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Oxygen Involvement in the Partial Oxidation of Methane on Supported and Unsupported V_2O_5

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O exchange of O_2 with V_2O_5/SiO_2, V_2O_5/Al_2O_3, V_2O_5, SiO_2, and Al_2O_3 was studied using steady-state isotopic transient kinetic analysis. It was found that bulk V_2O_5, V_2O_5/SiO_2, V_2O_5/Al_2O_3, and Al_2O_3 exhibited some oxygen exchange capability, whereas SiO_2 exhibited negligible oxygen exchange capability under the conditions used. Oxygen exchange reactions were also studied over supported vanadia catalysts under steady-state oxidation reaction conditions. O exchange of O_2 with V_2O_5/SiO_2 increased significantly in the presence of methane. This is attributed to a redox reaction making the surface more active for O exchange in the presence of the methane. The involvement of catalyst oxygen in the formation of the products HCHO, CO, and CO_2 was demonstrated. However, an estimation of the contribution of the lattice oxygen in the formation of the products is complicated by the presence of secondary O exchange. The total amount of ^{16}O exchanged with the feed O_2 and the products indicates that the oxygen associated with silica or the vanadia–silica interface is also involved in the exchange process. In general, O exchange behavior of various product species with V_2O_5/Al_2O_3 was found to be similar to that with V_2O_5/SiO_2. However, unlike V_2O_5/SiO_2, the O exchange of O_2 with V_2O_5/Al_2O_3 did not increase significantly in the presence of methane. This was attributed to the differences in the interactions of vanadia with silica and alumina. It is speculated that the O associated with highly dispersed tetrahedral surface vanadia is involved in a primary oxidation reaction, whereas O associated with the bulk-like vanadia and with the support is involved either in secondary oxidation reactions of HCHO or CO or in secondary O exchange of various O containing product species. Caution must be taken in making any conclusions about the source of reactive oxygen during partial oxidation on oxide catalysts based on isotopic oxygen studies due to the ease of secondary oxygen exchange.

INTRODUCTION

The catalytic conversion of methane to ethane or oxygenates over oxide catalysts has acquired increased importance in recent years due to a worldwide surplus of methane. However, few studies have been reported on the direct conversion of methane to oxygenates such as methanol and formaldehyde (1–6, 36, 37). In addition, while the mechanism for the conversion of methane to ethane via an oxidative coupling reaction has been heavily investigated, there have been few studies which examine the reaction mechanism for the partial oxidation of methane to oxygenates (3, 5, 6).

One of the major issues in a partial oxidation reaction over oxide catalysts is the role of the catalyst oxygen. It is widely accepted that most partial oxidation reactions follow a Mars–van Krevelen-type mechanism in which the catalyst is partially reduced by the hydrocarbon forming oxygenated products (7–9). The catalyst is then reoxidized by gas-phase oxygen. However, little is known about the role of various oxygen species on the catalyst.

Much of the earlier research has concentrated on investigations of various isotopic exchange reactions in static systems (10–15). For example, Winter (10) and Klier and co-workers (11–12) have formulated exchange reactions for O_2 with a catalyst in terms of the number of catalyst oxygens involved in the exchange process. This subject has also been addressed in terms of a comparison of oxygen binding capacity and oxygen mobility for various catalysts (16, 17). More recently, several researchers have used isotopic tracers to establish the type of oxygen species involved in partial oxidation reactions (17–23). For example, Keulks and co-workers (20, 21) have studied the contribution of lattice oxygen to the partial oxidation of propylene to acrolein. However, in such studies secondary exchange reactions of oxygen after the formation of the products from a primary species have often been ignored. Patterson and Parker (17, 18) have successfully demonstrated the use of isotopic tracer studies for determination of the contribution of lattice and adsorbed oxygen on bulk Sn–Sb-oxide catalysts, taking into account the secondary O exchange reactions. However, very little is known about O exchange behavior over supported oxide catalysts (24).

The feasibility of using isotopic transient techniques for studying the role of catalyst oxygen has been shown (22, 25–27). With this technique the mechanistic information can be obtained without perturbing the steady state of the

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system (28). Recently, we have demonstrated the use of this technique for examining carbon reaction pathways during the partial oxidation of methane on V_2O_5/SiO_2 (29). We have also reported preliminary results of a study on the role of secondary O exchange during the partial oxidation of methane (30). This paper presents the final results of our investigation into the oxygen pathway for the partial oxidation of methane over supported vanadia catalysts using isotopic transient techniques.

In an accompanying paper we have reported on the nature of the vanadia species on silica- and alumina-supported vanadia catalysts (31). In particular, we have shown that the 1.6% V_2O_5/SiO_2 catalyst possesses bulk-like vanadia and tetrahedral surface vanadia species, whereas the 2% V_2O_5/Al_2O_3 catalyst possesses only tetrahedral surface vanadia species. In another accompanying paper, we have also reported on the reactivity of various vanadia species for methane oxidation (35). There it was concluded that a tetrahedral V site is essential for the abstraction of H atom from methane, whereas secondary oxidation reactions may occur on the bulk-like vanadia (32). Based on these conclusions and the oxygen transient data reported here, we have speculated on the role of O associated with different vanadia species in oxidation and/or exchange reactions occurring during methane oxidation.

EXPERIMENTAL

Silica- (Cab-O-Sil, M5, Cabot Corp., BET surface area = 170 m^2/g) and gamma alumina- (Vista Chemicals, BET surface area = 205 m^2/g) supported vanadia catalysts were prepared by wet impregnation starting from ammonium metavanadate (Aldrich Chemical Company, Inc., 99.99% purity). A detailed description of the preparation can be found elsewhere (31). The catalysts were dried at 100°C overnight, ground, and then calcined at 580°C for 8 h. Blank supports, SiO_2 and Al_2O_3, were subjected to a treatment similar to that of the impregnated catalysts. Bulk V_2O_5 (BET surface area = 30 m^2/g) was bought from Aldrich and used as received. The BET surface areas of the 1.6 wt% V_2O_5/SiO_2 and the 2 wt% V_2O_5/Al_2O_3 catalysts were found to be 152 m^2/g and 200 m^2/g, respectively.

