Catalysis Letters 21 (1993) 201–207

Oxygen pathways in methane selective oxidation over silica-supported molybdena

Roy Mauti and Charles A. Mims[1]

Department of Chemical Engineering and Applied Chemistry, University of Toronto,
Toronto, Ontario, Canada M5S 1A4

Received 28 April 1993; accepted 17 July 1993

Oxygen pathways for CH_4 partial oxidation over a silica-supported molybdena catalyst were investigated using a series of oxygen isotopic exchange experiments and steady state oxygen isotope transients. The initial source of oxygen in the products is masked by rapid and extensive oxygen exchange between the catalyst and the products CO_2 and HCHO. This exchange process occurs at the surface molybdena site and is accompanied by rapid O interchange between the surface and support phases which allows access to the bulk of the support. Laser desorption Fourier transform mass spectra, LDFTMS, indicate equal enrichment of ^{18}O in both the silica and molybdena fragments.

Keywords: Methane selective oxidation; silica supported molybdena catalyst; oxygen isotopic exchange; laser desorption Fourier transform mass spectra (LDFTMS)

1. Introduction

The best current HCHO yields in the direct partial oxidation of methane over heterogeneous catalysts are only several percent [1–4]. An understanding of the oxygen pathways and the active oxygen species responsible for selective and non-selective reactions is required in order to understand the current yield limits and aid in the search for improved catalysts. Dynamic isotope tracing using an $^{16}O_2 \rightarrow {}^{18}O_2$ feed switch is a powerful tool for studying oxygen pathways at steady state reaction conditions [5–8]. After switching the reactant O_2 to the new ^{18}O isotope, the only sources of the old ^{16}O isotope are the various catalyst-bound oxygen species (adsorbed on surface, in surface silica and molybdena phases, and in bulk silica). Monitoring the fraction of ^{16}O evolved in each of the products yields information on the size of the oxygen pools involved and the reaction pathways. Interpretation of these results requires information about post-formation exchange of

---

[1] To whom correspondence should be addressed.

oxygen between the products and the catalyst. These processes can mask the identity of the active oxygen species [5,9].

Silica-supported molybdena catalysts have received much attention for selective methane oxidation and have shown the most promise to date. SiO_2 supported molybdena catalysts like those studied here have been characterized by others [10–12]. It is generally agreed that at low Mo loadings ($<2\%$ Mo) a well dispersed and stable Mo surface species is formed. These species have been reported to be monomeric tetrahedrally coordinated MoO_4^{2-} species [10], and octahedrally coordinated Mo species such as polymolybdates and silicomolybdic acid (Mo_{12}) [11]. It has been shown that the formation of the above structure is dependent on preparation and treatment procedures such as calcination and hydration [12]. This dispersed surface phase has been correlated to methane partial oxidation activity. At higher Mo loadings less stable and less active crystalline MoO_3 is observed on the catalyst surface.

2. Experimental

The supported catalyst was prepared by the method described in ref. [1]. Fumed silica (Cabosil M5, Cabot Corp.) was wetted with an ammonium heptamolybdate (Baker) solution of appropriate strength. After drying and calcining in air at 500°C, the catalyst was pressed, crushed and sieved to produce particles of 80–120 μm diameter. The catalyst used in this study contained 1.8 wt% Mo and the total surface area was 125 m^2/g. Based on previous extensive characterization of similar catalysts [10–12], and the lack of any bulk MoO_3 X-ray diffraction features in ours, the MoO_3 was assumed to be fully dispersed in an active surface layer.

