono}}\right), \tag{1}$$

where a_m and ρ_b are the specific surface area and bulk density of the MoO_x/SiO_2 catalyst, respectively, and a_m^0 and ρ_b^0 are the corresponding parameters for the bare SiO_2. The term in parentheses accounts for the fraction of the surface of MoO_x/SiO_2 occupied by MoO_x. c_m is the surface concentration of Mo, and c_m^{mono} is the theoretical monolayer coverage of MoO_x, taken as 8.2 $Mo\,nm^{-2}$ [17]. The porosity ε is calculated from the bulk density ρ_b and skeletal density ρ_s of each catalyst as

$$\varepsilon = \frac{\rho_b}{\rho_\varepsilon} = 1 - \frac{\rho_b}{\rho_s}, \tag{2}$$

where ρ_b was measured by volumetry, and ρ_s was estimated from linear summation of skeletal densities of the SiO_2 and MoO_x, assuming the MoO_x to be present as bulk MoO_3:

$$\rho_s = (2.20\ g\,cm^{-3})(1 - \omega_{MoO_3}) + (4.62\ g\,cm^{-3})\omega_{MoO_3}, \tag{3}$$

where ω_{MoO_3} is the weight fraction of MoO_x as MoO_3.

Raman spectra were recorded with a Kaiser Optical HoloLab 5000 series Raman spectrometer equipped with a Nd:YAG laser that was frequency-doubled to 532 nm and operated at 7 mW. Catalyst samples (50–100 mg) were ground into powder and pressed into discs 1 cm in diameter at 10,000 psi. The discs were placed in a sealed rotary cell and rotated at 400 rpm during laser exposure to distribute the beam over a greater area and reduce local heating. The cell was heated to 923 K with air flowing over the samples to examine the state of the catalysts at a temperature relevant to CH_4 oxidation. Cubic splines were utilized to remove background fluorescence. Raman peak positions were reproducible to within 1 cm^{-1} for strong peaks and 2 cm^{-1} for all peaks.

Flow experiments were conducted by supporting the catalyst on a plug of quartz wool in a quartz reactor with a quartz-sheathed thermocouple inserted halfway into the bed

Table 1
Catalyst physical properties

Catalyst	Mo surface concentration c_{Mo} ($Mo\,nm^{-2}$)	Specific surface area a_m ($m^2\,g^{-1}$)	Bulk density ρ_b ($g\,cm^{-3}$)	Skeletal density ρ_s ($g\,cm^{-3}$)	Porosity ε	Residual exposed surface area ζ
SiO_2	–	460	0.570	2.20	0.741	1
MoO_x/SiO_2	0.44	426	0.660	2.28	0.711	1.01