Catalysis Letters 21 (1993) 209–214

Transient experiments on the selective oxidation of methane to formaldehyde over V_2O_5 / SiO_2 studied in the temporal-analysis-of-products reactor

B. Kartheuser, B.K. Hodnett

Department of Chemical and Life Sciences, University of Limerick,
Limerick, Ireland

H. Zanthoff and M. Baerns

Lehrstuhl fur Technische Chemie, Ruhr-Universität Bochum,
PO Box 10 21 48, D-4630 Bochum 1, Germany

Received 2 June 1993; accepted 16 June 1993

Methane oxidation to formaldehyde was studied over a vanadium oxide catalyst supported on silica at 630°C using the technique known as temporal analysis of products with sequential pulsing of methane and oxygen. This work shows that methane interacts very weakly and oxygen very strongly with the catalyst surface and it is concluded that the initial activation of methane involves an adsorbed oxygen species. Methyl radicals formed in the first step subsequently extract lattice oxygen to yield formaldehyde.

Keywords: Methane; formaldehyde; oxidation; vanadium oxide; silica

1. Introduction

A number of studies have now appeared relating to the selective oxidation of methane into formaldehyde over heterogeneous catalysts at ambient pressure [1–17]. In these conditions methanol is not usually detected among the reaction products, unless large amounts of steam are added to the feed gas [16]. A number of mechanistic studies have also appeared. Although different mechanisms have been proposed for the two major catalyst systems applied to this problem, namely molybdenum oxide on silica and vanadium oxide on silica, some common features appear. The most important of these is that CH_3 radicals and surface methoxy species have been cited in most mechanisms [1–4,11,12,16]. Recent evidence shows that when a mixture of CH_4 and $^{18}O_2$ is contacted with MoO_3/SiO_2 the product HCHO featured almost exclusively ^{16}O, evidently extracted from the lattice [18]. Some ambiguity remained regarding the nature of the species, adsorbed oxygen or lattice oxygen, which affects the primary activation of the methane to form the methyl radical and the stage of the mechanism in which the oxygen is inserted into the hydrocarbon. Here we report the results of a study of methane oxidation to formaldehyde over a vanadium oxide catalyst supported on silica using the experimental technique known as temporal analysis of products (TAP) [19] in which these questions are addressed.

2. Experimental

A catalyst with 1 wt% vanadium was prepared by impregnation of SiO_2 (Cabosil) with an aqueous solution of $(NH_4)_2VO_3$. Prior to use the catalyst was calcined at 550°C for 8 h in air. Previous work in conventional fixed bed reactors operated at atmospheric pressure indicated that the best yields of formaldehyde were obtained at 1 wt% vanadium on the support [8]. 150 mg of this catalyst was loaded into the reactor of a TAP apparatus, held in place by two layers of inert sand, and maintained under vacuum for 2–3 h prior to pulsing. The reaction temperature was 630°C throughout this study. A mixture of methane, oxygen and argon (9 : 1 : 1) (pulse sizes $= 3.6 \times 10^{15}$ molecules) was passed through the reactor. These conditions correspond to the Knudsen diffusion regime so that gas phase collisions were largely eliminated. The TAP profile was established as the average of 100 individual pulses for each product and 20 pulses for each reactant.

Two series of sequential pulsing experiments were performed. In the first of these a pulse of oxygen was passed over the catalyst (1.8×10^{15} molecules per pulse) followed at a precise delay by a pulse of methane (1.8×10^{15} molecules per pulse). The separation between the pulses will be referred to below as the pulse interval (PI), and was varied between 0 and 5 s. The total cycle time between pulses of oxygen was maintained at 5 s throughout, and usually a total of 100 cycles were required to achieve satisfactory signal to noise ratio and establish the TAP profiles.

In the second series of experiments the sequence was reversed so that the methane was pulsed first followed by oxygen at a precise pulse interval. All other features were the same. In practice HCHO, CO and CO_2 products were monitored, but HCHO profiles only are presented in this publication.

Formaldehyde production in these sequential pulsing experiments was always compared with the amounts produced when the methane and oxygen pulse were passed through the reactor simultaneously.