The partial oxidation of methane was studied by allowing a mixture of CH_4 and O_2 to react on V_2O_5/SiO_2 and V_2O_5/Al_2O_3 catalysts in a quartz microreactor system. Detailed descriptions of the characterization of the catalysts and the experimental setup are given elsewhere (29, 31). The reaction conditions used were total flow rate = 31 cm^3/min, CH_4 flow rate = 10 cm^3/min, $CH_4/O_2 = 5$–10, $T = 550$–600°C, $P = 1$ atm. Helium was used as a diluent in all cases. All lines were heated in order to avoid condensation of products and polymerization of formaldehyde. All the gases used were of 99.99+% purity except $^{18}O_2$ (Isotec, Inc.), which was 98.4% pure. Prior to an isotopic switch, the reaction was carried out for ca. 1 h, and the steady-state activity and selectivity were measured using online GC (TCD and FID).

Oxygen transients were obtained by switching abruptly from $^{16}O_2$ to $^{18}O_2$ at steady state and monitoring the products continuously using mass spectrometry. The reaction system was connected to the mass spectrometer using a differentially pumped interface (25). A very fast data-acquisition rate was able to be realized by using an automatic computerized data-acquisition system. The electron energy was adjusted to about 20 eV in order to minimize excessive fragmentation of ions, thus avoiding any overlap in the mass numbers for the species of interest. In some cases, where an overlap of masses of the products was unavoidable, a fragment of the corresponding molecular ion was followed. For example, CO was followed at $m/e = 28$, whereas HCHO (or $HCH^{18}O$) was followed at $m/e = 29$ (or 31) (a fragment of HCHO (or $HCH^{18}O$)). Thus, it was possible to follow the evolution or decay of all the oxygen-containing effluent species by following the molecular ions corresponding to a species containing either ^{16}O or ^{18}O. For reaction on the V_2O_5/SiO_2 catalyst at 550°C, a lower CH_4/O_2 ratio of 5 was necessary in order to form sufficient CO to be detected in the mass spectrometer, whereas at 600°C a higher CH_4/O_2 ratio of 10 was necessary to form sufficient C_2H_6 and HCHO to be detected by the mass spectrometer (29).

Ar was used as a tracer in order to determine the gas-phase holdup of the system. All transients are represented as normalized effluent flow rates, $F(t)$ vs time. The total amount of ^{16}O in a particular product species desorbed from the catalyst up to a particular time was obtained by multiplying the area under the normalized curve for the ^{16}O containing species (after subtraction of the gas-phase hold up) by the total flow rate of that species.

An analysis of error in the measurements of ^{16}O exiting the reactor in the various products was done. Error in the measurement of all O containing species except water was estimated to be ca. ±12%. Error in the determination of ^{16}O exiting the reactor as H_2O was estimated to be ca. ±25%.

RESULTS

Steady-State Reaction

The steady-state activity and selectivity were measured for the supports, bulk V_2O_5, and the supported-V_2O_5 catalysts. It was found that neither SiO_2 nor bulk V_2O_5 exhibited any appreciable activity under the conditions used. On the other hand, Al_2O_3 exhibited significant activity for methane oxidation to CO and CO_2 only at 600°C and above (see Table 1). For the 1.6 wt% V_2O_5/SiO_2 catalyst, HCHO and CO were the major products observed at 550°C,

TABLE 1

Conversions and Product Selectivities for Various Catalysts

Catalyst	Temp (°C)	Conv (%)	Rate (μmol/g s)[a]	Selectivity (%)			
				HCHO	CO	CO_2	C_2H_6
1.6% V_2O_5/SiO_2	550	1.0	1.7	45	55	—	—
	600	5.1	8.5	6	80	10	4
2.0% V_2O_5/Al_2O_3	550	1.1	1.9	—	63	37	—
	600	3.0	5.1	—	60	40	—
Al_2O_3	600	0.4	0.7	—	70	30	—

[a] Rate of CH_4 conversion/g of catalyst.

whereas CO_2 and C_2H_6 could also be detected at 600°C. The activities and selectivities for the V_2O_5/SiO_2 catalyst are summarized in Table 1. For the 2% V_2O_5/Al_2O_3 catalyst, CO and CO_2 were the only products observed under the conditions used in these experiments. The activities and selectivities for this catalyst are also listed in Table 1. It is important to note that the activity measurements were carried out at atmospheric pressure and at temperatures where homogeneous gas-phase reactions are negligible. A detailed analysis of the steady-state activities of bulk and supported vanadia catalysts for methane partial oxidation have been reported in an accompanying publication (35). In general, the trends in the steady-state activities and selectivities of supports, bulk vanadia, and supported vanadia catalysts are in agreement with that observed by Spencer and co-workers (1, 2) for similar catalysts.

Steady-State Isotopic Transient Kinetic Analysis (SSITKA)

SiO_2, Al_2O_3, and bulk V_2O_5. The oxygen transients obtained by switching from $^{16}O_2$ to $^{18}O_2$ under steady-state conditions for SiO_2, Al_2O_3, and bulk V_2O_5 at 600°C are shown in Fig. 1. Since there was no source of ^{16}O after the isotopic switch other than the adsorbed and catalyst oxygen, the formation of the scrambled product $^{16}O\,^{18}O$ can be considered to be a measure of the oxygen exchange capability of the catalyst. It can be seen that SiO_2 exhibited negligible O exchange capacity. Bulk V_2O_5 and Al_2O_3, on the other hand, exhibited a low rate of O exchange. The amount of ^{16}O desorbed from the catalyst during the 5.5 min following the $^{16}O_2$ to $^{18}O_2$ switch was calculated and is listed in Table 2. The oxygen transients for SiO_2,

