JOURNAL OF CATALYSIS **124**, 336–348 (1990)

Oxygen Isotope Transfer Rates during the Oxidative Coupling of Methane over a Li/MgO Catalyst

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Received November 16, 1989; revised February 13, 1990

The rates of various oxygen isotope transfer processes over Li/MgO catalysts have been investigated in a flow system under conditions relevant to methane coupling. Using $^{16}O_2/^{18}O_2$ mixtures, mixing to form $^{16}O^{18}O$ reached equilibrium at 700 and 750°C when helium was used as the carrier. The extent of equilibration was greatly reduced when the same mixture was used to oxidize methane. The inhibition occurs because mixing requires that the catalytic sites be in oxide form and these sites are converted to carbonate by the carbon dioxide formed from methane concurrently with ethane and ethylene. The same inhibition could be demonstrated directly when using an inert carrier by including $C^{18}O_2$ in the feed. When $C^{18}O_2$ was added during methane coupling with $^{16}O_2$ as the sole oxidant, there was complete equilibration between added $C^{18}O_2$ and $C^{16}O_2$ derived from methane. In addition some ^{18}O was transferred into unreacted $^{16}O_2$. This exchange did not produce $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ in equilibrium. There was a slight excess of $^{18}O_2$ due to the occurrence of some two-place exchange. Transient experiments in which $C^{18}O_2$ alone was carried over Li/MgO showed that only a small fraction of the total oxygen pool of the catalyst participated in exchange. It is probably associated with lithium. When $C^{18}O$ was included in reacting $CH_4/^{16}O_2$ mixtures, approximately one-half of it was oxidized to carbon dioxide. Some exchange of ^{18}O out of unreacted $C^{18}O$ took place but the rate of this process was much slower than transfer from carbon dioxide to oxygen. Calculations indicate that the catalyst is able to carry out exchange reactions of oxygen molecules faster than it reacts oxygen with methane. Hence methane coupling is unlikely to be limited by the supply of oxygen to the catalyst surface when the Li/MgO system is used.

INTRODUCTION

The catalytic conversion of methane to ethane and ethylene is a subject of extensive current investigation. Much of the work is in the context of the utilization of natural gas in remote areas by conversion to liquid fuels or chemicals (*1*). Many oxide systems are now known to oxidize methane–oxygen mixtures with an efficiency similar to that of the Li/MgO catalyst first described by Ito *et al.* (*2*). Among the most promising are lead oxide (*3*), various combinations of Group I and Group II oxides (*4*, *5*), and rare earth oxides, particularly samaria and lanthana (*6*, *7*). It is likely that the basic reaction steps are similar with all systems and some aspects are now well understood. The initial step is hydrogen abstraction from methane with release of a methyl species into the gas phase. Direct detection of methyl has been possible using matrix isolation electron spin resonance (*8*, *9*). The quantities found are sufficient to account for at least half, and probably all, the ethane formed on the assumption that methyl coupling occurs in the gas phase alone (*8*). Evidence for direct coupling is also provided by the oxidation of CH_4/CD_4 mixtures which yield CH_3CH_3, CH_3CD_3, and CD_3CD_3 almost exclusively (*10*, *11*). Further reaction then gives predominantly CH_2CH_2, CH_2CD_2, and CD_2CD_2 but with some exchanged ethylenes as well (*12*). Experi-

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0021-9517/90 $3.00

ments with added ^{13}C-labeled ethane and ethylene show that a considerable fraction of the carbon dioxide byproduct is derived from them under severe conditions (*13*, *14*). However, such successive oxidation is not significant over Li/MgO at lower temperatures when ethane is the predominant C_2 hydrocarbon produced from methane (*14*).

Thus the steps involved in carbon–hydrogen and carbon–carbon bond breaking and bond forming are reasonably clear, although the extent to which catalytic processes, as distinct from purely gas-phase ones, are involved in secondary reactions is still uncertain. By contrast pathways involving oxygen are little known. Ito *et al.* (*2*) reported a correlation between Li^+O^- site density (as determined by ESR after quenching heated samples to -196°C) and catalytic activity in the Li/MgO system and suggested that these were the catalytic centers. Such sites are known to react rapidly with methane and it was therefore concluded that water desorption or catalyst reoxidation rather than methane activation is the slow step (*2*). This now seems unlikely since the relative oxidation rates of CH_4 and CD_4 show a normal kinetic isotope effect (*15*) which requires that bond breaking in methane be rate determining. Even more directly it has been reported recently (*16*) that the rate of generation of methyl from CH_4 versus CD_4 shows the same kinetic isotope effect.

There have been two recent transient isotope studies which used ^{18}O to probe interchange between lattice and gaseous oxygen (*13*, *17*). Ekstrom and Lapszewicz (*13*) found that the lattice oxygens of Sm_2O_3 and Pr_6O_{11} were rapidly and completely exchanged under methane-coupling conditions. By contrast, Peil *et al.* (*17*) showed that the extent of ^{18}O exchange with a Li/MgO catalyst at 600°C was very slow after the equivalent of about 12 atom layers had been replaced. As opposed to these transient studies the purpose of the present work was to determine the rate of ^{18}O interchange between gaseous oxygen-containing species during methane coupling over Li/MgO. The system was optimized for steady-state operation under conditions of high selectivity (700–770°C). However, measurements on some types of exchange reactions with the catalyst were also possible and these lead to conclusions which supplement those of Peil *et al.* (*17*).

