Temperature programmed isotopic exchange of lattice oxygen during methane oxidative coupling

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Temperature programmed isotopic exchange (TPIE), has been applied in the studies of the oxidative coupling of methane. Results presented in this paper show that the addition of strontium oxide to lanthanum oxide changes a structure of La_2O_3 by creating oxygen vacancies in its lattice. TPIE experiments indicate that an exchange between gas phase and lattice oxygen for the 1% Sr/La_2O_3 starts below 400 °C and a starting exchange temperature (SET), is around 100 °C lower than in the case of unpromoted La_2O_3. In this paper the effect of other operating variables (oxygen partial pressure, presence of methane, and carbon dioxide), on the isotopic exchange rates for lanthanum oxide based catalysts is also demonstrated.

Keywords: Isotopic exchange; oxidative coupling of methane

1. Introduction

The role of lattice oxygen is an important consideration in the design of new catalysts for the oxidative coupling of methane. Isotopic labelling is a well known technique which has been used in many catalytic studies including the early work by Emmett on ammonia synthesis [1], and by many others [2–4]. Happel [5] proposed the use of isotopic switches to perform steady state experiments under transient isotopic conditions. This line of inquire proved to be very useful, and has been applied in CO hydrogenation studies by Biloen et al. [6], Mims and McCandlish [7], Nwalor et al. [8], and Yokomizo and Bell [9]. A number of transient techniques with and without isotopes have been used recently to study the reaction pathways of several of the reactants during methane dimerization by oxidative coupling. These include the use of pulses and steps of reactants with different oxygen concentrations by Miro et al. [10,11], as well as the use of isotopic switches performed by Peil et al. [12], and Kalenik and Wolf [13]. More traditional isotopic labelling techniques have been applied to study CH_4/CD_4 exchange during the oxidative coupling of methane by

Nelson et al. [14], Ekstrom and Lapszewicz [15], Mims et al. [16], and also by Mirodatos [17]. While these techniques have provided significant insights into the various pathways involved in methane oxidative coupling, the role of lattice versus adsorbed oxygen still remains elusive. Recently we have focussed on studying the role of oxygen mobility in La_2O_3 and Sr/La_2O_3 catalysts by using step changes in $^{16}O_2$ and $^{18}O_2$ feeds at conditions similar to those utilized in oxidative coupling reactions [13]. From these results it was concluded that Sr promotion increased the oxygen diffusivity in the lattice, presumably by creating oxygen vacancies in the La_2O_3 structure. Similar conclusions have been reached by Peil et al. [12] regarding the role of Li promotion in MgO catalysts. Since the increase in mobility also coincided with an increase in activity for methane coupling, it follows that understanding the pathways of gas phase and lattice oxygen could be relevant to the design of more active and selective catalysts.

To broaden the range of operating variables and to understand better the role of lattice oxygen participation in catalytic reactions, we have applied a variant of our previous isotopic exchange experiments by combining them with temperature programming and called the resulting combination: temperature programmed isotopic exchange or TPIE. While temperature programmed reaction in the presence of isotopes has been used by Yokomizo and Bell [9] and Bertucco and Bennett [18] to investigate the nature of adsorbed species during CO hydrogenation over Ru/TiO_2, it has not been used to measure the isotopic exchange with lattice oxygen. The TPIE method has an important application in the field of catalytic oxidation reactions involving lattice oxygen, since it provides much more information regarding the rates of lattice oxygen exchange, than steady state isotopic methods. While the experiments are still in progress, the authors feel that the technique itself is a useful contribution to the study of reactions involving the participation of lattice oxygen and warrants an early communication.

2. Experimental procedure

The two catalysts used in the exchange experiments for which results are presented in this letter were La_2O_3 and 1% Sr promoted La_2O_3. The catalyst preparation technique and the experimental apparatus which consists of a small volume quartz flow reactor connected to a UTI 100C mass spectrometer have been described previously [11,13]. Consequently only its modification for the TPIE experiments are described here.

