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# A Temperature Programmed Isotope Exchange Study of Ca–Ni–K and Mg–Li Oxide Catalysts Used for Oxidative Coupling of Methane

YUN-FENG CHANG, GABOR A. SOMORJAI, AND HEINZ HEINEMANN

*Center for Advanced Materials, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720*

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A temperature programmed isotope exchange (TPIE) technique was used to study the isotope exchange between gas phase oxygen and lattice oxygen of two Ca–Ni–K oxide, and a Mg–Li oxide catalysts at temperatures up to 750°C. Two types of active surface sites were found: one responsible for single exchange between gas phase oxygen and lattice oxygen and the other responsible for multiple exchange between gas phase oxygen and lattice oxygen. The multiple exchange reaction takes place at lower temperature than the single exchange reaction. The number of active sites responsible for multiple exchange of oxygen is only a fraction (<20%) of that responsible for single exchange. The amount of lattice oxygen exchanged by gas-phase oxygen depends on both the nature of the catalyst and exchange temperature. At temperatures ≤750°C, Mg–Li oxide has the highest exchange capacity (>20%). Ca–Ni–K (A) oxide prepared from the corresponding nitrate and Ca–Ni–K (B) oxide made by physical mixing of CaO, NiO, and $KNO_3$ have a comparable amount (~10%) of lattice oxygen exchanged by gas phase oxygen. 

## INTRODUCTION

The oxidative coupling of methane over Ca–Ni–K oxide catalysts at 600°C in the presence of steam and at low space velocity was first reported in 1990 (*1*), but the active sites responsible for the coupling activity and the role played by water in facilitating the coupling reaction have not been understood. Recently, similar beneficial effects of water were also observed for the oxidative coupling of methane over Mg–Li oxides under similar conditions (*2*). The presence of steam has been shown to enhance both the conversion of methane and the selectivity to higher hydrocarbons, however, its role in changing the reaction pathway remains unclear. The present work was intended to characterize active oxygen species present on the catalyst surface and to understand the role of water in the oxidative coupling of methane by using temperature programmed isotope exchange (TPIE) and temperature programmed desorption (TPD) techniques. In the TPIE experiments, the exchange between gas phase oxygen and lattice oxygen was studied, while in the TPD experiments, water and carbon dioxide were used as probes. The $H_2O$-TPD can provide information about the interaction between water molecules and catalyst surface while $CO_2$-TPD should reveal the possible formation of carbonate.

TPIE has been used for the study of oxidative coupling of methane over $Sr/La_2O_3$ catalysts (*3*). It has given information on active surface oxygen species. It was found that the temperature required for isotope exchange between gas phase oxygen and lattice oxygen was lower on Sr-promoted $La_2O_3$ catalyst than on the parent $La_2O_3$, in other words, the activation energy for isotope exchange was lowered by introducing strontium into the lattice of $La_2O_3$ oxide. This decrease in activation energy corresponds to a significant increase in both conversion and selectivity for the oxidative coupling of methane. In this study, we address the involvement of water in the oxidative coupling of methane and its interaction with lattice oxygen.

## EXPERIMENTAL

The catalysts used in this study were two Ca–Ni–K oxides: one was prepared by decomposition of a mixture of the corre-



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sponding nitrates ($Ca(NO_3)_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, Aldrich, AR grade; $KNO_3$, Mallinckrodt, AR grade at 700°C, denoted Ca–Ni–K (A); the other was a physical mixture of CaO (Aldrich, AR grade), NiO (Aldrich, AR grade), and $KNO_3$ (Mallinckrodt, AR grade), denoted Ca–Ni–K (B). Mg–Li oxide was prepared by decomposition of a mixture of the corresponding nitrates ($Mg(NO_3)_2 \cdot 6H_2O$, Mallinckrodt, AR grade; $LiNO_3$, Aldrich AR grade) at 700°C.

$H_2{}^{18}O$ (99.5%, Isotec) was used as the source of oxygen-18 isotope.

The isotope exchange experiments were carried out in a tubular quartz flow reactor (I.D. 0.36 cm) containing 0.2 g of catalyst. In order to avoid interference from adsorbed oxygen, which might have remained after calcination, the catalysts were degassed in helium flow over a period of 2 h at 680°C. High purity helium (99.999%, Alfagaz) was used as carrier gas. Due to the unavailability of oxygen-18 gas, we explored the possibility to use $H_2{}^{18}O$ instead of $^{18}O_2$ for the TPIE Experiments. First, an isotope exchange of the oxide catalysts (in the form of $^{16}O$) with $H_2{}^{18}O$ was conducted to convert them to $^{18}O$-labeled oxides followed by a TPIE to exchange lattice $^{18}O$ by gas phase $^{16}O_2$. In the $H_2{}^{18}O$-exchange experiments, the flow rates of steam ($H_2{}^{18}O$) and carrier helium were 2 and 100 $cm^3 \cdot min^{-1}$, respectively. This in effect is equivalent to an experiment to exchange an oxide catalyst (in the form of $^{16}O$) by gas phase $^{18}O_2$ provided that the $H_2{}^{18}O$ treatment resulted in equilibration between lattice oxygen and water. To ensure maximal exchange of lattice $^{16}O$ by $H_2{}^{18}O$, the exchange was conducted at 680°C until no further isotope exchange product was detected in the effluent gas. The $^{18}O$-exchanged oxide catalysts were purged by helium at 680°C until no detectable amount of water in the effluent before cooling down to room temperature. The amount of isotope exchanged was also estimated after proper calibration of the system. The fast exchange of lattice oxygen ($^{16}O$) with $H_2{}^{18}O$ at high temperatures allowed the TPIE experiments to be performed with significant economy in the use of $H_2{}^{18}O$. After the isotope exchange, the reactor was brought to room temperature, and the gas stream containing oxygen has ($^{16}O_2$) was introduced while the temperature program was started. The signals of $^{16}O^{18}O$ and $^{18}O_2$ were monitored as a function of temperature. In the TPIE experiments, the flows of oxygen and carrier gas helium were 2 and 100 $cm^3 \cdot min^{-1}$, respectively. A heating rate of 10°C $\cdot$ $min^{-1}$ was used throughout this work.