EXPERIMENTAL

The catalytic measurements were carried out in a single pass flow system using 100- or 200-mg samples of Li/MgO catalyst in the form of 0.6- to 1.2-mm particles. The reactor and flow system was similar to that described previously (*10*, *12*, *14*). As before, chemical and isotopic analyses were carried out by a combination of on-line mass spectrometry and gas chromatography with off-line FTIR. The operating procedure following each switch in feed composition was to monitor the reactor exit stream until the mass spectrometer indicated constant composition (5 to 15 min) and then for a further 10 to 15 min during which time the exit stream flushed a 10-cm gas cell. The cell was removed and the gas stream sampled into the chromatograph immediately, thus enabling cross comparison between the three methods of analysis with the same sample.

The mass spectrometer (Vacuum Generators SX-200) was operated in multiple ion monitoring mode with 16 peaks recorded on a cycle time of 20–30 s. The FTIR measurements used a Digilab Model 15/80 instrument with 256 scans at 0.25 cm^{-1} resolution. The $^{16}O/^{18}O$ isotopic compositions of carbon monoxide and oxygen were provided accurately by the FTIR and mass spectrometric measurements, respectively. Both methods also provided an isotopic analysis for carbon dioxide but each was of somewhat limited accuracy. In the case of the mass spectrometer it exhibited a significant background peak at $m/e = 44$ (due to $C^{16}O_2$) and the extent to which this apportioned to 46 ($C^{16}O^{18}O$) and 48 ($C^{18}O_2$) with ^{18}O-containing mixtures was somewhat uncertain. The unmixed carbon dioxides ($C^{16}O_2$ and $C^{18}O_2$) could be obtained accurately from the FTIR spectra of mixtures by successive subtraction of scaled spectra of known pressures of the individual compounds. However, in the absence of a pure sample of $C^{16}O^{18}O$ to permit calibration, its content in the carbon dioxide could be obtained only by difference between the sum of the $C^{16}O_2$ and $C^{18}O_2$ values and the total carbon dioxide content determined by gas chromatography. The accuracy of the isotopic analyses for carbon dioxide is best estimated by comparison between the results obtained by the m/s and FTIR methods as shown in the later tables.

The oxygen-18 ($<1.0\%$ ^{16}O) was obtained from Cambridge Isotope Laboratories, Massachusetts, in a 150-cm^3 cylinder at sufficient pressure to enable direct delivery. The carbon monoxide–^{18}O (Liquid Carbonic, IL, $<1\%$ ^{16}O) and carbon dioxide–^{18}O (Merck, Sharp and Dohme, Canada, $>92\%$ ^{18}O) were supplied at subatmospheric pressure. To facilitate delivery, known pressures of each were transferred to 75-cm^3 cylinders and pressurized to 20 atm with ultrahigh purity methane or helium. Gases of the same purity were used for the main reactant streams.

The catalyst was prepared by slurrying appropriate amounts of Li_2CO_3 and $MgCO_3$ in water followed by drying at 170°C and calcination in air for 4 h at 900°C. The lithium content, as determined by atomic absorption spectroscopy, was 0.77% as prepared. However, as noted later this had declined to 0.095% after 40 h of reaction. The surface area was then 0.45 m^2/g as determined by the BET method with krypton as the adsorbate.

RESULTS

Most experiments were carried out on a single Li/MgO sample giving the product distribution and oxygen conversions shown in Table 1. Over an operating period of 40 h, which included ^{13}C-labeling experiments described elsewhere (*14*), both selectivity and conversion declined slightly. The decrease is undoubtedly due to loss of lithium since its content in the sample fell from 0.77 wt% initially to 0.095 wt% for the final used one. It is likely that some of the loss is retained on the walls of the reactor and thermocouple wells since, as may be seen from the data, blank tests on the used reactor show activity and selectivity higher than those of the starting system.

Exchange between Oxygen Molecules

Results for $^{16}O^{18}O$ formation from a 5% $^{16}O_2$, 5% $^{18}O_2$ mixture diluted by helium or methane are given in Table 2. In series A, with helium as carrier, equilibrium is reached over Li/MgO at both 750 and 700°C. The reaction quotient, Q_p, defined as $[^{16}O^{18}O]^2/[^{16}O_2][^{18}O_2]$ reaches 4 and X_m (the fractional approach to equilibrium) is indistinguishable from unity. In the same series there is also substantial mixing in the used empty reactor. The activity probably originates from lithium stripped from the catalyst and retained on the reactor walls as noted above, since the new reactor shows negligible activity for isotope mixing. The situation is quite different in series B under methane coupling conditions. The fractional conversion over the catalyst is 0.64 at 750°C and 0.32 at 700°C with equivalent drops in the used reactor tests.

Two explanations can be considered for the reduced extent of $^{16}O_2/^{18}O_2$ mixing with methane present. One is that methane scavenges the catalyst for oxygen, reducing the surface concentration of it and hence the probability of forming $^{16}O^{18}O$. Alternatively, carbon dioxide formed by oxidation of methane could convert oxide to carbonate thus reducing exchange if it were substantially confined to the oxide portion of the catalyst. The latter proposition can be tested by inclusion of carbon dioxide in the feed stream when helium is the carrier. Series C in Table 2 shows the result of such a test at 750°C with carbon dioxide (as $C^{18}O_2$) added in an amount approximately equal to that formed from methane in series B. Exchange is very greatly reduced compared to that of the carbon dioxide-free situation. Indeed

TABLE 1

Product Distributions and Oxygen Conversions for Reaction of 90% Methane, 10% Oxygen Mixtures over 200 mg Li/MgO and Corresponding Reactor Blanks[a]

Sample[b]	Temperature (°C)	% Oxygen conversion	% in exit stream				% Selectivity to C_2H_4 + C_2H_6
			CO	CO_2	C_2H_4	C_2H_6	
New reactor	750	≈1	0.04	0.04	0.003	0.037	52
	700	≈0.5	<0.01	0.02	<0.001	0.01	<50
Li/MgO	750	69	0.40	2.55	2.40	2.83	78
(3 h)	700	27	0.16	0.98	0.43	1.46	77
Li/MgO	750	57	0.28	1.99	1.59	2.29	77
(35 h)	700	16	0.15	0.84	0.22	1.00	71
Used reactor	750	10	0.18	0.51	0.09	0.42	61
(40 h)	700	5	0.07	0.25	0.01	0.14	49

[a] All measurements with total flow rate of ≈25 cm^3 (STP)/min.