The experiments were performed in an apparatus similar to one described previously [13]. A quartz-lined downflow tubular reactor (4 mm inside diameter) held the catalyst charge (0.11 g, 0.38 cm^3 bed volume). Temperatures were monitored by a quartz-sheathed thermocouple imbedded in the top of the catalyst bed. Reactant gas mixtures were produced with flow controllers, and two separate streams (for the two isotopic variants) were produced simultaneously for the pulse and transient experiments. The gases were used without further purification: CH_4 (99.99%, Matheson) and O_2 (ultrahigh purity, Matheson), $C^{18}O_2$, $C^{18}O$, and $^{18}O_2$ (ICON, 99 at% ^{18}O). A small amount of either argon or neon in one stream provided a time mark for comparison of the transient behavior of the products. Switches between reactant streams and data collection were under PC control. The product composition was analyzed by mass spectrometry. The inlet, just under the bed and made of quartz, showed no discernible propensity to hold up the oxygenated products. A multi-loop sampling valve allowed the collection of time-resolved samples for more detailed isotopic analysis (GCMS, NMR) when desired.

3. Results and discussion

The results of an isotopic switch ($^{16}O_2$–$^{18}O_2$) are shown in fig. 1. From the slow decays in the ^{16}O content of oxygen containing products it is clear that large quantities of catalyst ^{16}O appear in the products CO, CO_2, and HCHO well after the gas phase O_2 has been switched to the new ^{18}O label. The amount of ^{16}O incorporated into the products (1100 μmol/g by the end of the experiment) far exceeds that associated with the surface molybdena phase (600 μmol/g). At this point, the fact that the products still contain 80% ^{16}O indicates that most of the bulk catalyst oxygen (including the silica support) participates in the reaction. Such results have been seen in several investigations of selective oxidation reaction mechanisms in non-steady state experiments (for examples see ref. [14]). Often such results are interpreted as showing that the bulk catalyst oxygen is responsible for the oxidation pathway(s). However, post-reaction oxygen exchange between the catalyst and the products can erase the connection between the initial reactive oxygen and that leav-

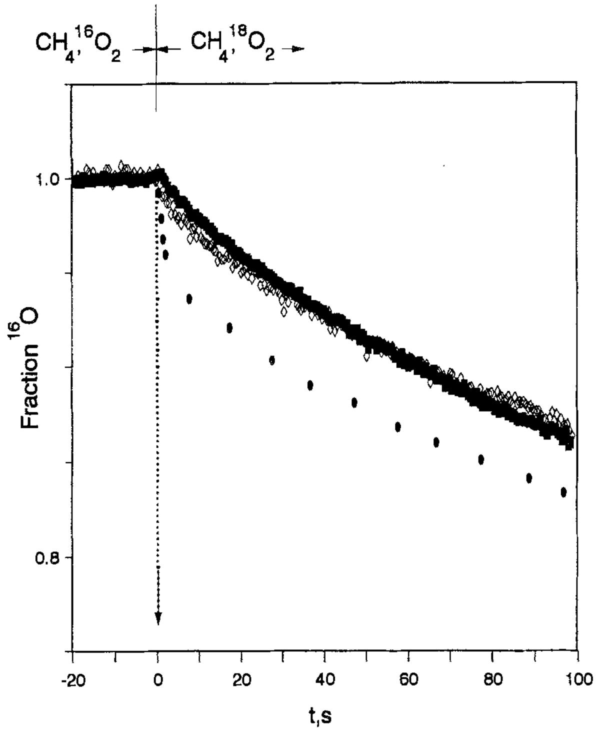


Fig. 1. Transient isotopic response in products CO (●), CO2 (◇), and HCHO (■) to an abrupt reactant change ($CH_4(0.63)/^{16}O_2(0.07)/Ar$ with Ne tracer $(0.30) \rightarrow CH_4(0.63)/^{18}O_2(0.07)/Ar(0.30)$) at $t = 0$ s. The dashed line represents the decay in $^{16}O_2$ and the Ne tracer which both go to zero in the first 5 s of the transient. Reaction conditions: $T = 650°C$, 0.15 g catalyst, total reactant flow 45 ml(STP)/min, CH_4 conversion = 0.03, selectivities: HCHO = 0.75, CO_2 = 0.10, CO = 0.15.

ing with the products (for a complete discussion of earlier work, see ref. [15]). The following oxygen exchange results demonstrate that this is in fact the case here.