Gases used in isotope exchange experiments were analyzed by a Hewlett–Packard 5971A quadrupole mass spectrometer. The interface between the outlet of reactor and the inlet of the selective mass detector was a piece of deactivated silica capillary (I.D. 0.11 mm × 2 m, SGE Pty., Australia). The use of this type of ultra-thin capillary tubing allows a continuous and fast-response. To avoid possible condensation of water in the transfer line, it was kept at 120°C.

In $H_2O$-TPD experiments, 0.2 g of oxide catalysts were used. The catalysts were saturated with water vapor at 45°C. The flow rates of water vapor and carrier helium were 2 $cm^3 \cdot min^{-1}$ and 100 $cm^3 \cdot min^{-1}$ respectively. A temperature programmed desorption was started at 45°C with a heating rate of 10°C $\cdot$ $min^{-1}$ and a carrier helium flow of 100 $cm^3 \cdot min^{-1}$.

XPS measurements were carried out in a Perkin–Elmer Phi 5300 ESCA system. The samples were prepared by pressing powdered catalysts between a folded precleaned gold foil and then unfolding it. A layer of catalysts sample stuck on the foil and was analyzed. The conditions employed to collect XPS data were: Al anode (400 W); passing energy, 35.7 eV; acquisition time $\geq$20 min; angle 45°.

Surface area measurements were made with a Quantasorb surface area apparatus (QuantaChrome Co.).

TABLE 1

Results of Surface Analysis and Isotope Exchange

| Catalyst | Composition (atomic ratio) | | BET surface area ($m^2 \cdot g^{-1}$) | Lattice O exchanged[a] (%) |
|---|---|---|---|---|
| | Nominal | XPS | | |
| Li–Mg oxide | 1:2 | 1:3 | 0.7 | >20 (68)[d] |
| Ca–Ni–K oxide (A)[b] | 31:10:1 | 15:5:1 | 1.8 | >8 (42) |
| Ca–Ni–K oxide (B)[c] | 29:9:1 | 13:4:1 | 2.1 | >10 (54) |

[a] Amount of lattice oxygen exchanged by gas-phase oxygen at temperature ≤750°C during the temperature programmed exchange experiment.
[b] Prepared by decomposition of a mixture of $Ca(NO_3)_2$, $Ni(NO_3)_2$, and $KNO_3$ at 700°C.
[c] A physical mixture of CaO, NiO, and $KNO_3$.
[d] Values in brackets are the amount of lattice oxygen exchanged after $H_2{}^{18}O$-treatment.

## RESULTS

Bulk and surface composition, and BET surface area of the three catalysts studied are given in Table 1. Table 1 also contains the degree of lattice oxygen exchanged by gas phase oxygen calculated from TPIE data.

The temperature programmed isotope exchange profiles of single exchange oxygen (signal $^{16}O^{18}O$) and multiple exchange oxygen ($^{18}O^{18}O$) for Li/MgO catalyst are given in Fig. 1. Figures 2 and 3 give the corresponding profiles obtained for Ca–Ni–K (A) and Ca–Ni–K (B) oxides, respectively.

Figure 4 presents the temperature programmed desorption (TPD) profiles of water over Li/MgO oxide, Ca–Ni–K (A), and Ca–Ni–K (B) oxides.

To check on the potential formation of

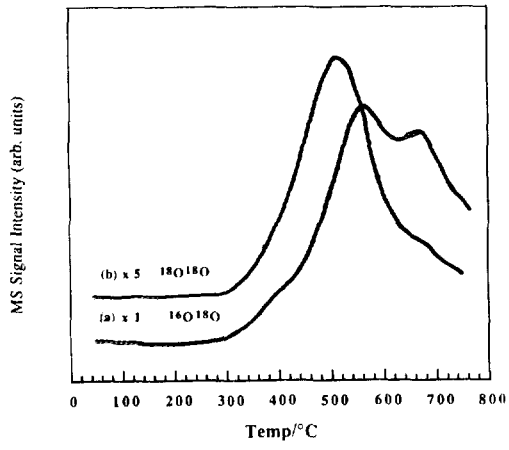


FIG. 1. Temperature programmed exchange of lattice oxygen ($^{18}O$) by gas phase oxygen ($^{16}O_2$) over Mg–Li oxide catalyst: (a) $^{16}O^{18}O$ and (b) $^{18}O^{18}O$.