[b] Time in parenthesis is the total period for which the reaction had been run. The value for the used reactor corresponds to the period of use with Li/MgO present prior to unpacking.

the fractional mixing (X_m = 0.50) is slightly below that found under methane coupling conditions at the same temperature (X_m = 0.64). The difference is probably caused by the different carbon dioxide concentration gradients along the catalyst beds in the two situations. The gradient is flat when carbon dioxide is carried by helium but steadily increases from entrance to exit when it is made from methane. In the latter situation it is likely that a small section at the front of the bed remains carbonate free and the additional mixing occurs there.

Analysis of the ^{18}O disposition in the carbon dioxide (by m/s and FTIR) and carbon monoxide (by FTIR) was carried out for most of the runs in series B and C. For reasons given earlier the accuracy of the carbon dioxide measurements was considerably less than that for oxygen but as far as could be judged the three carbon dioxides were at equilibrium ($[C^{16}O^{18}O]^2/[C^{16}O_2][C^{18}O_2]$ in the range 2.5 to 4). There was a tendency for the ^{18}O content of the carbon dioxides to fall somewhat below the value of 0.50 expected for equal reaction of $^{16}O_2$ and $^{18}O_2$ in series B. The deviation was greatest in those runs producing the least carbon dioxide. Given the high temperature, this is unlikely to arise from an oxygen kinetic isotope effect (*18*). It may reflect a small extent of continuous exchange with a large pool of ^{16}O on the catalyst or reactor walls. The ^{18}O content of the carbon monoxide showed a similar trend.

Exchange between Oxygen and Carbon Dioxide

It may be seen from the results for series C in Table 2 that the overall ^{18}O content of the oxygen (≈54%) exceeds that for the input $^{16}O_2/^{18}O_2$ mixture (≈50%). The corresponding carbon dioxide is depleted in ^{18}O (≈56% versus 92% in the input stream). Thus oxygen transfer between carbon dioxide and oxygen is significant. This process was studied separately from oxygen mixing using $^{16}O_2/C^{18}O_2$ mixtures diluted with helium or methane. Results are summarized in Table 3. As with $^{16}O_2/^{18}O_2$ mixing, the extent of exchange of ^{18}O from $C^{18}O_2$ into oxygen is lower in the presence of methane coupling (series A and B) than that when an inert carrier is used (series C and D). Somewhat surprisingly the distribution between the three oxygens does not seem to be exactly at equilibrium since the reaction quotient for exchange between these species, Q_p, is 1.1 ± 0.4 rather than the equilibrium value of 4 observed in all the experiments of Table 2.

TABLE 2

Catalysis of Isotope Exchange between $^{16}O_2$ and $^{18}O_2$ by Li/MgO under Various Conditions

Feedstream[a]	Sample[b]	Temperature (°C)	Oxygen composition (%)[c]			Extent of[d] mixing, X_m
			$^{16}O_2$	$^{16}O^{18}O$	$^{18}O_2$	
Series A	Li/MgO	750	24.5	51.0	24.4	1.02
5% $^{16}O_2$, 5% $^{18}O_2$	Li/MgO	700	25.8	49.3	24.9	0.98
Balance He	New reactor	750	49.0	2.11	48.9	0.013
	New reactor	700	49.2	1.77	49.0	0.01
	Used reactor	750	29.6	41.1	29.2	0.82
	Used reactor	700	39.1	23.9	36.9	0.47
Series B	Li/MgO	750	32.5	32.7	34.9	0.64
5% $^{16}O_2$, 5% $^{18}O_2$	Li/MgO	700	41.0	17.1	41.8	0.32
Balance CH_4	New reactor	750	49.4	1.44	49.2	<0.01
	New reactor	700	49.4	1.44	49.1	<0.01
	Used reactor	750	40.2	18.8	41.0	0.36
	Used reactor	700	46.4	7.8	45.8	0.13
Series C						
5% $^{16}O_2$, 5% $^{18}O_2$	Li/MgO	750	32.5	25.6	42.0	0.50
1.8% $C^{18}O_2$, balance He						

[a] The total flow rate was ≈24 cm^3 (STP)/min in each series.

[b] The Li/MgO (200 mg) had been used for approximately 35 h prior to these measurements. The catalyst was unpacked and the used reactor blank runs made immediately after the Li/MgO runs.

[c] The composition of the input stream was $^{16}O_2$ = 49.4%, $^{16}O^{18}O$ = 1.40%, $^{18}O_2$ = 49.2%.

[d] Calculated as $X_m = ([^{16}O^{18}O]_{out} - [^{16}O^{18}O]_{in})/([^{16}O^{18}O]_\infty - {}^{16}O^{18}O]_{in})$, where the equilibrium concentration, $[^{16}O^{18}O]_\infty$, is given by $2f_{18}(1 - f_{18})$ with f_{18} the fraction of ^{18}O in the exit molecular oxygen.