3. Results and discussion

When methane was pulsed over the catalyst surface in the absence of gas phase oxygen, formaldehyde was not produced even after the surface had been freshly reoxidized. This result was generally observed provided a 60 s interval was allowed between exposure to oxygen and passage of the methane pulse. When methane and oxygen were pulsed simultaneously, methane, oxygen, formaldehyde, carbon monoxide and carbon dioxide were detected at 630°C, the standard temperature used for this study. The observed TAP profile is indicated in fig. 1. Methanol was never detected in these reaction conditions, and when $^{18}O_2$ was used as oxidant formaldehyde appeared exclusively as $HCH^{16}O$. The extent of exchange between the catalyst and $^{18}O_2(g)$ was very small. Bearing in mind that these experiments were performed in the Knudsen diffusion regime, wherein gas phase collisions are largely eliminated, the TAP profile shown in fig. 1 is consistent with the following reaction network:

$$CH_4 \rightarrow HCHO \rightarrow CO \rightarrow CO_2 .$$

Fig. 2 summarises the sequential pulsing experiments in which the oxygen pulse preceded the methane pulse by a precise interval. Typically formaldehyde was produced in sequential pulsing experiments when a pulse of methane was passed through the reactor up to 5 s after the oxygen pulse had been administered. Extending the cycle time to 60 s eliminated formaldehyde associated with the methane pulse. Formaldehyde was not produced when the oxygen pulse was passed through the reactor, indicating that all the hydrocarbon related species from the previous cycle had desorbed from the catalysts surface, prior to the passage of the oxygen pulse. These results point to different lifetimes for hydrocarbon and oxygen species on the catalyst.

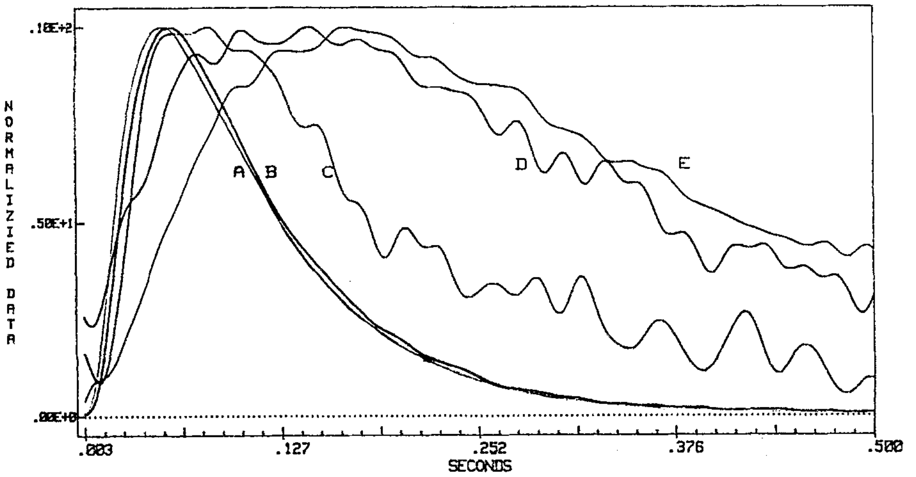

Fig. 1. TAP profiles for A = CH_4 (amu: 15), B = O_2 (amu: 32), C = HCHO (amu: 31), D = CO (amu: 28), E = CO_2 (amu: 44). T = 630°C, 150 mg 1V Cabosil, pulse size 2.6×10^{15} molecules, average of 100 pulses.

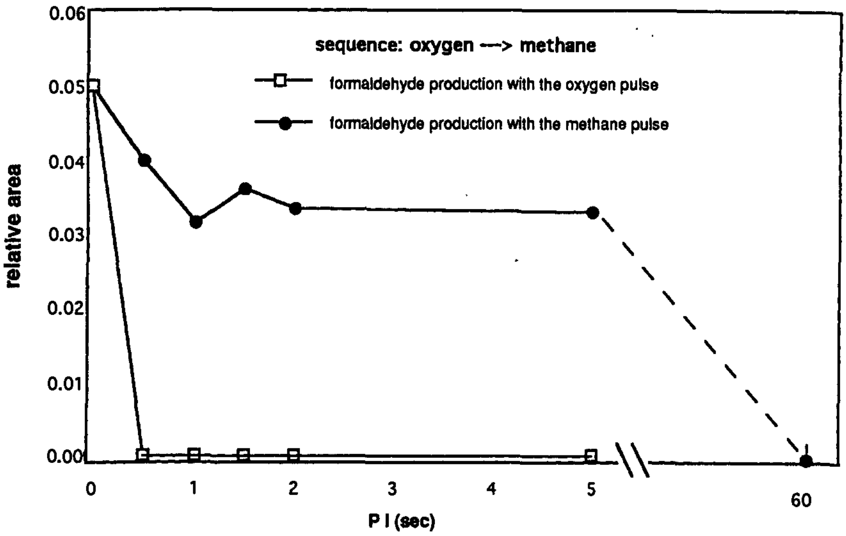

Fig. 2. Influence of pulse interval (PI) on formaldehyde production during sequential pulsing of oxygen followed by methane over 1-Cabosil at 630°C.