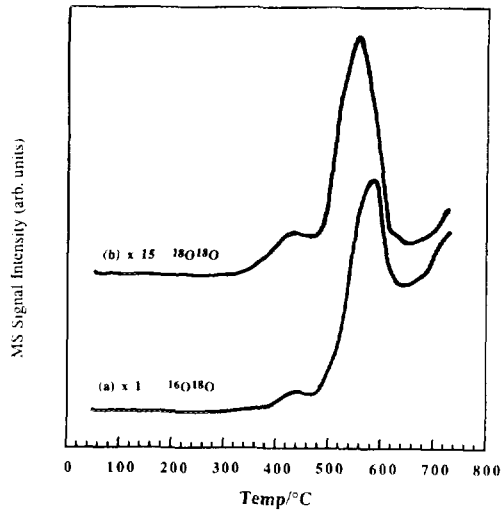


FIG. 2. Temperature programmed exchange of lattice oxygen ($^{18}O$) by gas phase oxygen ($^{16}O_2$) over Ca–Ni–K (A) oxide catalyst: (a) $^{16}O^{18}O$ and (b) $^{18}O^{18}O$.

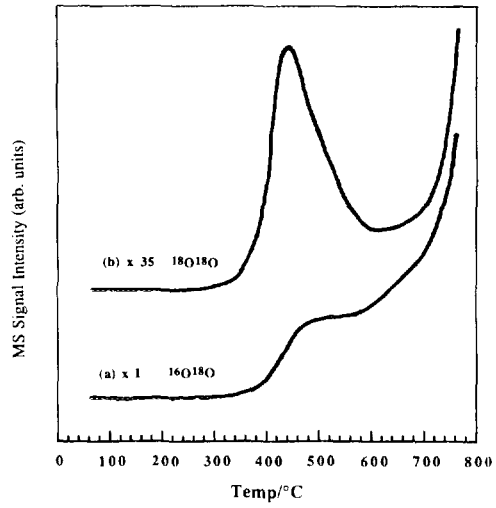


FIG. 3. Temperature programmed exchange of lattice oxygen ($^{18}O$) by gas phase oxygen ($^{16}O_2$) over Ca–Ni–K (B) oxide catalyst: (a) $^{16}O^{18}O$ and (b) $^{18}O^{18}O$.

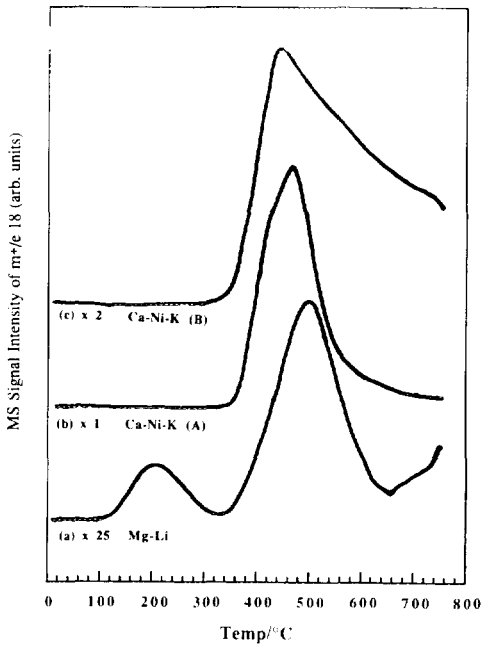


FIG. 4. Temperature programmed desorption profiles of water over (a) Mg–Li, (b) Ca–Ni–K (A) oxide, and (c) Ca–Ni–K (B) oxide catalysts.

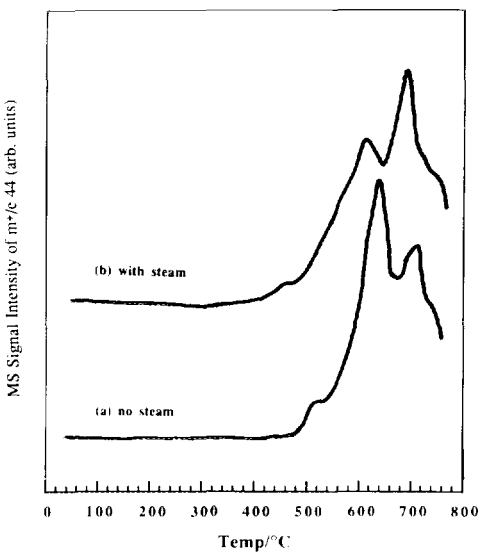


FIG. 5. The effect of steam on the decomposition of carbonate species formed on Mg–Li oxide catalyst (a) in the absence of steam and (b) in the presence of steam ($H_2O$ vapor: 2.7 $cm^3 \cdot min^{-1}$).