There is a slight excess of $^{18}O_2$ above equilibrium, indicating the presence of some two-place exchange (type R_2 according to the classification of Winter (*19*)). This can occur if the pool through which exchange proceeds is equilibrating faster with carbon dioxide than with oxygen. In that case the ^{18}O, content of the pool is high and an incoming $^{16}O_2$ molecule has an increased chance of evolving $^{18}O_2$ over $^{16}O^{18}O$ as long as both its oxygens are transferred to the pool. Peil *et al.* (*17*) have observed a similar nonequilibrium distribution during exchange of $^{18}O_2$ with Li/MgO itself.

Figure 1 shows the FTIR spectrum of the product gas from series B of Table 3 in the carbon monoxide and carbon dioxide regions. The latter exhibits the *Q* branches of $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ at 668.1, 663.0, and 657.7 cm^{-1}, respectively. Thus mixing between added $C^{18}O_2$ and $C^{16}O_2$ derived from methane is extensive. The carbon monoxide spectrum shows both $C^{16}O$ and $C^{18}O$, the *P* and *R* branches of the latter being perfectly revealed in the difference spectrum (b). Thus the set of oxygen exchange processes includes carbon monoxide. The ^{18}O disposition in the carbon oxides for all series are listed in the last three columns of Table 3. The FTIR and m/s results for carbon dioxide agree reasonably well and correspond quite closely to the FTIR values for carbon monoxide. Thus ^{18}O exchange between added $C^{18}O_2$ and the small amounts of $C^{16}O$ made by methane oxidation seems to be complete under these conditions. Information on the rate of this process with larger quantities of carbon monoxide present is given later.

The final entry in Table 3 shows that the

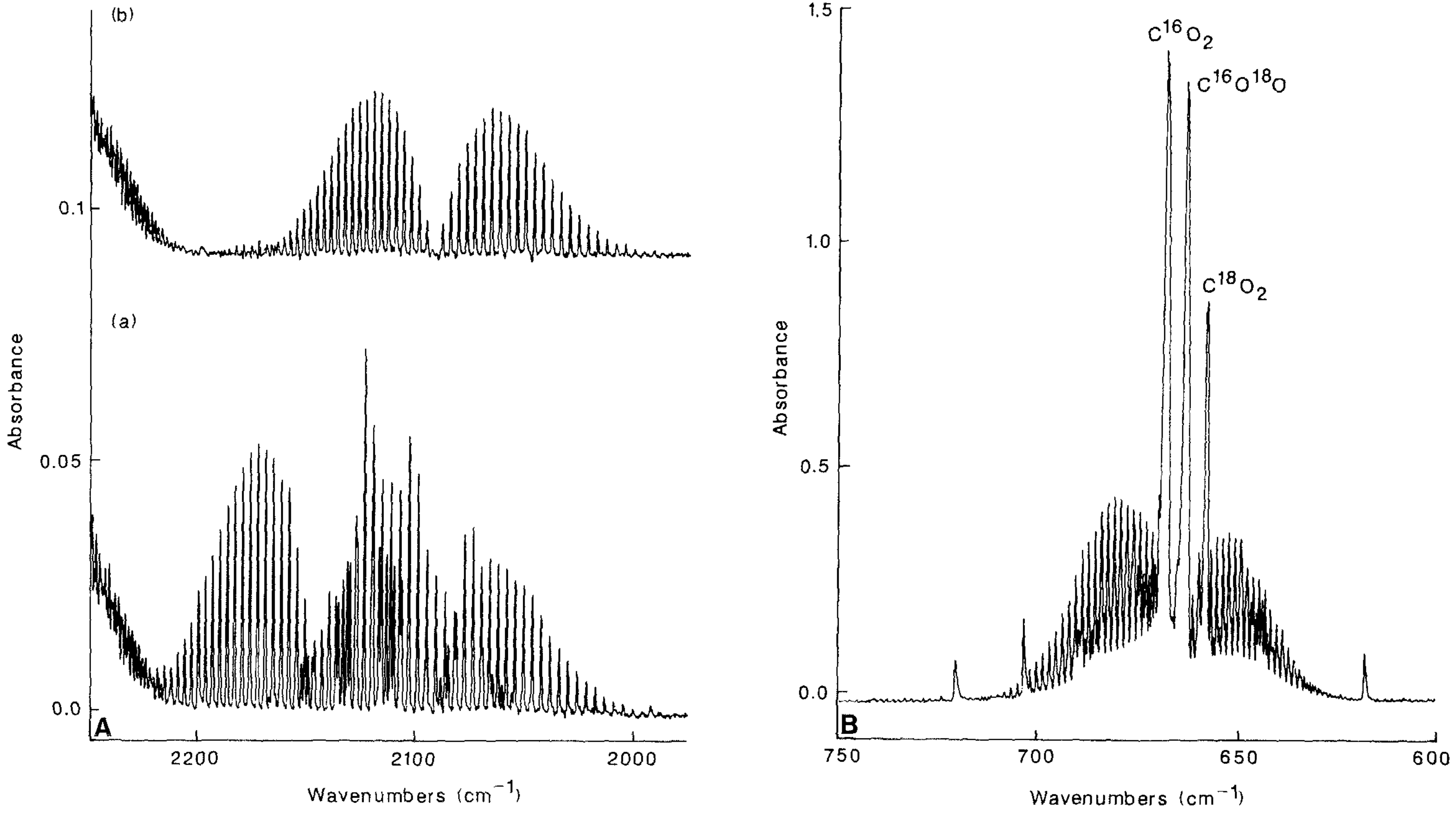

FIG. 1. (A) FTIR spectrum in carbon monoxide region for product of reaction of $CH_4/O_2/C^{18}O_2$ mixture over Li/MgO with conditions as per series B of Table 3: (a) product gas; (b) difference spectrum corresponding to (a) less contribution from $C^{16}O$. (B) FTIR spectra in carbon dioxide region for product gas from same reaction.