Oxygen exchange between CO_2 and the silica-supported molybdena catalyst was examined by introducing a pulse of $C^{18}O_2$ over the catalyst at reaction conditions and monitoring the isotope distribution of the resulting effluent CO_2. The results are shown in fig. 2. The injection of CO_2 into an empty reactor results in a pulse in the *m/e* 48 signal as expected. When repeated over the catalyst, no response at *m/e* 48 is observed, but instead a similar response in the *m/e* 44 signal occurs. Carbon dioxide thus undergoes a large number of exchange events during its residence time in the reactor, and acquires the isotopic make-up of this catalyst oxygen pool, initially all ^{16}O. This exchange continues with time and eventually

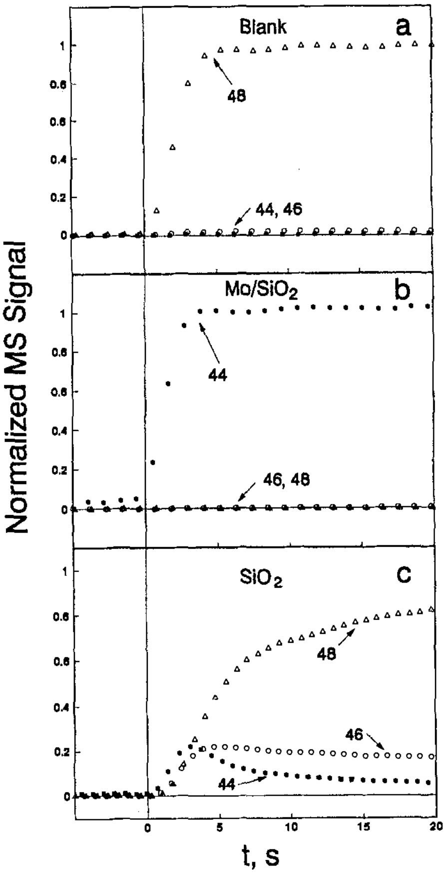


Fig. 2. Mass spectrometer response to a pulse of $C^{18}O_2$ (4% of total gas flow) added to a mixture $CH_4(0.63)/^{16}O_2(0.07)/Ar(0.30)$ fed at 650°C to (a) an empty reactor, (b) 0.15 g of 1.8% Mo/SiO_2 and (c) 0.15 g of SiO_2 support only: *m/e* = 44 (■), 46 (○) and 48 (△).

involves a large fraction of the catalyst oxygen, a result similar to that in the isotopic transient. This rapid exchange also persists to temperatures well below reaction conditions. Oxygen exchange between CO_2 and various methane coupling catalysts has been observed [5,9] but the extensive involvement of the support here is unusual. Although a surface carbonate is a likely intermediate in this exchange process, previous ^{12}C–^{13}C transient studies [13] show that the surface abundances of all carbon containing intermediates (including any surface carbonates) are extremely small under these conditions. That the molybdenum phase is responsible for most of this exchange is shown by a similar exchange measurement with the silica support alone (fig. 2c). By comparison with the supported molybdena catalyst, the initial exchange rates are at least 100 times slower on the support and this exchange involves a much smaller amount of oxygen (~ 150 μmol/g).