In order to provide a linear increase of the reactor temperature, typically from 25 to 750 °C, a programmable temperature controller (Omega 2012), has been added to the original unit. Of importance in the design of the reactor is its low volume, which was accomplished by the use of two concentric tubes at the reactor inlet and a tapered exit which minimized both, the pre- and post reactor

volumes. The $^{18}O_2$ isotope was first transferred to an evacuated lecture bottle, which was then pressurized with He up to 100 psi. Since the isotopic exchange rates are sensitive to the reactor pressure as well as the oxygen partial pressure (P_{O_2}), a pressure transducer was mounted at the reactor inlet, and an electronic indicator (Omega DP-354) was used to monitor pressure changes inside the reactor. A metering valve at the reactor exit provided an easy way to control and adjust total reactor pressure.

An important aspect of the experimental procedure consists of exchanging *first* $^{18}O_2$ isotope with the $^{16}O_2$ of the oxide catalyst at 750 °C by sending a step of $^{18}O_2$/He mixture into the reactor (100 cc/min total flow rate) over a predetermined period of time. In the case of La_2O_3 catalyst, a period of seven minutes was sufficient to achieve 80% exchange between the isotope and the unlabeled lattice oxygen. The first exchange of the $^{18}O_2$ with the lattice oxygen permits the TPIE, experiment to be performed with significant economy in the isotope use. Monitoring of the signals for $^{16}O_2$ (referred hereafter as O_2), $^{18}O_2$ isotope, and $^{16}O^{18}O$ scrambled oxygen permits to determine the amount of isotope exchanged as well as its mobility in the lattice [13]. After exchanging the isotope, the reactor is brought to room temperature, and the gas stream containing O_2 and He is introduced over a sample while the temperature program is started. Of interest is to follow the signals corresponding to $^{18}O_2$ and $^{16}O^{18}O$ as a function of temperature (time). It should be noted that the location of the maximum temperature of these peaks is *not* important since it depends on the amount of isotope exchanged during the first stage of experiment. Due to the fluctuations in the reactor heating rates and changes in the isotope feed concentration this amount is not identical in all experiments. The temperature at which isotopic exchange starts or (SET), is reproducible and it is used as an indication of the activation energy of the exchange reaction. The oxygen flow rate can be varied, mixed with other gases, or substituted by another oxygen containing species such as CO_2 or N_2O. The results of such experiments on La_2O_3 and Sr/La_2O_3 catalysts are presented below.

3. Results and discussion

The initial results obtained by applying the TPIE technique, revealed immediately the usefulness of this method. Figs. 1a and 1b present responses of the $^{16}O^{18}O$ and $^{18}O_2$ signals for the Sr/La_2O_3 and La_2O_3 catalysts. These results were obtained using 0.5 cc/min of O_2 diluted in 100 cc/min of the helium carrier and by programming the temperature increase from room to 750 °C in 30 minutes. Two important observations can be made from these results: (i) for both catalysts the starting exchange temperature or SET at which $^{16}O_2/^{18}O_2$ isotopic exchange first can be observed is much lower than the temperatures typically used in oxidative coupling of methane (> 750 °C), and (ii) Sr promo-