TABLE 3

Isotope Distribution for Products of Exchange between $C^{18}O_2$ and $^{16}O_2$ over 200 mg Li/MgO at 750°C

Feedstream[a]	Oxygen distribution (%)			Q_p[b]		Fraction ^{18}O in[c]		
	$^{16}O_2$	$^{16}O^{18}O$	$^{18}O_2$	O_2	CO_2	O_2	CO	CO_2
Series A 10% $^{16}O_2$, 1.5% $C^{18}O_2$ Balance CH_4	85.1	12.9	1.9	1.0	4	0.08	(0.12)	0.12(0.14)
Series B 7.2% $^{16}O_2$, 2.3% $C^{18}O_2$ 67% CH_4, 24% He	80.3	15.5	4.2	0.7	5	0.12	(0.41)	0.31(0.39)
Series C 9% $^{16}O_2$, 3% $C^{18}O_2$ Balance He	72.7	21.6	5.7	1.1	6	0.17	(0.28)[d]	0.36(0.39)
Series D 5% $^{16}O_2$, 1.7% $C^{18}O_2$ Balance He	67.3	25.9	6.8	1.5	3	0.20	-	0.27(−)
Same, new reactor	99.4	0.6	—	—	—	≈0.003	—	0.89(−)

[a] With total flow rates of 20, 30, 22, and 23 cm^3 (STP)/min in series A, B, C, and D, respectively.

[b] Q_p is the reaction quotient for mixing in an individual chemical species defined as $[^{16}O^{18}O]^2/[^{16}O_2][^{18}O_2]$ for oxygen and similarly for carbon dioxide.

[c] Defined as $^{18}O/(^{16}O + {}^{18}O)$ in each chemical species calculated from m/s and/or FTIR measurements with the latter in parentheses. The values for the input streams were <0.005 for oxygen and ≈0.92 for carbon dioxide.

[d] The amount here was very small but still measureable by FTIR.

reactor itself has negligible activity for $C^{18}O_2/{}^{16}O_2$ exchange when new.

Amount of Exchangeable Material on Catalyst

Several transient experiments were carried out to assess the size of the oxygen pool on the catalyst which is used during exchange between the gaseous species. The flow system was not well optimized for observation of direct isotope switches, from $C^{16}O_2$ to $C^{18}O_2$ for example, which might reveal the amount of carbon dioxide adsorbed on the catalyst. Nevertheless the amount of oxide readily exchangeable with carbon dioxide could be ascertained by commencing with the catalyst in oxide form in He and switching to He/$C^{18}O_2$. Exchange then produces $C^{16}O_2$ and $C^{16}O^{18}O$ which are initially adsorbed but are then displaced by further $C^{18}O_2$. The pool size for exchangeable oxide can be found by appropriate integration of the ^{16}O evolved. Figure 2 shows the results of one such experiment over Li/MgO at 750°C from the time $C^{16}O_2$ was detected. In the period immediately following the switch $C^{16}O_2$ dominates over $C^{16}O^{18}O$. Either two-place exchange is important, or, much more likely, the carbon dioxide undergoes a long series of oxygen transfers during its passage down the bed of Li/MgO. The quantity of $C^{16}O^{18}O$ passes through a maximum as the ^{16}O in the pool is depleted. After ≈400 s the relative amounts of $C^{16}O^{18}O$ and $C^{18}O_2$ are stable and fairly close to the values for the input streams (shown as open symbols). It should be noted here that the time evolution of the plots of Fig. 2 is substantially determined by the input rate of $C^{18}O_2$ to the system rather than by the chemical exchange rate. Integration of the ^{16}O content over a period of 400 s indicated a pool size of 0.9 ± 0.2 mg of oxygen, which is far short of the total oxygen content of 80 mg in the

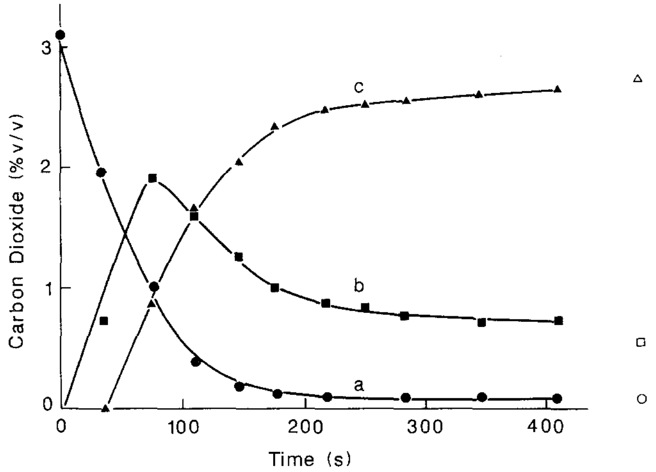

FIG. 2. Volume percent of individual carbon dioxides in exit gas as a function of time following switch of feed composition from helium alone to 3.2% $C^{18}O_2$ in helium: (a) $C^{16}O_2$; (b) $C^{16}O^{18}O$; (c) $C^{18}O_2$.

Li/MgO sample. The integration was carried out with correction of the $C^{16}O^{18}O$ curve, assuming its shape in the absence of catalyst would have been the inverse of the $C^{16}O_2$ evolution curve in Fig. 2. This is unlikely to be exactly true leading to the uncertainty specified above. Additional oxygen exchange beyond that estimated may also have occurred on a time scale beyond that detectable here. The amount estimated is approximately equal to that expected from the Li_2O content (≈0.8 mg of oxygen initially). Thus it seems likely that lithium provides the component through which exchanging oxygens are cycled.