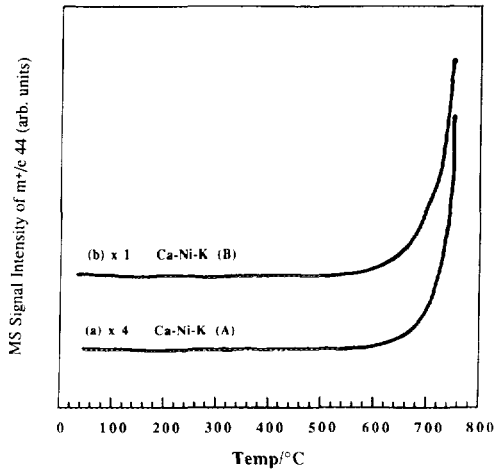


FIG. 6. Temperature programmed desorption profiles of $CO_2$ from (a) Ca–Ni–K (A) and (b) Ca–Ni–K (B) oxide catalysts pretreated with $CO_2$ at 600°C.

carbonate and its dissociation behavior, temperature programmed decomposition of carbon dioxide adsorbed on Li/MgO, Ca–Ni–K (A), and Ca–Ni–K (B) oxide catalysts at 600°C (the reaction temperature used for the oxidative coupling of methane in the presence of steam) was carried out. The results obtained for Li/MgO catalyst are given in Figure 5 ((a) in the absence of steam and (b) in the presence of steam, $H_2O$ vapor: 2.7 $cm^3 \cdot min^{-1}$). Figure 6 gives the corresponding results for both Ca–Ni–K (A) and Ca–Ni–K (B) oxide catalysts.

For comparison, temperature programmed decomposition of $Li_2CO_3$ and $CaCO_3$ was also undertaken. The results are presented in Fig. 7.

## DISCUSSION

### *Mechanistic Considerations of Isotope Exchange of Oxygen*

The isotope exchange of oxygen between gas phase oxygen and lattice oxygen of metal oxides can occur. This reaction process is called heterophase exchange (scheme (A)). Normally, it requires high reaction temperatures (≥300°C). The degree

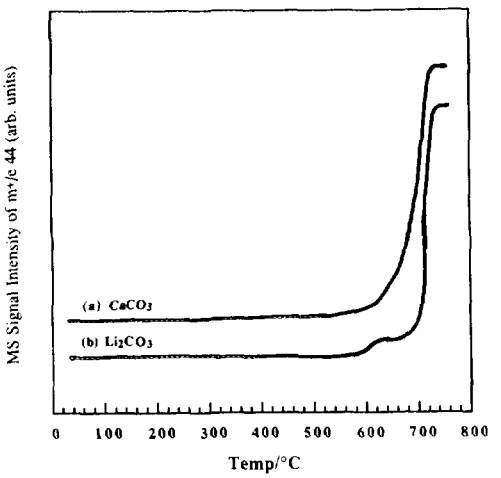


FIG. 7. Evolution of $CO_2$ during the temperature programmed decomposition of (a) $CaCO_3$ and (b) $LiCO_3$.

of exchange at a given temperature depends on the nature of the oxides:

$$^{16}O_2(g) + |^{18}O|_{cat} = {}^{16}O^{18}O + |^{16}O|_{cat}. \quad (A)$$

The symbol $|O|_{cat}$ represents adsorbed or lattice oxygen.

In order to show that the formation of isotopic species ($^{16}O^{18}O$, $^{18}O^{18}O$) is due to isotope exchange between gas phase oxygen and lattice oxygen and not to evolution of molecular oxygen ($^{18}O_2$, $^{16}O^{18}O$) from the catalyst, TPD experiments on $^{18}O$-labeled catalysts were carried out. In the TPD experiments, the $^{18}O$-labeled Mg–Li or Ca–Ni–K oxide catalysts were heated from room temperature to 800°C at a heating rate of 10°C · $min^{-1}$ under constant helium flow (100 $cm^3$ · $min^{-1}$). No evolution of oxygen ($^{16}O_2$, $^{18}O_2$, $^{16}O^{18}O$) was observed. Isotope exchange in the absence of catalyst (under identical conditions as in the presence of a catalyst) was conducted. The amount of isotope exchange was found to be negligible. Therefore, the isotope exchange must be due to heterophase exchange. Thus, we do not need to deal with gas phase exchange in this work. Only heterophase exchange was considered.

For heterophase exchange it is possible to distinguish two cases: single exchange and multiple exchange based on experimental observations of either the time dependence or the temperature dependence of the isotope distribution of molecular oxygen species $^{16}O^{16}O$, $^{16}O^{18}O$, and $^{18}O^{18}O$. For a single exchange, there is only one oxygen atom of the molecule exchanged for one lattice oxygen atom of the catalyst during the residence time on the catalyst surface as described in scheme (B),

$$^{16}O^{16}O(g) + |^{18}O|_l = {}^{16}O^{18}O(g) + |^{16}O|_l, \quad (B)$$

where $|O|_l$ represents lattice oxygen on the catalyst surface. Likewise, the multiple exchange involves both oxygen atoms of the gas phase oxygen molecule exchanged for one stay on the catalyst surface for two lattice oxygen atoms as depicted in scheme (C):

$$^{16}O^{16}O(g) + 2|^{18}O|_l = {}^{18}O^{18}O(g) + 2|^{16}O|_l, \quad (C)$$

Details about distinguishing among single exchange, multiple exchange, and homophase equilibration mechanisms using kinetic analysis methods were given by Klier *et al.* (*4*) and Muzykantov *et al.* (*5*). We used the temperature programmed isotope exchange technique, to study the isotope exchange between lattice oxygen and gas phase oxygen, and tried to correlate it with the catalyst's reaction performance. The use of temperature programming was designed to differentiate these sites responsible for single exchange reaction from those responsible for multiple exchange reaction because the temperature required (which reflects the activation energy for the exchange reaction) for the two reactions may be different.