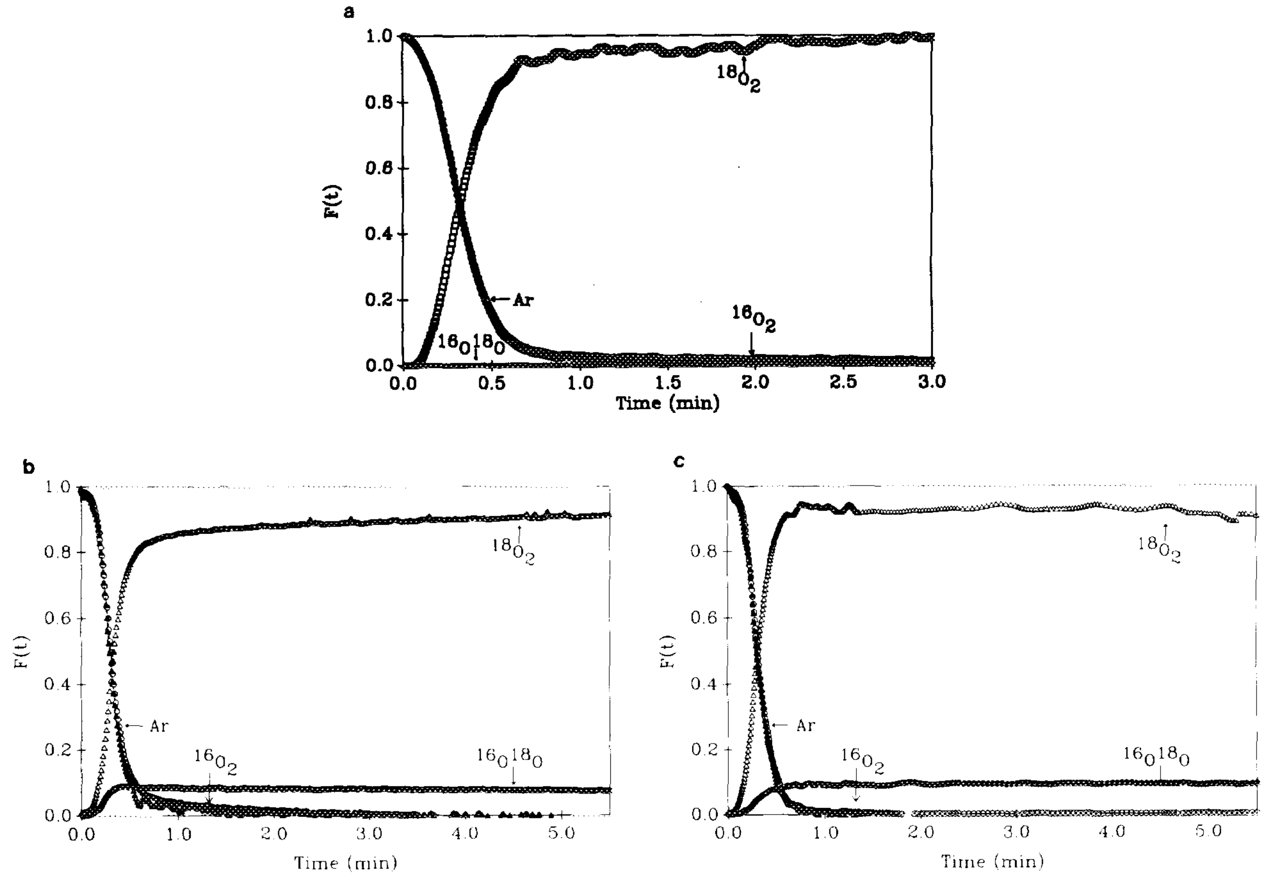

FIG. 1. (a) Oxygen transients for SiO_2 at 600°C. (b) Oxygen transients for Al_2O_3 at 600°C. (c) Oxygen transients for bulk V_2O_5 at 600°C.

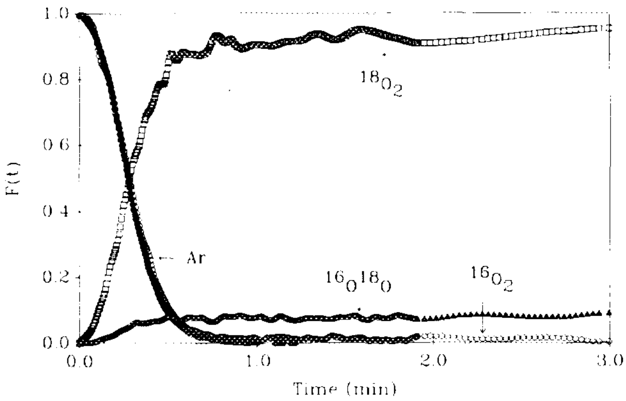

FIG. 2. Oxygen transients without reaction over V_2O_5/SiO_2 at 600°C.

TABLE 2

Summary of O Exchange with O_2 during 5.5 Min for the Catalysts Studied

Catalyst	Feedstream	^{16}O mmol/g of catalyst[a]	
		550°C	600°C
SiO_2	$^{18}O_2$, He	—	—
Al_2O_3	$^{18}O_2$, He	0.35	0.45
V_2O_5 (bulk)	$^{18}O_2$, He	0.40[b]	0.50
V_2O_5/SiO_2	$^{18}O_2$, He	0.44[b]	0.40
	$^{18}O_2$, CH_4, He	1.70[b]	1.10
V_2O_5/Al_2O_3	$^{18}O_2$, He	0.35	0.45
	$^{18}O_2$, CH_4, He	0.45	0.56

[a] In $^{16}O_2$ and $^{16}O^{18}O$ only; total flow rate = 31 cm³/min, CH_4 flow rate = 10 cm³/min, O_2 flow rate = 1 cm³/min.

[b] Conditions same as above except O_2 flow rate = 2 cm³/min (see text for details).

Al_2O_3, and bulk V_2O_5 under reaction conditions were also obtained by switching $^{16}O_2$ to $^{18}O_2$ at steady state. Since no measurable activity was seen for SiO_2 and bulk V_2O_5 under the conditions used, the transients were essentially similar to those without reaction and hence are not presented here. Al_2O_3 exhibited some activity for methane oxidation at T = 600°C (see Table 1). However, CO and CO_2 transients could not be obtained since the amounts of CO and CO_2 formed during methane oxidation on Al_2O_3 even at 600°C were insufficient to provide a stable mass spectrometer signal, especially at the low electron energy used in our studies. The O_2 transient, however, was similar to that without reaction and is not presented here due to space constraints.