Exchange Involving Carbon Monoxide

The results of Table 3 indicate that small amounts of carbon monoxide can fully interchange oxygen with $C^{18}O_2$. It was of interest to determine the extent of this process with larger amounts of $C^{18}O$ in feed streams. In principle such measurements can be used to place limits on the speed of the water–gas shift equilibria and the extent to which carbon dioxide may be derived by carbon monoxide oxidation. Two such experiments, one at 750°C with 1.07% $C^{18}O$ added, the second at 770°C with 3.2% $C^{18}O$ added, were carried out. Both used a 100-mg sample of Li/MgO which had been previously operated for 40 h. Product yields in control experiments (columns 1 and 2 of Table 4) were somewhat lower than those of Table 1 due to the lesser mass of Li/MgO. In the two experiments with added $C^{18}O$ (columns 3 and 4 of Table 4), the yields of ethane and ethylene are reduced relative to the control experiments. Mass balance calculations indicated that production of the two carbon oxides from methane was inhibited to a similar extent. Of course their absolute quantities in the product stream are larger than in the control experiments due to the added $C^{18}O$ and carbon dioxide derived from it. Calculations showed that ≈59% of the $C^{18}O$ added at 750°C was converted to carbon dioxide. The corresponding figure for the experiment at 770°C with a larger amount of $C^{18}O$ added was 46%.

FTIR spectra of the product mixture from the experiment at 750°C are shown in Fig. 3. The carbon monoxide region shows similar amounts of $C^{16}O$ and $C^{18}O$ but $C^{16}O_2$ dominates among the carbon dioxides. As can be seen from the numerical values for ^{18}O content listed in the final columns of Table 4, a similar picture emerges for the experiment at 770°C with 3.2% $C^{18}O$ added. This is unlike the results of Table 3 which show apparently

TABLE 4

Product Analysis for the Oxidation of Methane over 100 mg Li/MgO in the Presence and Absence of Added $C^{18}O$[a]

Reaction temperature	Chemical analysis (vol %)				$^{18}O/(^{16}O + ^{18}O)$[b]	
	750°C	770°C	750°C	770°C	750°C	770°C
Feed analyses						
$C^{18}O$	Nil	Nil	1.07	3.21	>0.98	>0.98
O_2	10.2	10.2	10.1	9.9	<0.01	<0.01
Product analyses						
O_2	7.2	6.9	7.4	7.3	0.025	0.061
CO	0.18	0.25	0.59	1.90	(0.52)	(0.65)
CO_2	1.07	0.16	1.52	2.35	0.058	0.147
C_2H_4	0.57	0.60	0.41	0.33	—	—
C_2H_6	1.52	1.37	1.28	0.95	—	—

[a] With a basic feedstream of ≈90% methane, ≈10% oxygen at a total flow rate of 18 cm^3 (STP)/min.

[b] As determined by mass spectrometry or, in parentheses, FTIR.

complete equilibration between added $C^{18}O_2$ and the small amount of $C^{16}O$ derived from methane. It appears there is an inverse correlation between the amount of carbon monoxide present and the extent of equilibration between the two carbon oxides.

The isotope analyses of Table 4 show that the water–gas shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2,$$

which acts to equalize ^{18}O content, is far from equilibrium. Indeed the results show that ^{18}O equilibration between carbon monoxide and carbon dioxide must be considerably slower than other exchange processes. This can be demonstrated as follows using the results for the experiment at 750°C as an example. Assuming that inclusion of carbon monoxide inhibits methane oxidation to all products equally, as indicated above, then the quantity of carbon monoxide derived from methane should be 0.15 vol% and in the absence of exchange the fraction ^{18}O in the carbon monoxide (0.59 vol% in total) would be 0.75. The quantity of $C^{18}O$ oxidized to carbon dioxide is 0.63 vol% and again in the absence of exchange this should produce an ^{18}O fraction of 0.26 in the carbon dioxide as a whole. Hence rapid oxygen exchange between carbon monoxide and carbon dioxide along would give ^{18}O contents in each between 0.75 and 0.26. The actual value for carbon dioxide is ≈0.06. Thus ^{18}O is being exchanged out of carbon dioxide faster than it is being introduced from $C^{18}O$. This follows since the ^{18}O content corresponding to total equilibration between oxygen, carbon monoxide, and carbon dioxide is ≈0.04. The conversion of carbon dioxide from its starting value of 0.27 to this point is ≈90% whereas the corresponding figure for carbon monoxide is ≈32%.

Isotope balance calculations indicated that most of the ^{18}O lost from carbon monoxide and carbon dioxide left the reactor as molecular oxygen with water as a significant, but lesser recipient. The ^{18}O analysis for oxygen showed that the distribution between $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ was not at equilibrium. As with the results in Table 3 for exchange with $C^{18}O_2$ there was a significant excess of $^{18}O_2$ ($Q_p \approx 1.2$).