Oxygen scrambling between HCHO and the supported molybdena is also extremely rapid. This exchange process was examined by passing an inert gas stream containing approximately 1% HCHO over the catalyst bed after the catalyst had been ^{18}O doped by an isotopic transient. Fig. 3 shows the results of this experimental sequence. The GCMS results in panel c show that HCHO acquires the same ^{18}O content as the catalyst, indicating very rapid exchange similar to the CO_2 behavior. This rapid equilibration persists to temperatures as low as 300°C. The survi-

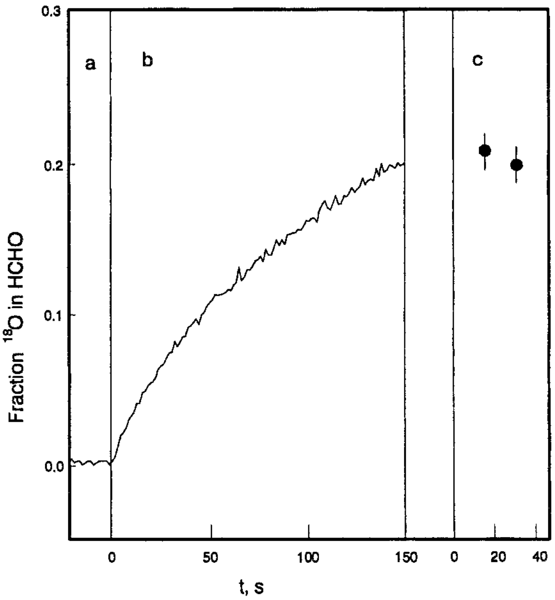
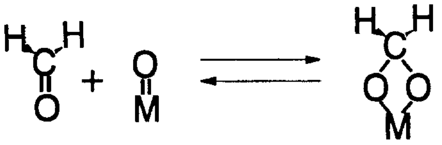


Fig. 3. Fraction of ^{18}O found in formaldehyde (a) during reaction with $CH_4(0.63)/^{16}O_2(0.07)$ followed by (b) $CH_4/^{18}O_2$ as in fig. 1, (c) as 1% $HCH^{16}O$ in Ar is fed to the resulting labelled catalyst. Between (b) and (c) the reactor was purged with Ar for 30 s.

val of formaldehyde under these severe reaction conditions while undergoing multiple oxygen exchange reactions is surprising, but can be explained by the reversible formation of a dioxymethylene (surface acetal) intermediate:


(1)

Oxygen scrambling between formaldehyde and a ferric molybdate catalyst has been reported in the literature [16], although experimental details were not presented. Similar oxygen scrambling at low temperatures (200–300°C) between acetone and silica-supported vanadia [17] and also between propylene oxide and a CuO catalyst have been documented [18].

Oxygen exchange between $C^{18}O$, $^{18}O_2$ and the catalyst was also investigated. By contrast to the HCHO and CO_2 results, CO and O_2 show no measurable oxygen exchange under these conditions.

As previously mentioned, the silica support must be involved to supply the amounts of exchangeable oxygen seen in these experiments. Further evidence of involvement of both the silica support and the surface molybdena phase was obtained by laser desorption Fourier transform mass spectroscopy (LDFTMS) performed on a sample of the catalyst enriched in ^{18}O during the course of CH_4 oxidation reactions using $^{18}O_2$. The spectra indicate equal ^{18}O enrichment in silica and molybdena ions [#1]. Although oxygen exchange involves both molybdena and silica phases, the exchange experiments show that the molybdena phase is responsible for the overwhelming majority of the exchange activity. This overall phenomenon may be described as a "spill-through" effect, whereby a rapid flow of oxygen between CO_2 and bulk silica is channelled through the surface molybdena sites where the gas–solid exchange occurs. For the rate of CH_4 oxidation in our experiment, the self-diffusion coefficient of oxygen atoms in bulk silica of approximately 10^{-15} cm^2/s (coefficient for fused silica) is sufficient to mix the oxygen atoms within the primary (15 nm) silica particles, thus making the entire oxygen inventory in the catalyst available for exchange at the surface.