V_2O_5/SiO_2. Figure 2 shows the oxygen transients without reaction for the 1.6% V_2O_5/SiO_2 catalyst at 600°C. It can be seen that the V_2O_5/SiO_2 catalyst exhibited some slight O exchange capability similar to that for bulk V_2O_5. Figure 3 shows the O exchange of O_2 under reaction conditions at 600°C. It can be seen that the O exchange capability of O_2 with the catalyst increased significantly in the presence of methane, i.e., under reaction conditions (see Table 2). Figure 4a shows the transients obtained for the products HCHO and CO after the switch from $^{16}O_2$ to $^{18}O_2$ under steady-state reaction. It can be seen that the products HCHO and CO exhibited slow decreases in ^{16}O content with time. Figure 4b shows the transients for CO_2 after switching from $^{16}O_2$ to $^{18}O_2$ under steady-state reaction. As was the case for O_2, CO_2 exhibited a large scambled product signal, $C^{16}O^{18}O$, which did not decay to zero in the time span studied.

The total amount of ^{16}O desorbed from the catalyst for each species during the 5.5-min span of the isotopic transient was calculated and is listed in Table 3. The amount of ^{16}O desorbed as H_2O was calculated from the

TABLE 3

Total ^{16}O Desorbing from the 1.6 wt% V_2O_5/SiO_2 Catalyst under Reaction during 5.5 Min

Species	Total ^{16}O atoms desorbing (mmol/g)[a]	
	550°C	600°C
HCHO	0.08	0.05
CO	0.07	0.40
CO_2	—	0.05
H_2O	0.15	0.90
$^{16}O^{18}O$	1.70	1.10
Total	2.00	2.50

[a] For t = 5.5 min. Total ^{16}O in vanadia for 1.6 wt% V_2O_5/SiO_2 = 0.45 mmol/g.

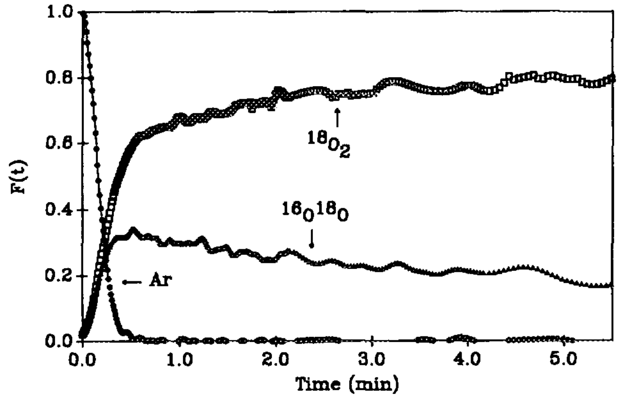

FIG. 3. Oxygen transients for O_2 during partial oxidation of methane on V_2O_5/SiO_2 at 600°C.

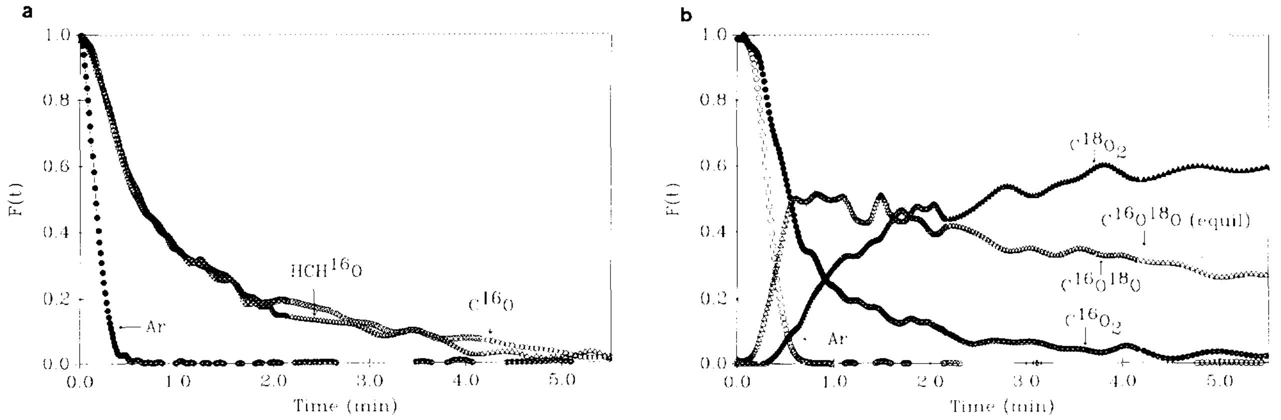

FIG. 4. (a) Oxygen transients for CO and HCHO during partial oxidation of methane on V_2O_5/SiO_2 at 600°C. (b) Oxygen transients for CO_2 during partial oxidation of methane on V_2O_5/SiO_2 at 600°C.

flow rate of H_2O (estimated by carbon mass balance, e.g., each mol of CO_2 or CO results in 2 mol of H_2O being formed) and the H_2O transient. It should be noted that such an indirect estimation of the rate of water formation, coupled with the errors in the H_2O transient (since water can be easily held up in the system and the mass spectrometer) makes the estimation of ^{16}O evolved in water subject to greater error than that for the other species.

V_2O_5/Al_2O_3. Figure 5 shows the O_2 transients without reaction for the 2% V_2O_5/Al_2O_3 catalyst at 600°C. It can be seen that the V_2O_5/Al_2O_3 catalyst exhibited some O exchange capability which was equivalent to the O exchange capability for alumina (see Table 2). Figure 6 shows O exchange of O_2 with the V_2O_5/Al_2O_3 catalyst under reaction conditions at 600°C. It can be seen that O exchange capability of O_2 with the catalyst increased only slightly in the presence of methane, i.e., under reaction conditions (see Table 2). Figures 7a and 7b show the transients obtained for the products CO and CO_2 after the switch from $^{16}O_2$ to $^{18}O_2$ under steady-state reaction. It can be seen that the scrambled product signal, $C^{16}O^{18}O$, did not decay to zero even after 5.5 min, as was also the case for V_2O_5/SiO_2. The total amount of ^{16}O desorbed from V_2O_5/Al_2O_3 catalyst during the 5.5-min span of the isotopic switch for each species was obtained and is listed in Table 4. Again, some error was involved in the estimation of the amount of ^{16}O corresponding to water due to reasons explained above.