DISCUSSION

The present results show that interchange of oxygen atoms between gaseous oxygen

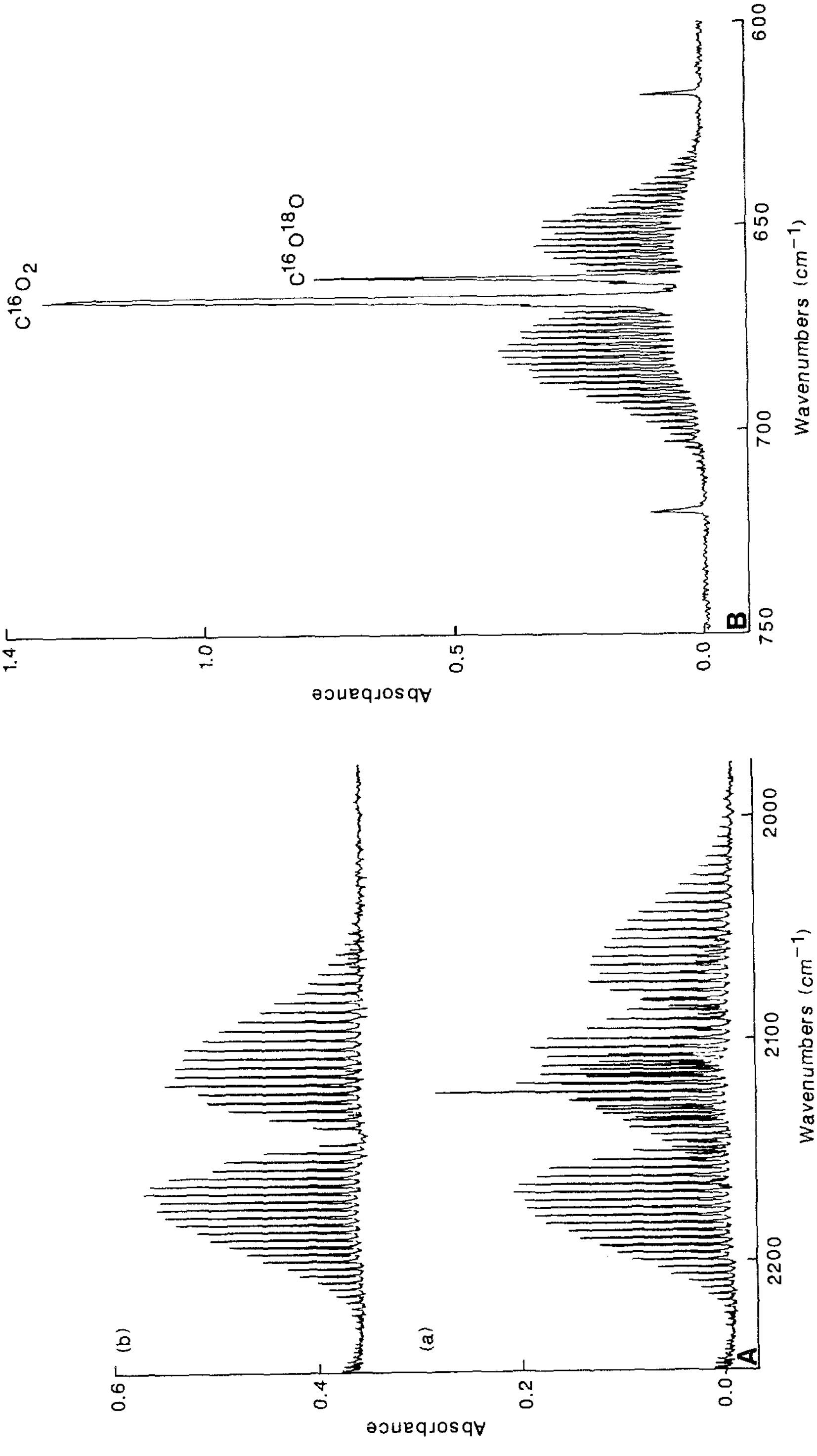

FIG 3. (A) FTIR spectrum in carbon monoxide region for product of reaction of $CH_4/O_2/1.07\%$ $C^{18}O$ mixture over Li/MgO with conditions as per Table 4: (a) product gas; (b) difference spectrum corresponding to (a) less contribution from $C^{18}O$. (B) FTIR spectra in carbon dioxide region for product gas from same reaction.

and carbon dioxide occurs readily over Li/MgO catalysts under methane coupling conditions. The process uses only a small fraction of the catalyst oxygen, probably that associated with lithium. Carbon dioxide presumably exchanges via rapid oxide–carbonate transformations, i.e.,

$$\mathrm{Li_2{}^{16}O + C^{18}O_2 \rightarrow Li_2C^{16}O^{18}O_2}$$

$$\mathrm{Li_2C^{16}O^{18}O_2 \rightarrow Li_2^{18}O + C^{16}O^{18}O}.$$

Exchange with and between oxygen molecules requires the pool to be in oxide form since it is greatly inhibited by carbon dioxide. The results show that single-place (R_1) and to a much lesser extent two-place (R_2) exchange of oxygen are both possible but provide no direct information on the species involved. One possibility following the nomenclature of Winter (*19*) is that single-place exchange involves single vacancies ($\square_s^-$) and adsorbed atoms (O_a)

$$\mathrm{{}^{18}O_2} + (e_2^- \mid \square_s^-) \rightarrow (\mathrm{{}^{18}O^{2-}} \mid \square_s^-) + \mathrm{{}^{18}O}_a$$

$$\mathrm{{}^{16}O_2} + (e_2^- \mid \square_s^-) \rightarrow (\mathrm{{}^{16}O^{2-}} \mid \square_s^-) + \mathrm{{}^{16}O}_a$$

$$\mathrm{{}^{16}O}_a + \mathrm{{}^{18}O}_a \rightarrow \mathrm{{}^{16}O^{18}O}$$

or

$$\mathrm{{}^{16}O}_a + (\mathrm{{}^{18}O^{2-}} \mid \square_s^-) \rightarrow (e_2^- \mid \square_s^-) + \mathrm{{}^{16}O^{18}O},$$

while two-place exchange (observable here only when using $C^{18}O_2/^{16}O_2$ or $C^{18}O/^{16}O_2$ mixtures) involves adjacent vacancies:

$$(\mathrm{{}^{18}O^{2-}} \mid \square_s^-) + (\mathrm{{}^{18}O^{2-}} \mid \square_s^-) \rightarrow (e_2^- \mid \square_s^-) + (e_2^- \mid \square_s^-) + \mathrm{{}^{18}O_2}$$

$$(e_2^- \mid \square_s^-) + (e_2^- \mid \square_s^-) + \mathrm{{}^{16}O_2} \rightarrow 2(\mathrm{{}^{16}O^{2-}} \mid \square_s^-).$$