*Mg–Li Oxide*

The TPIE profile (Fig. 1a) of a single exchange of oxygen on Li/MgO catalyst shows two major peaks positioned at 550 and 660°C, plus a low temperature shoulder

at ca. 400°C. This suggests that there are at least two different types of lattice oxygen site present on the surface of this catalyst which are responsible for the isotope exchange between gas phase oxygen ($^{16}O_2$) and lattice oxygen ($^{18}O$). There was no isotope exchange occurring at temperatures below 300°C. The amount of single isotope exchange of oxygen occurring at temperatures $\leq$440°C was very small. Most of the exchange took place at temperatures $\geq$500°C.

In the TPIE profile of doubly exchanged oxygen (Fig. 1b), there is basically only one single peak centered at 510°C. This temperature is 40°C lower than the temperature of the lower one of the two single exchange peaks. As for the single exchange, there was no significant multiple oxygen exchange at temperatures $\leq$300°C.

Now let us consider the formation of doubly exchanged oxygen. There are two processes leading to the formation of doubly exchanged oxygen species: the secondary exchange of singly exchanged oxygen ($^{16}O^{18}O$) and direct one-step multiple exchange via scheme (C). If the doubly exchanged oxygen is formed via the two-step single exchange, there should be at least two peaks corresponding to the two single exchange peaks at 550 and 660°C, and more importantly, the temperature at which the secondary exchange occurs is expected to be the same if not higher than the primary exchange. Also, the area under these corresponding peaks should be proportional to that of the singly exchanged peaks because the amount of corresponding secondary exchange product formed should be proportional to the amount of primary exchange product. The fact that the temperature (510°C) required for the formation of doubly exchanged oxygen was lower than that required for the single exchange at low temperature (550°C) suggests that the doubly exchanged oxygen ($^{18}O^{18}O$) was probably solely formed via a single step multiple exchange process. This can be achieved, for instance, over a peroxide site. A scheme was proposed by Novakova *et al.* (*6*) for the multiple exchange mechanisms, in which a gas phase oxygen molecule adsorbs on an oxygen vacancy while two lattice oxygen atoms leave the oxide surface and combine to form a molecule. Winter (*7*) suggested a different mechanism, assuming that in the course of the exchange reaction, a reversible decomposition of the oxide surface takes place which is partly responsible for the formation of doubly exchanged oxygen. Most recently, McCarty (*8*) has presented an excellent review on the subject of kinetics and mechanisms of oxidative methane coupling. This review contains a detailed discussion of the nature and thermodynamics of reactive oxygen species on alkali and alkaline-earth oxide catalyst surfaces. From his thermodynamic calculation of thermochemical properties of oxide, carbonate, and hydroxide, and based on the TPD results which suggest the involvement of surface carbonate species, McCarty suggested that superoxide anion ($O_2^-$) and peroxide anion ($O_2^{2-}$) are probably responsible for the coupling reaction on alkali and alkaline-earth oxide catalysts. It was estimated that a concentration of surface active oxygen equivalent to 0.1—1% of a monolayer exists on these catalysts. It was concluded that superoxide anion is the more likely active oxygen center responsible for the coupling reactions on alkali oxide catalysts, while peroxide anion is the more likely reactive center for the coupling reaction on alkaline-earth oxide catalysts. These reactive centers have been previously proposed by others (superoxide, Lunsford (*9*); peroxide anion, Otsuka (*10*), Kharas and Lunsford (*11*), and Korf *et al.* (*12*)).

Based on the signal intensity of $^{16}O^{18}O$ and $^{18}O^{18}O$ as well as the calibration data for oxygen, we estimated that there is one in four active sites responsible for multiple exchange. The exchange reaction occurring on the multiple exchange active sites requires a lower activation energy than the single exchange reactions occurring on active sites responsible for single exchange.

From the isotope exchange data in Table 1, we calculated that the amount of lattice oxygen exchanged by gas phase oxygen is equivalent to approximately 20 atomic oxygen layers by assuming that each oxygen atom occupies 12.5 $Å^2$ (derived from a bond length of Mg–O of 2 Å and the crystal structure of MgO), or expressed in another way: there are $10^{19}$ oxygen atoms per $m^2$ of surface. The number of layers of oxygen exchanged is in excellent agreement with the result of Peil *et al.* (*13*) obtained at around ≥600°C using steady-state isotope transient kinetic analysis (SSITKA) method. They concluded that there were approximately 20 atomic oxygen layers participated in the exchange at temperatures around 600°C.