DISCUSSION

Analysis of Oxygen Transients

SiO_2, V_2O_5, and V_2O_5/SiO_2. The O exchange of O_2 in the absence of CH_4 was found to be negligible for SiO_2 as indicated by the absence of the scrambled product signal (see Fig. 1). However, bulk V_2O_5 and silica-supported vanadia exhibited some oxygen exchange capability, indicating that the O exchange capability is indeed due to vanadia. This is consistent with earlier studies in which bulk V_2O_5 was found to exhibit an exchange capability at temperatures above 430°C (10–12). Although our results in general are consistent with the observations made earlier, it should be noted that most of the earlier

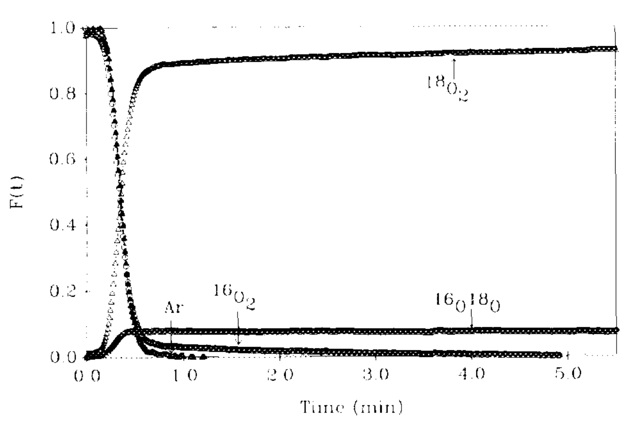

FIG. 5. Oxygen transients without reaction on V_2O_5/Al_2O_3 at 600°C.

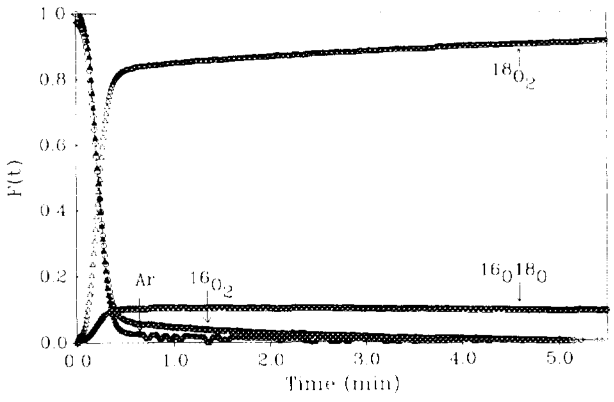

FIG. 6. Oxygen transients for O_2 during partial oxidation of methane on V_2O_5/Al_2O_3 at 600°C.

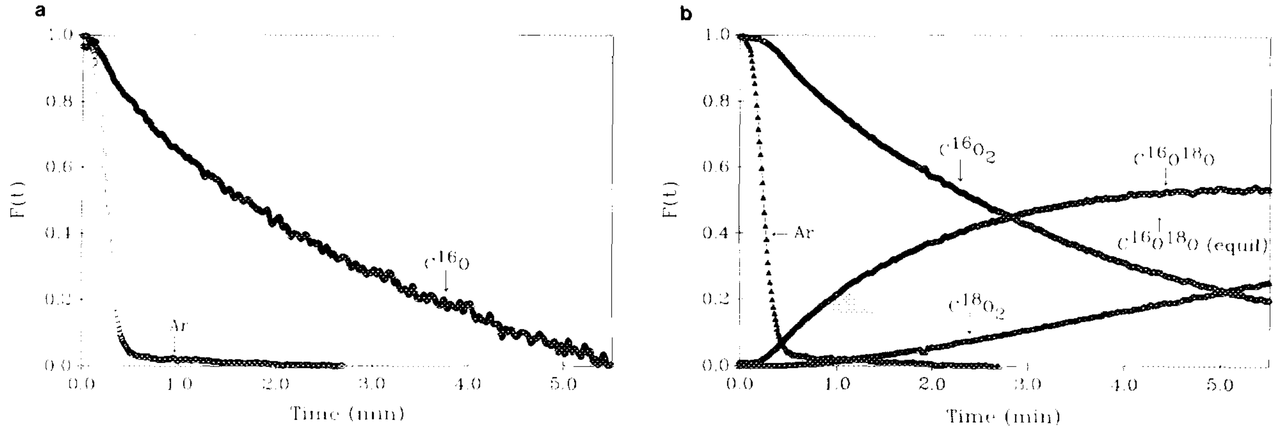

FIG. 7. (a) Oxygen transients for CO during partial oxidation of methane on V_2O_5/Al_2O_3 at 600°C. (b) Oxygen transients for CO_2 during partial oxidation of methane on V_2O_5/Al_2O_3 at 600°C.

studies were carried out in static systems and the isotopic concentrations followed for several hours (10–16). This creates a difficulty in comparing rates of O exchange obtained by other researchers with the rates obtained in our studies. Also, few studies have reported results for the O exchange of O_2 with supported vanadia catalysts (24).

As can be seen from Figures 2 and 3, and Table 2, O exchange of O_2 increased significantly in the presence of methane for silica-supported V_2O_5. This behavior is very different from the O exchange behavior observed for catalysts for the oxidative coupling of methane, such as Li/MgO, wherein the catalyst exhibited significant O exchange capability even in the absence of a reducing agent (26). Several authors have reported that in vapor-phase partial oxidation of hydrocarbons by dioxygen over metal oxides a Mars–van Krevelan-type mechanism may be operative in which the oxidic surface might first be reduced by the hydrocarbon species followed by its reoxidation by O_2 (7–9). Application of a mechanistic hypothesis along these lines could explain the observed increased O exchange capability in the presence of methane. The presence of methane may create more active "sites" due to partial reduction for the reversible dissociative chemisorption of O_2 on the V_2O_5/SiO_2 catalyst resulting in a higher O exchange capability.