It is not possible to be certain if the catalyst oxygen species involved in exchange are also those which induce methane oxidation. However, a direct connection is likely since methane coupling over Li/MgO, like oxygen exchange, is inhibited by carbon dioxide (*20*).

It is of interest to compare the rate of $^{16}O_2/^{18}O_2$ mixing with that of methane coupling. The desorption of any $^{16}O^{18}O$ during methane coupling with $^{16}O_2/^{18}O_2$ mixtures is evidence that oxygen is being supplied to the surface at a rate in excess of that required for methane oxidation. In calculating the overall oxygen desorption rate it is necessary to allow for the fact that exchange is reversible and that $^{16}O^{18}O$ represents only one-half the total oxygen actually desorbing (the atoms involved in the remainder have traversed the same steps but give $^{16}O_2$ and $^{18}O_2$ by random recombination). If there is no net oxygen consumption (i.e., when helium is used as carrier) then the mixing reaction will be first order in the distance from equilibrium with an oxygen desorption rate given by

$$\text{rate} = -F_{O_2} \ln(1 - X_m), \qquad (1)$$

where F_{O_2} is the input molar flow rate of oxygen and X_m is the fractional approach of mixing to equilibrium as defined in Table 2. Table 5 compares oxygen desorption rates calculated according to this equation with the chemical conversion rate given by $F_{O_2} X_R$, where X_R is the fractional conversion of oxygen by reaction with methane. It is clear that the desorption rate of oxygen molecules which have undergone the exchange processes is approximately twice the reaction rate. The desorption rate is much faster again when the carrier is inert. Equation (1) is not universally true under conditions of oxygen consumption and calculations based on several extended models were carried out. None overturned the basic conclusion that oxygen desorption was faster than chemical reaction during methane coupling. The conclusion is that methane conversion over Li/MgO is not substantially restricted by the rate of catalyst reoxidation. This is in accord with our conclusions reached previously on the basis of the relative oxidation rates of CH_4 and CD_4 (*15*). The existence of a normal kinetic isotope effect requires that the rate-determining step be bond breaking in methane.

TABLE 5

Comparison of Desorption Rates for Exchanging Oxygen with the Conversion Rate for Reaction of Oxygen with Methane over 200 mg Li/MgO[a]

Temperature (°C)	Carrier	Rates in μmol(O_2)/min	
		For desorption[b]	For reaction
750	He	>500[c]	—
750	CH_4	110	66
700	He	500	—
700	CH_4	42	24

[a] With flow rates and reactant compositions as shown in Table 1 and 2.

[b] Calculated using Eq. (1) with values for X_m from Table 2.

[c] The limit here corresponds to $X_m = 0.99$. The measured value for X_m was 1.02 with an uncertainty of 0.03.

Most of the results reported here pertain to net atom transfer rates between gaseous species during methane coupling for which no comparison measurements are available. However, the transient experiment of Fig. 2 does confirm the recent results of Peil *et al.* (*17*) that exchange involves only a small fraction of the oxygen atoms in Li/MgO. However, our interpretation differs from theirs. They imply that the exchange process is restricted to the outer layer of the entire sample by a slow rate of diffusion into the solid. It is our belief that the observed exchange is largely confined to the lithium component. It is difficult to explain the large difference in exchange activity between new and used reactors other than by lithium stripped from the catalyst. However, it may be noted that the lithium retained by the catalyst after prolonged use is substantially less than that volatilized from it and yet the activity of the depleted Li/MgO for $^{16}O_2$/$^{18}O_2$ mixing is much greater than that of the used reactor (Table 2). This may indicate that the exchange activity of Li/MgO is intrinsically higher than that of the Li/reactor (Al_2O_3) combination or simply that the lithium in the latter has been deposited in a zone at lower temperature.

There is little direct information to indicate whether the results and conclusions reported here for Li/MgO apply to other methane coupling catalysts. Ekstrom and Lapszewicz (*13*) have recently carried out experiments involving $^{18}O_2$, $C^{18}O$, and $C^{18}O_2$ over Sm_2O_3 and Pr_6O_{11}, but they are predominantly of the transient type. Their results with $^{18}O_2$ show rapid exchange of all lattice oxygen even under conditions of high oxygen consumption. Thus like Li/MgO, the rate of methane oxidation over these catalysts is unlikely to be limited by supply of oxygen. The results of Ekstrom and Lapszewicz (*13*) also show that the fraction of added $C^{18}O$ which is oxidized is similar to that found here for Li/MgO and that CO_2 adsorbs strongly on Li/Sm_2O_3 (as expected from the results here) but not on Pr_6O_{11} or Sm_2O_3 itself. They did not report measurements of the rates of ^{18}O transfer between oxygen molecules or between oxygen and carbon oxides.

ACKNOWLEDGMENTS

This project was supported by the CSIRO/Macquarie University Collaborative Fund and a NERDDP grant to the Broken Hill Proprietary Co., Melbourne Research Laboratories. We thank R. J. Tyler for his enthusiastic encouragement.

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