Fig. 3 summarises the results of the sequential pulse experiments corresponding to the second series where methane was pulsed before oxygen. The following features are important: HCHO was produced when the methane pulse, at PI = 0, was passed over the surface, corresponding to methane and oxygen being pulsed simul-

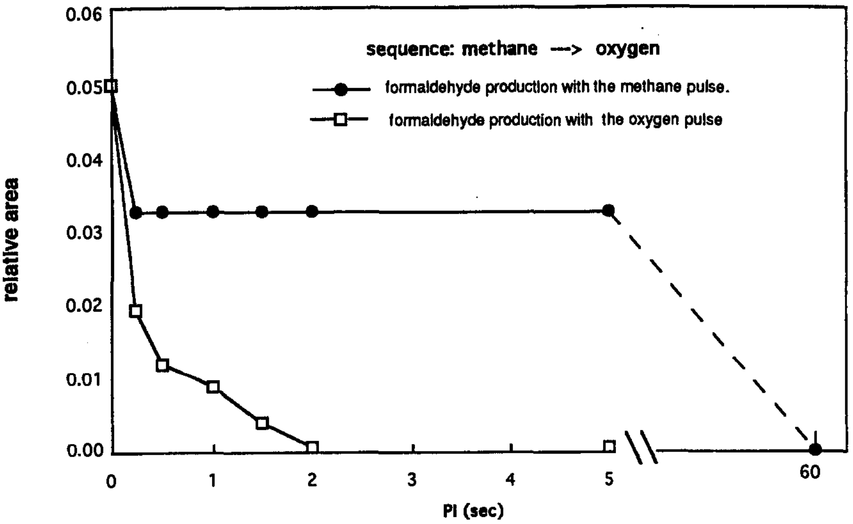

Fig. 3. Influence of pulse interval (PI) on formaldehyde production during sequential pulsing of methane followed by oxygen over 1-Cabosil at 630°C.

taneously. Some formaldehyde was detected during passage of the O_2 pulse, but the amount was small, and in this case was strongly dependent on the PI. As shown in fig. 3 formaldehyde was produced during passage of the oxygen pulse through the reactor only if the PI was less than 2 s. At longer PIs there was insufficient residual methane, or methane derived species, still on the surface to facilitate reaction. These data indicate that some residual carbon containing species, possibly a reaction intermediate, remained on the catalysts surface for up to 2 s. By contrast, the amount of formaldehyde emanating from the methane pulse was essentially constant and probably reflected the presence on the catalyst surface of a level of oxygen species with a lifetime of greater than the cycle time, namely 5 s. When the cycle time was extended to 60 s (fig. 3) formaldehyde was not detected when methane was pulsed.

One essential conclusion to be drawn from this work is that there is a very weak interaction between the catalyst surface and methane, whereas interaction with oxygen involved the formation of surface species with lifetimes between 5 and 60 s, which were capable of activating the methane, resulting ultimately in the production of formaldehyde. Given the formaldehyde is not produced from methane pulses when up to 60 s is allowed for the flushing of oxygen species from the catalyst surface, it seems reasonable to conclude that methane is initially activated through interaction with a form of adsorbed oxygen, most likely O_2^- or O^-, with the formation of methyl radicals and that further reaction of these species leading ultimately to the formation of formaldehyde, occurs via a reaction with lattice oxygen leading to its incorporation into the product. The following sequence can be written to describe the steps involved:

$$CH_4 + O^-_{n(ads)} \rightarrow CH_3\cdot + OH\,,$$

$$CH_3 + {}^{16}O_{(latt)} \rightarrow HCH^{16}O + H\cdot\,.$$

Acknowledgement

This work has been supported in part by the European Community Joule Programme under contract number JOUF-0044-C.

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