It can be seen that the HCHO, CO, and CO_2 transients exhibited slow decays in their ^{16}O contents (see Fig. 4), indicating the participation of adsorbed and/or catalyst oxygen in the exchange process for both selective and nonselective products (see Fig. 4). Similar observations have been made for the partial oxidation of propylene over bismuth molybdate catalysts (20–21). Attempts have also been made in the past to delineate the contribution of the lattice oxygen vs that of the adsorbed oxygen species in the formation of the products based on oxygen exchange reactions (20–21). Since, in this case, the total amount of ^{16}O evolved for 5.5 min (see Table 2) is greater than the total amount of ^{16}O that can be accounted for by considering the catalyst covered completely with adsorbed oxygen (0.3 mmol/g of ^{16}O) it would appear that lattice oxygen is directly involved in the formation of the products. However, such an interpretation is not entirely valid. It is possible that a product species could be formed initially by reaction of CH_4 with an adsorbed oxygen species but that secondary O exchange of its oxygen with the catalyst oxygen could then occur. Such secondary O exchange reactions would mask the origin of the oxygen responsible for the formation of the selective and the nonselective products.

Several studies have reported O exchange for CO and CO_2 for various oxides (15–18, 27) including vanadia (32,

TABLE 4

Total ^{16}O Desorbing from the 2% V_2O_5/Al_2O_3 Catalyst under Reaction during 5.5 Min

	Total ^{16}O atoms desorbing (mmol/g)[a]	
Species	550°C	600°C
CO	0.08	0.25
$C^{16}O^{18}O$	0.08	0.25
$C^{16}O_2$	0.17	0.55
H_2O	0.34	0.95
$^{16}O^{18}O$	0.45	0.56
Total	1.12	2.56

[a] For t = 5.5 min. Total ^{16}O in Vanadia for 2 wt% V_2O_5/Al_2O_3 = 0.55 mmol/g.

33). In an earlier study, we have produced evidence for such secondary exchange reactions (30). In that study, the isotopic composition of CO_2, in a gas stream containing CO_2 with and without CH_4, was switched from $C^{16}O_2$ to $C^{18}O_2$ at steady state over V_2O_5/SiO_2. Unlike O exchange of O_2, O exchange of CO_2 with V_2O_5/SiO_2 was found to be rapid both in the presence and in the absence of methane, thus providing evidence for O exchange of CO_2 with the catalyst under CH_4 reaction conditions. The activation energy for the reaction for primary CH_4 oxidation on V_2O_5/SiO_2 catalyst is about 50 kcal/mol, while for CO or HCHO oxidation it is about 15–30 kcal/mol (1, 2). However, the activation energy for secondary exchange reactions, such as O exchange of CO_2 or CO, has been reported to be much lower (0–2 kcal/mol) for various oxides such as ZnO, CuO, and Cr_2O_3 (17, 22). In our studies of the secondary O exchange of CO_2, the rate of O exchange was only slightly affected by a change in temperature. This suggests that the activation energy of O exchange with V_2O_5/SiO_2 is also very low. Thus, the secondary exchange reactions take place very rapidly, i.e., at a rate much higher than the formation of the product species.

Patterson and Parker (17, 18) have attempted to measure the "true" lattice oxygen contributions in the total oxidation of methane to CO_2 and H_2O on Sn-Sb-oxide catalysts by trapping the products immediately after their formation, thus minimizing secondary O exchange between various product species. However, even in a microreactor, the exchange reaction can be so fast that trapping the products at the exit of the catalyst bed would be too late for preventing secondary exchange reactions during collisions of the product molecules with the catalyst. Thus, the presence of secondary oxygen exchange complicates the determination of the oxygen source involved in primary oxidation.

The total amount of ^{16}O exchanged was found to be greater than the total amount of ^{16}O in the supported vanadia (see Table 3). This suggests that oxygen associated with silica or with the vanadia–silica interface may also be involved in O exchange with V_2O_5 and/or the primary products. It should be noted that, although silica did not exhibit significant O exchange capability with O_2, the possibility of ^{16}O in silica exchanging with the product species, i.e., secondary O exchange, at these high temperatures cannot be ruled out. Recently, Mims and co-workers (34) have reported on a study involving isotopic oxygen transients during the partial oxidation of methane over MoO_3/SiO_2 catalysts. They also found that the total amount of labeled oxygen in the products was higher than that which could be accounted for by only MoO_3. Thus, we believe that the oxygen associated with the support also participates in the exchange process under reaction conditions, either directly or via a SiO_2–V_2O_5 exchange of oxygen.

For the reaction $C^{16}O_2 + C^{18}O_2 \rightleftharpoons C^{16}O^{18}O$ the equilibrium constant equals 4. The equilibrium amount of $C^{16}O^{18}O$ was calculated from the experimental values of $C^{16}O_2$ and $C^{18}O_2$ and is also shown in Fig. 4b (dotted line). Near-equilibrium conditions were achieved at all times. This suggests that gas-phase CO_2 was completely equilibrated under reaction conditions. It is important to note that, although the gas-phase product CO_2 is equilibrated, the exchange process occurs on the catalyst surface where the catalyst oxygen probably gets involved as seen by the presence of a large scrambled product signal for CO_2. Similar surface-catalyzed exchange processes resulting in gas-phase equilibration are also likely to occur for HCHO and CO. In such a case, the determination of the primary oxygen source responsible for the formation of the products becomes even more difficult.