The activity and selectivity shown by this catalyst at 600°C for the oxidative coupling of methane in the presence of steam (*2*) may be attributed to the presence of both low temperature active sites (≤600°C) for single exchange and one step multiple exchange reactions, while the activity and selectivity observed at higher temperatures (≥700°C) by Kimble and Kolts (*14*, *15*) may relate to the active sites responsible for the high temperature single exchange reaction (≥600°C) in addition to the contribution from the low temperature sites.

*Ca–Ni–K Oxides*

From Fig. 2a, one can see that the starting exchange temperature (SET) of Ca–Ni–K (A) oxide catalyst is 380°C and that there are three $^{16}O^{18}O$ peaks at temperatures 430, 580, and ≥750°C, suggesting that there are probably three different types of active sites present on Ca–Ni–K (A) oxide catalyst which are responsible for the single exchange of oxygen. The low temperature peak is less significant than the high temperature ones. Due to the limitation of the furnace used for the temperature programmed experiment, we were unable to get a complete peak at ≥750°C. However, from the curve shape, we expect that the area under this high temperature peak (≥750°C) would be comparable to that of the 580°C peak, thus, the number of active sites responsible for the single exchange of oxygen at 580 and ≥750°C is approximately the same.

The TPIE profile (Fig. 2b) of doubly exchanged oxygen on Ca–Ni–K (A) oxide catalyst consists of three peaks, a relatively small one at ca. 400°C, a dominant one centered at 540°C, and an incomplete one at ≥720°C. The SET is ca. 320°C, which is 60°C lower than that of the single exchange. Again, in addition to the temperature differences between the three single exchange peaks (430, 580, and ≥750°C) and the three double exchange peaks (400, 540, and ≥720°C), the area under each peaks of the latter is also different from that of the former. Thus, the formation of these doubly exchanged oxygen may be due to a single step multiple exchange mechanism rather than a secondary single exchange. From the signal intensity of single exchange active sites and multiple exchange active sites, the number of active sites responsible for multiple exchange is less than 10% of that responsible for single exchange. From the exchange data presented in Table 1, it is calculated that the amount of lattice oxygen exchanged by gas phase oxygen is equivalent to approximately 5 atomic oxygen layers based on the assumption that each square centimeter of oxide surface contains $10^{19}$ oxygen atom which was estimated from MgO (this value is very close to the universal number $6 \times 10^{18}$ oxygen atoms per $m^2$ of oxide surface suggested by Whalley and Winter (*16*)).

TPIE profiles of oxygen on Ca–Ni–K (B) catalyst (Fig. 3a) show that there are probably two not well resolved single exchange peaks, one at ca. 480°C, and the other at ≥750°C. Though the high temperature peak is not complete due to the temperature limitation of the furnace it appears that the low temperature peak is relatively less significant compared to the high temperature one. The doubly exchanged profile (Fig. 3b) shows two distinct peaks at 440 and ≥750°C. Judging from the area under the

low temperature peak and the curve shape of the high temperature one, it can be concluded that the two peaks are comparable. It appears that there are two types of oxygen sites present on the catalyst surface which are responsible for the single exchange reaction. The low temperature $^{18}O^{18}O$ peak is 40°C lower than the low temperature $^{16}O^{18}O$ peak. This seems to suggest that this low temperature $^{18}O^{18}O$ peak is due to multiple exchange rather than two step single exchange process. However, it is inconclusive about the mechanism for the formation of doubly exchanged oxygen occurred at high temperature because the temperature required for its formation is the same as for the single exchange oxygen formed at high temperatures. Due to this complication, it is difficult to give an exact value of the number of active multiple exchange sites relative to that of single exchange sites. The number of active sites responsible for multiple exchange is probably around 5 ~ 10% of that responsible for single exchange. The amount of lattice oxygen exchanged by gas phase oxygen at temperatures ≤750°C is equivalent to approximately 4–5 atomic layers of lattice oxygen.