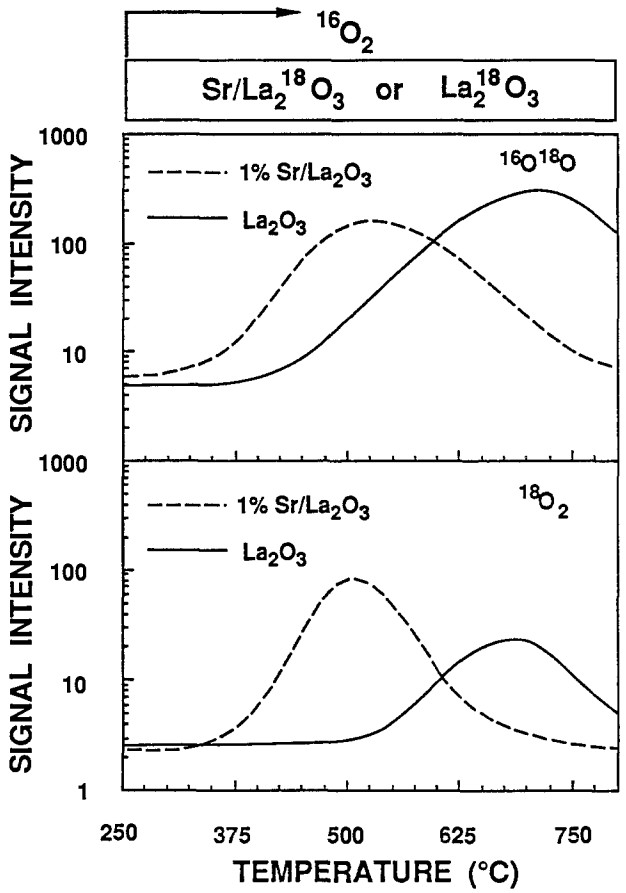

Fig. 1. The effect of Sr promotion on starting exchange temperature (SET), during temperature programmed isotopic exchange (TPIE), on 1% $Sr/La_2^{18}O_3$ and $La_2^{18}O_3$ catalysts. Oxygen and carrier flow rates: 0.5 and 100 cc/min respectively, mass of the catalyst 10 mg.

tion lowers by about 100 °C the temperature at which isotopic exchange takes place, representing a *decrease* in activation energy for this reaction. The $^{18}O_2$ signal appears in both catalysts later (i.e. at a higher temperature) than the $^{16}O^{18}O$ signal. This apparently occurs because the oxygen readily available on the surface top layers has a higher probability of forming $^{16}O^{18}O$ species than the one for recombination of ^{18}O atoms. Both, the $^{16}O^{18}O$ and the $^{18}O_2$ signals reach a maximum and then decrease with time due to the depletion of ^{18}O oxygen from the lattice. Prior to the initial exchange all catalysts samples had been degassed for 30 min in helium flow at 600 °C. Subsequent temperature programmed desorption (TPD) experiments conducted in the temperature range of the TPIE experiments, showed no desorption of oxygen from the catalyst surface. Furthermore, no signal of oxygen evolution from the surface or the lattice was detected in the *absence* of gas phase oxygen, nor any detectable C_2

products appear when the experiment was conducted without gas phase oxygen when methane is added to a pure helium stream [13]. The results of the TPIE experiment presented above clearly show that oxygen mobility in the lattice of La_2O_3 is rapid, and that Sr promotion decreases further the activation energy for the oxygen exchange as compared to the unpromoted La_2O_3.

The different response in these two catalysts can be attributed to the increase in the number of oxygen vacancies which are formed in the structure of lanthanum oxide after promotion with strontium oxide. The bulk concentration of oxygen vacancies depends on the amount of strontium oxide dissolved in the lattice of the La_2O_3.

Besides the Sr promoter added to the lanthanum oxide catalyst, several other factors also affect isotopic exchange rates and to a lesser extent the starting exchange temperatures. One of them is the effect of oxygen partial pressure which of course may be a consequence of the total reactor pressure. Fig. 2 shows the results of TPIE experiment on Sr/La_2O_3 catalyst at two different partial pressures of oxygen (P_{O_2}). It can be clearly seen that the starting exchange temperatures for the $^{16}O^{18}O$ and $^{18}O_2$ signals remain almost unchanged while the rate of the exchange (measured by the slope of the response versus time curve) increases as partial pressure of oxygen increases. This kind of behavior is expected since the increase in O_2 concentration does not change significantly the total number of oxygen vacancies. However, some of them are dissolved by the gaseous oxygen which maybe the cause of the changes observed in fig. 2.