It is evident that isotopic tracing of the origin of oxygen in HCHO and CO_2 is completely dominated by post-formation oxygen exchange between these products and the catalyst and *no* information about the original oxygen source remains. The CO product does not suffer from this limitation, but since the majority of CO forms sequentially from HCHO [4], its transient behavior in fig. 1 is also dominated

---

[#1] LDFTMS data indicates that the molecular species $[^{28}Si^{16}O_2{}^{18}O]^-$, m/e 77.9659, has an abundance of 9.9% relative to $[^{28}Si^{16}O_3]^-$, m/e 75.9617. Similarly species $[^{100}Mo^{16}O_2{}^{18}O]^-$, m/e 149.8970, has an abundance of 8% relative to $[^{100}Mo^{16}O_3]^-$, m/e 147.8923. These data indicate that within experimental error equal enrichment of both silica and molybdena phases occurs, however the possibility of oxygen scrambling during sample handling and treatment cannot be ruled out.

by HCHO oxygen exchange. The small amount of CO which shows a prompt ^{18}O uptake could result from a minor direct CH_4 oxidation channel.

Acknowledgement

We wish to thank the Natural Sciences and Engineering Research Council (NSERC) of Canada, Exxon Corporation and Imperial Oil, Ltd. for their support of this work. We also wish to thank Dr. Zhenmin Liang of Extrel FTMS, Inc., Madison WI for obtaining the LDFTMS results.

References

[1] N.D. Spencer J. Catal. 109 (1988) 187.
[2] M.Yu. Sinev, V.N. Korshak and O.V. Krylov, Russ. Chem. Rev. 58 (1989) 22.
[3] J.J. Brown and N.D. Parkyns, Catal. Today 8 (1991) 305.
[4] J.H. Lunsford, in: *Methane Conversion*, eds. D.M. Bibby, C.D. Chang, R.F. Howe and S. Yurchak (Elsevier, Amsterdam, 1988) p. 359.
[5] C.A. Mims, R.B. Hall, A.J. Jacobson, J.T. Lewandowski and G. Myers, in: *Surface Science of Catalysis: In-Situ Probes and Reaction Kinetics*, ACS Symp. Series 482, eds. F. Hoffmann and D. Dwyer (ACS, Washington, 1991) p. 230.
[6] C. Mirodatos, Catal. Today 9 (1991) 83.
[7] A. Ekstrom and J.A. Lapszewicz, J. Am. Chem. Soc. 110 (1988) 5226.
[8] K.P. Peil, J.G. Goodwin and G. Marcelin, J. Phys. Chem. 93 (1989) 5977.
[9] N.W. Cant et al., J. Catal. 124 (1990) 336.
[10] A.N. Desikan, L. Huang and S.T. Oyama, J. Phys. Chem. 95 (1991) 10050.
[11] S. Kasztelan, E. Payen and J.B. Moffat, J. Catal. 112 (1988) 320.
[12] J.M. Stencel, J.R. Diehl, J.R. D'Este, L.E. Makovsky, L. Rodrigo, K. Marcinkowska, A. Adnot, P.C. Roberge and S. Kaliaguine, J. Phys. Chem. 90 (1986) 4739.
[13] R. Mauti and C.A. Mims, ACS Preprints, Petroleum Chemistry Division, Symposium on Natural Gas Upgrading, 1992, Vol. 37 (ACS, Washington) p. 65.
[14] G.W. Keulks, J. Catal. 19 (1970) 232;
K.M. Sancier, P.R. Wentrcek, and H. Wise, J. Catal. 39 (1975) 141;
K. Otsuka and M. Hatano, Chem. Lett (1992) 2397.
[15] A. Ozaki, *Isotopic Studies of Heterogeneous Catalysis* (Kodansha/Academic Press, Tokyo/New York, 1977).
[16] C.J. Machiels, U. Chowdry and A.W. Sleight, ACS Preprints, Petroleum Chemistry Division, 1983, Vol. 28 (ACS, Washington) p. 1293.
[17] T. Tanaka, R. Tsuchitani, M. Ooe, T. Funabiki and S. Yoshida, J. Phys. Chem. 90 (1986) 4906.
[18] Tezuka and Takeuchi, Z. Phys. Chem. NF 97 (1975) 321.