The above results clearly show that the amount of lattice oxygen exchanged by water is quite substantial (~10 oxygen atomic layers) though it varies with catalyst composition. This degree of exchange is much higher than that previously reported. In a study of isotope exchange between the oxygen in water ($H_2{}^{18}O$) and lattice oxygen of metal oxides (e.g., $\gamma$-$Al_2O_3$, $ThO_2$, $TiO_2$) at 100°C by Whalley and Winter (*16*), it was found that a fast equilibration step involved the oxygen atoms at the surface (from nitrogen adsorption isotherms) and a second, much slower exchange involved the "second layer of oxygen" in the framework. Whalley and Winter found that the fast exchange with water was faster than the reaction with $^{18}O_2$ under comparable conditions. A similar scheme was claimed for Si–OH, Al–OH, Al–O–Al, and Si–O–Si exchanged with $H_2{}^{18}O$ by Mills and Hindin (*17*) who also found a rather fast first step (Si–OH, Al–OH exchange) and a slower second reaction (Si–O–Si, Al–O–Si, Al–O–Al exchange). Solbakken *et al.* (*18*) showed that the exchange of $H_2{}^{18}O$ vapor with oxygen promoters on an iron oxide catalyst at 450°C yielded oxygen exchange per surface area comparable to nitrogen adsorption. Peri (*19*) studied $H_2{}^{18}O$ exchange with various oxide catalysts (including zeolites) but found the method non-selective for surface OH detection. The study of isotopic exchange between $H_2{}^{18}O$ and various ZSM-5 zeolites (including Al-free ZSM-5 zeolite) and amorphous $SiO_2$ by van Ballmoos (*20*) found that the degree of isotope exchange between $H_2{}^{18}O$ and lattice oxygen ($^{16}O$) was temperature dependent. At moderate temperatures, the isotope exchange occurs at oxygen associated with aluminum sites (Al–O–Si). At high temperatures, the exchange is no longer limited to just lattice oxygen associated with framework aluminum. Exchange with other lattice oxygen (Si–O–Si) also takes place. Basically, at high temperatures the differentiation between surface or structural OH groups and lattice oxygen is lost because sufficient activation energy is available for both kinds of exchange. Thus, the high degree of isotope exchange between $H_2{}^{18}O$ and lattice oxygen observed in our experiments reflects the use of high reaction temperature (680°C) which permits multiple layer isotope exchange rather than the presence of surface hydroxyl groups. The data in Table 1 clearly show that the isotope exchange of lattice oxygen is far from completion. Obviously, the temperature used in the isotope exchange experiments is not high enough to completely exchange all the lattice oxygen by $H_2{}^{18}O$. It should be pointed out that the degree of exchange depends on the structure of the catalyst. Mg–Li oxide has the highest degree of isotope exchange while Ca–Ni–K oxide (A) has the lowest.

### *TPD–$H_2O$*

The TPD profile of Li/MgO catalyst (Fig. 4a) shows a big peak at 500°C and a relatively small peak at 200°C, plus a spread

high temperature peak at ca. 750°C. It is estimated from the TPD data that there are 20 monolayers of water molecules adsorbed on the catalyst surface assuming that one square meter of oxide surface contains $10^{19}$ oxygen sites and each oxygen site adsorbs one water molecule. This means that this Li/MgO catalyst has a significant capacity to adsorb water. While most of the water molecules desorb at 600°C, there remains a significant amount (1 ~ 3 monolayer) of water on the surface. It is probably these strongly adsorbed water molecules which are responsible for the enhanced selectivity to form higher hydrocarbons in the oxidative coupling of methane at 600°C previously reported (*2*).

Basically, there is only a single peak (at 450°C) in the TPD profile (Fig. 4b) of Ca–Ni–K (A) catalyst apart from the high temperature shoulder spreading from 550 up to 750°C. Using the same assumption, the amount of water adsorbed from TPD data is on the order of 100 monolayers. This suggests that the capacity of this material to adsorb water is five times greater than that of Li/MgO catalyst.

For Ca–Ni–K (B) catalyst, its TPD profile (Fig. 4c) is similar to that of Ca–Ni–K (A) except that its high temperature shoulder was more significant, suggesting that the interaction between water molecules and the catalyst surface is stronger than that of Ca–Ni–K (A). Its capacity to adsorbed water is also greater than that of Ca–Ni–K (A) (150 monolayers vs 100 monolayers).

*TPD–$CO_2$*

The TPD profile (Fig. 5a) of Li/MgO catalyst which had been treated in a $CO_2$ stream (10 $cm^3 \cdot min^{-1}$) at 600°C for 5 h shows that no desorption of $CO_2$ occurred at temperatures below 500°C. Most of the desorption occurred at above 600°C. There are at least two dominant peaks at 640 and 710°C plus a minor low temperature shoulder at 520°C and a high temperature shoulder at ≥750°C. This suggests that there are probably four different types of active sites which are responsible for the adsorption of carbon dioxide at 520, 640, 710, and ≥750°C. The high temperature (>640°C) required to remove the adsorbed $CO_2$ implies that the interaction between $CO_2$ and these active sites is quite strong. Based on TPD and calibration data, the amount of $CO_2$ adsorbed by this catalyst is calculated to be $\geq 1.3 \times 10^{21}$ molecules $\cdot g^{-1}$. If we assume that adsorbed $CO_2$ is in the form of $Li_2CO_3$ because $MgCO_3$ is unstable at temperature above 350°C then the amount of $CO_2$ adsorbed corresponds to a conversion of ca. 20% of the lithium present in the catalyst to carbonate. $Li_2CO_3$ is a very stable compound ($CO_2$ pressure of 760 Torr at 1310°C). Thus, the observed TPD peaks at 640 and 710°C are probably due to the decomposition of some carbonate species other than $Li_2CO_3$. We will address this issue in a following section.

To elucidate the possible role played by steam in the decomposition of the carbonated species, TPD experiments in the presence of steam (2.7 $cm^3 \cdot min^{-1}$) were carried out. The TPD profile (Fig. 5b) shows a decrease of decomposition temperature of more than 40°C. This difference cannot be attributed to a partial pressure effect because it has been offset by lowering the flow of carrier gas (in both cases, helium). Thus, the only possible explanation is that water participated in the process by interacting either with the adsorbed $CO_2$ molecules or those sites which adsorb the $CO_2$ molecules, or by interacting with both.