Al_2O_3 and V_2O_5/Al_2O_3. It can be seen from Figs. 1b and 5, and Table 2 that the O exchange capabilities of the alumina-supported vanadia catalyst and those of plain alumina are comparable. This is consistent with O exchange studies of Al_2O_3 and of bulk V_2O_5 carried out in static systems (16). There, the activation energy for O exchange with Al_2O_3 was reported to be slightly lower than O exchange with bulk V_2O_5 in the temperature range 400–550°C. The O exchange capability of the V_2O_5/Al_2O_3 catalyst increased somewhat in the presence of methane (see Figures 5 and 6, and Table 2). As was the case for V_2O_5/SiO_2, this can be attributed to the redox nature of the methane oxidation reaction.

As seen for V_2O_5/SiO_2, the CO and CO_2 transients for V_2O_5/Al_2O_3 exhibited slow decays in their ^{16}O contents, indicating the participation of adsorbed and/or catalyst oxygen in the formation of the products (see Fig. 7). A similar slow decay was seen for the CO transient on alumina at 600°C. Table 4 shows the total amount of ^{16}O exiting in the various effluent species during 5.5 min after the $^{16}O_2$ to $^{18}O_2$ switch during steady state of reaction on the V_2O_5/Al_2O_3 catalyst. As was the case for the V_2O_5/SiO_2 catalyst, the total amount of ^{16}O in all the species for the V_2O_5/Al_2O_3 exceeded the amount that can be accounted for by oxygen in V_2O_5 alone. Since alumina is not very active for the reaction of methane, it is likely that the oxygen of alumina is involved in secondary oxidation reactions such as oxidation of CO to CO_2, in the secondary O-exchange of products formed on vanadia sites, or in exchange of oxygen with the V_2O_5.

The equilibrium calculations for the CO_2 transients (see dotted line in Fig. 7b) indicated that gas-phase CO_2 was equilibrated as was the case for CO_2 formed on V_2O_5/SiO_2. However, in contrast to O exchange with O_2, the normalized scrambled product signal ($C^{16}O^{18}O$) for CO_2 was considerably higher than the scrambled product signal for O_2 ($^{16}O^{18}O$). This suggests that, for the V_2O_5/Al_2O_3 catalyst, O exchange with CO_2 occurs in preference to the reversible adsorption of O_2. Similar observations have been made by Cant *et al.* (22) for O exchange studies of Li/MgO catalysts during oxidative coupling of methane.

Comparison of O Exchange over the Various Catalysts

It is generally accepted that catalyst oxygen reactivity determines to a large extent the activities and selectivities for partial oxidation. The catalyst oxygen reactivity in turn is determined largely by the nature of support and the catalyst–support interaction. In an accompanying paper we have reported on the activity for methane oxidation of different V species on the supported and bulk vanadia catalysts (35). There we have suggested that the negligible activity of bulk vanadia for methane partial oxidation as compared to supported vanadia is due to differences in the structure of vanadia species in bulk vanadia and on supported vanadia. Also, we have shown earlier (31) that, in general, SiO_2- and Al_2O_3-supported vanadia catalysts are reduced at lower temperatures than bulk V_2O_5. This results in higher oxygen lability and hence higher activity of the supported catalysts than bulk V_2O_5 or the supports.

We have also reported on the nature of the V species on silica- and alumina-supported vanadia (31). We have shown that both tetrahedral and bulk-like vanadia are present on 1.6% V_2O_5/SiO_2, whereas only tetrahedral vanadia species are present on 2% V_2O_5/Al_2O_3. Since alumina is a more interacting support, i.e., vanadia binds more strongly to alumina than to silica, the oxidized tetrahedral V species on alumina appears to be more stable than on silica, as was seen from the lesser degree of reduction of V_2O_5/Al_2O_3 than of V_2O_5/SiO_2 during TPR (31). This perhaps explains why for V_2O_5/Al_2O_3, unlike for V_2O_5/SiO_2, the oxygen exchange capability did not increase significantly under reaction conditions. It would also appear that CO and CO_2 can interact more easily with V_2O_5/Al_2O_3 than O_2, probably due the formation of more stable surface intermediates. Evidence for the presence of a carbonate-type intermediate during O exchange of CO or CO_2 with bulk V_2O_5 has been reported earlier by Hirota *et al.* (32, 33) based on IR spectroscopic measurements. They also observed higher rates of O exchange of CO_2 with bulk V_2O_5 than O exchange of O_2 and attributed this to the greater ease of dissociative chemisorption of CO_2 as compared to O_2. Existence of such competitive chemisorption between O_2 and CO/CO_2 on V_2O_5/Al_2O_3 may also be the reason for the observed low increase in the O exchange capability of O_2 in presence of methane on V_2O_5/Al_2O_3.

Speculations on the Nature of O Species Involved in the Partial Oxidation of Methane

In our earlier studies on the partial oxidation of methane over supported vanadia catalysts, we have reached the following conclusions:

(a) O associated with a tetrahedral V site appears to be necessary for abstraction of H atom from CH_4 during the partial oxidation of methane, resulting in the formation of selective oxidation product, HCHO (35);

(b) an irreversible readsorption of product HCHO and its oxidation can occur during methane oxidation to form CO (29);

(c) secondary oxidation of HCHO or CO can also take place on the bulk-like vanadia of V_2O_5/SiO_2 and on alumina sites of V_2O_5/Al_2O_3 (35).

Based on the O transients given here and NMR characterization of the catalysts (31), three types of exchangeable O species can be hypothesized for the supported vanadia catalysts:

(a) O associated with highly dispersed tetrahedral surface vanadia,

(b) O associated with the bulk-like vanadia,

(c) O associated with the support or with the vanadia–support interface.

Isotopic tracer studies, such as this, cannot provide direct evidence for the existence of all intermediates involved in the primary reactions, secondary reactions, and secondary exchange processes. Thus, our speculations given below have to be based on indirect evidence from the oxygen transients and our previous conclusions listed above.

We speculate that the O associated with the different V species and with the support (as hypothesized above) play different roles in the oxidation/exchange of various effluent O containing species during the partial oxidation of methane. For example, since the O associated with the tetrahedral surface V species appears to be responsible for the abstraction of H atom from methane for both V_2O_5/SiO_2 and V_2O_5/Al_2O_3 catalysts (35), we believe that the O associated with the V tetrahedral species (adsorbed or catalyst) may be incorporated in the products via a primary oxidation reaction. This is depicted in the form of a schematic for silica-supported vanadia in Fig. 8. However, the possibility of either secondary oxidation or secondary O exchange reactions occurring on such a vanadia species cannot be ruled out. This is also depicted in Fig. 8.

We also believe that the O associated with the bulk-like vanadia and the support or the support–catalyst interface may be responsible for either secondary oxidation reactions or secondary O exchange or both. Since secondary oxidation reactions of HCHO or CO are believed to occur on bulk-like vanadia and on alumina (35), it is likely that

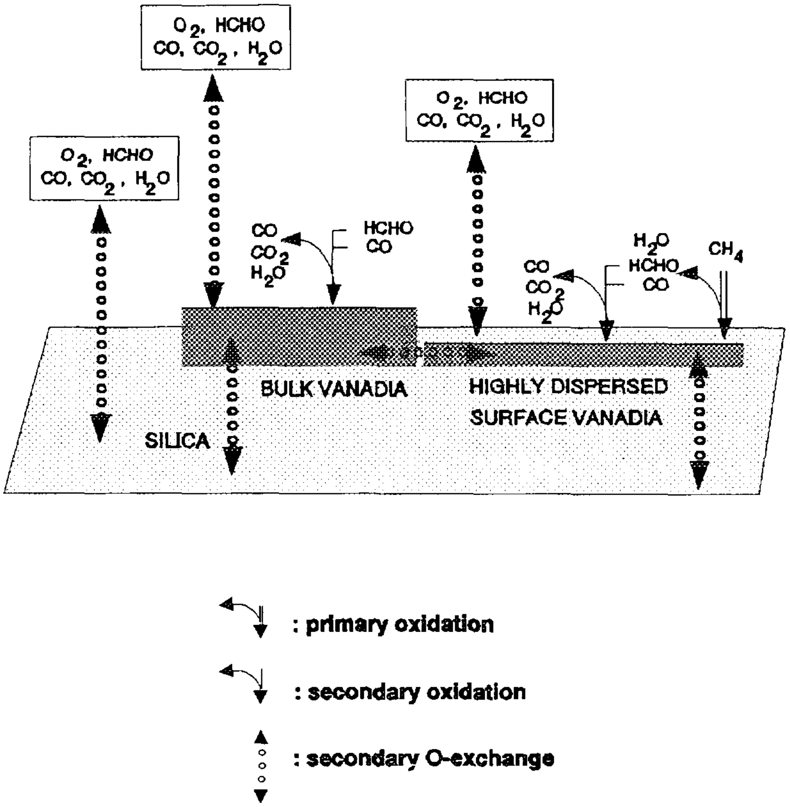

FIG. 8. Proposed O exchange pathway for the partial oxidation of methane.

the O associated with these species is incorporated in the products. Much evidence exists for the presence of secondary O exchange with O associated with bulk-like vanadia or with support. Secondary O exchange of CO and CO_2 with bulk V_2O_5 was shown to occur through adsorption and desorption of a carbonate-type intermediate (32, 33). We have provided evidence for the existence of secondary O exchange of CO_2 with V_2O_5/SiO_2 (30). In addition, as discussed in the preceding sections, O transients indicate that O associated with the support or the vanadia–support interface has to participate in the O exchange process. Thus, it appears that the O associated with the support and the bulk-like vanadia is involved either in a secondary O exchange process or in a secondary reaction. This is depicted for silica-supported vanadia in Fig. 8. A similar schematic can be drawn for alumina-supported vanadia.

Although these speculations explain qualitatively the role of exchangeable O species in methane partial oxidation, the quantification of the reactivity of these O species for oxidation and/or exchange is rather difficult. Obviously, secondary O exchange occurs readily on all the species hypothesized above. The reactivity of the O associated with the tetrahedral surface vanadia and with the bulk-like vanadia in secondary oxidation (which determines the selectivity to formaldehyde) would depend on the redox state of these species and the oxidation potential of the feed gases (29).

CONCLUSIONS

O exchange of O_2 with V_2O_5/SiO_2, V_2O_5/Al_2O_3, SiO_2, Al_2O_3, and V_2O_5 was studied using SSITKA. It was found that V_2O_5, V_2O_5/SiO_2, Al_2O_3, and V_2O_5/Al_2O_3 exhibited some oxygen exchange capability. Silica exhibited negligible oxygen exchange capability under the conditions used. Oxygen exchange reactions were also studied over supported vanadia catalysts under steady-state reaction conditions. O exchange of O_2 with V_2O_5/SiO_2 increased significantly in the presence of methane. This is attributed to a redox reaction making the surface more active for O exchange in the presence of the methane. The involvement of catalyst oxygen in the formation of the products HCHO, CO, and CO_2 was demonstrated. However, an estimation of the contribution of the lattice oxygen in the formation of the products is complicated by the presence of secondary O exchange reactions. The total amount of ^{16}O exchanged with the feed O_2 and the products indicates that the oxygen associated with silica or the vanadia–silica interface is also involved in the exchange process.

In general, O exchange behavior of various product species with V_2O_5/Al_2O_3 was found to be similar to that with V_2O_5/SiO_2. However, unlike V_2O_5/SiO_2, the O exchange of O_2 with V_2O_5/Al_2O_3 did not increase significantly in the presence of methane. This is attributed to the stabilization of surface vanadia on alumina due to greater alumina–vanadia interaction, making oxygens at the vanadia–alumina interface less available for exchange with O_2. It is speculated that the O associated with highly dispersed tetrahedral surface vanadia is involved in a primary oxidation reaction, whereas O associated with the bulk-like vanadia and with the support is involved either in secondary oxidation reactions of HCHO or CO or in secondary O-exchange of various O-containing product species.

Oxygen involvement in partial oxidation reactions, such as the partial oxidation of methane, is much more complex than a simple redox reaction with catalyst oxygen. Care has to be taken in the interpretation of data from isotopic tracer studies due to the presence of secondary oxygen exchange reactions.

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