The TPD profiles (Fig. 6) of Ca–Ni–K (A) and Ca–Ni–K (B) catalysts which were pretreated in a helium stream containing $CO_2$ ($CO_2$: 10 $cm^3 \cdot min^{-1}$) at 600°C for 5 h show that no significant desorption of $CO_2$ occurred at temperatures below 700°C. Major decomposition took place at temperatures above 740°C. Based on these TPD data, the amounts of $CO_2$ adsorbed by Ca–Ni–K (A) and Ca–Ni–K (B) catalysts were calculated to be $7.2 \times 10^{20}$ and $2.3 \times 10^{21}$ molecules $\cdot g^{-1}$, respectively. Assuming that the adsorbed $CO_2$ converts CaO into $CaCO_3$, there is approximately 10% of the

Ca in Ca–Ni–K (A) and 30% in Ca–Ni–K (B) converted into $CaCO_3$ by the treatment. Previous results obtained using an XRD technique (*21*) showed there was a significant formation of $CaCO_3$ over Ca–Ni–K (B) catalyst. To confirm that, we did a TPD of $CaCO_3$ under the same experimental conditions as that of Ca–Ni–K (A) and Ca–Ni–K (B) catalysts pretreated with $CO_2$ to see if its TPD profile matches with that of the latter. Figure 7 shows a profile (curve (a)) similar to that of TPD–$CO_2$ of Ca–Ni–K (A) and Ca–Ni–K (B), suggesting that the formation of $CaCO_3$ takes place on both catalyst. However, the amount of $CaCO_3$ formed on Ca–Ni–K (A) is only one third of that of Ca–Ni–K (B). In other words, the catalyst prepared by decomposition of their corresponding nitrates has better resistance against the formation of $CaCO_3$ than that made by physically mixing of CaO, NiO, and $KNO_3$. Because their elemental compositions are essentially the same, this difference can only be attributed to their structural differences. Indeed, TPIE results (Figs. 2 and 3) show that they are different. Ca–Ni–K (A) has more active sites for single oxygen exchange at low temperature than Ca–Ni–K (B).

Similarly, to check if these peaks (at 640 and 710°C) in the TPD—$CO_2$ profile of Li/MgO pretreated with $CO_2$ at 600°C are due to the decomposition of $Li_2CO_3$, temperature programmed decomposition of $Li_2CO_3$ was conducted. The result (Fig. 7b) shows that the decomposition of $Li_2CO_3$ at temperatures below 720°C was negligible. Thus, those peaks observed at temperatures $\leq$710°C (Fig. 5) must be due to the decomposition of carbonate species other than $Li_2CO_3$. The formation of $MgCO_3$ can be ruled out because it has dissociated well below the temperature $\geq$640°C. This is in agreement with XRD results showing negligible formation of $Li_2CO_3$.

## CONCLUSIONS

For Li/MgO catalyst, there are at least two kinds of surface sites which are responsible for the single exchange reactions occurred at 550 and 660°C respectively; there is probably only one type of active sites which are responsible for the multiple exchange reaction at 510°C. The minimum temperature required for the isotopic exchange is 300°C. However, the amount of isotopic exchange below 400°C is negligible. Active sites responsible for multiple exchange reactions represent ~20% of the total number of active sites.

For Ca–Ni–K (A) catalyst, there are three type of surface sites which are responsible for the single exchange reactions occurred at 430, 580, and $\geq$750°C. The active oxygen sites responsible for the exchange reaction at 430°C are far less important than those responsible for the exchanges at higher temperatures (580, $\geq$750°C). There seem to be three types of oxygen sites which are responsible for multiple exchange reactions at 450, 520, and $\geq$720°C. The active site responsible for the exchange reaction at 520°C is dominant. Among the surface active sites for oxygen exchange reactions ~7% are responsible for multiple exchange reaction.

For Ca–Ni–K (B) catalyst, there are two types of active site responsible for single exchange reactions at 480 and $\geq$750°C. The number of sites responsible for the high temperature exchange reaction is greater than that responsible for the low temperature reaction. Likewise, there two types of active sites responsible for multiple exchange reactions, occurring at 440 and $\geq$740°C. The number of multiple exchange sites is only a very small fraction (<3%) of that responsible for the single exchange reactions.

Formation of calcium carbonate in both Ca–Ni–K oxide catalysts was demonstrated using TPD technique. Its formation was confirmed by temperature programmed decomposition of calcium carbonate. The amount of carbonate formed in Ca–Ni–K (A) catalyst is much lower than that of Ca–Ni–K (B) catalyst, suggesting that Ca–Ni–K catalyst prepared by decomposition

method is more resistant against carbonate formation than that prepared by physically mixing of their corresponding oxides.

Adsorption of carbon dioxide on Li/MgO catalyst was found. Temperature programmed decomposition of $Li_2CO_3$ revealed that the carbonate species formed on Li/MgO catalyst is probably not $Li_2CO_3$ because its decomposition required significantly lower temperature than that of $Li_2CO_3$. Moreover, the amount of carbonate species formed on this catalyst is much smaller than the carbonate content on the Ca–Ni–K oxide catalysts.

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