When oxygen and methane were both introduced as reactants during TPIE experiments, the behavior of the Sr promoted catalyst was different than in the case of the unpromoted material. Response signals of the $^{16}O^{18}O$ and $^{18}O_2$ species presented in fig. 3a and 3b indicate that the presence of CH_4 decreases the exchange rates between gas phase and lattice oxygen, while the SET remains unchanged. The factor responsible for this type of behavior is related to the interaction of methane-oxygen reaction products with the surface of the catalyst. Although isotopic switch experiments conducted on the Sr/La_2O_3 at 750 °C did not show long lived methane or carbon oxides surface species [13], it is possible that at lower temperatures, CO_2 produced during methane oxidative coupling can form surface lanthanum carbonates. In order to confirm this hypothesis, TPD measurements on reactor used samples of Sr/La_2O_3 samples were performed. These samples were prepared by treating freshly prepared Sr promoted La_2O_3 in a reactant mixture containing methane and oxygen for three hours at 450 °C and at 100 cc/min total flow rate (methane/oxygen ratio of 4 and reactant partial pressure of 0.4). The TPD measurements were conducted after stopping the methane and oxygen flow and raising reactor temperature to 770 °C. The results of the TPD experiment revealed that carbon dioxide desorbed from the surface of the catalyst in the 375 °–750 °C temperature range. It can be concluded that the small traces of CO_2 produced during reaction of methane and oxygen on Sr/La_2O_3, at this temperature react on the

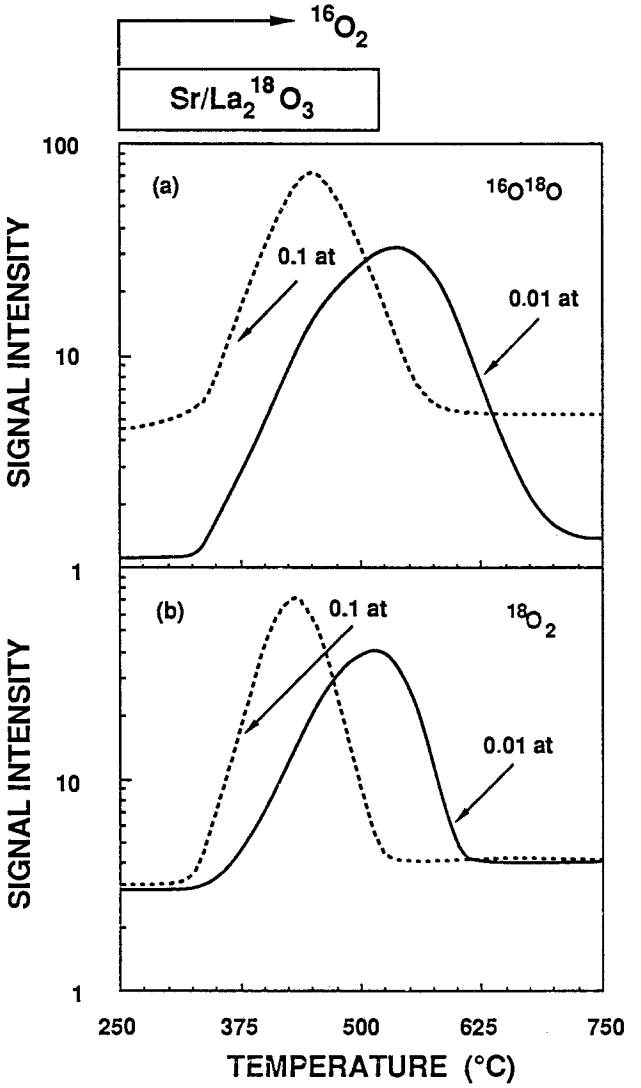

Fig. 2. The effect of oxygen partial pressure on the starting exchange temperature (SET), during TPIE experiments on Sr/La_2O_3 catalyst, (a).–$^{16}O^{18}O$ signal, (b)–$^{18}O_2$ signal. Mass of the catalyst 10 mg.

surface of the catalyst forming stable lanthanum carbonates. Since these carbonates are formed and remain on the surface of the catalyst up to 750 °C, their presence can influence the exchange rates between gas phase and lattice oxygen. It is well known that the presence of carbonates plays an important role in the deactivation of the sites for the oxidative coupling of methane [19]. The results of fig. 2 appear to confirm these findings by indicating that the presence of carbonate decreases the rate of oxygen exchange.

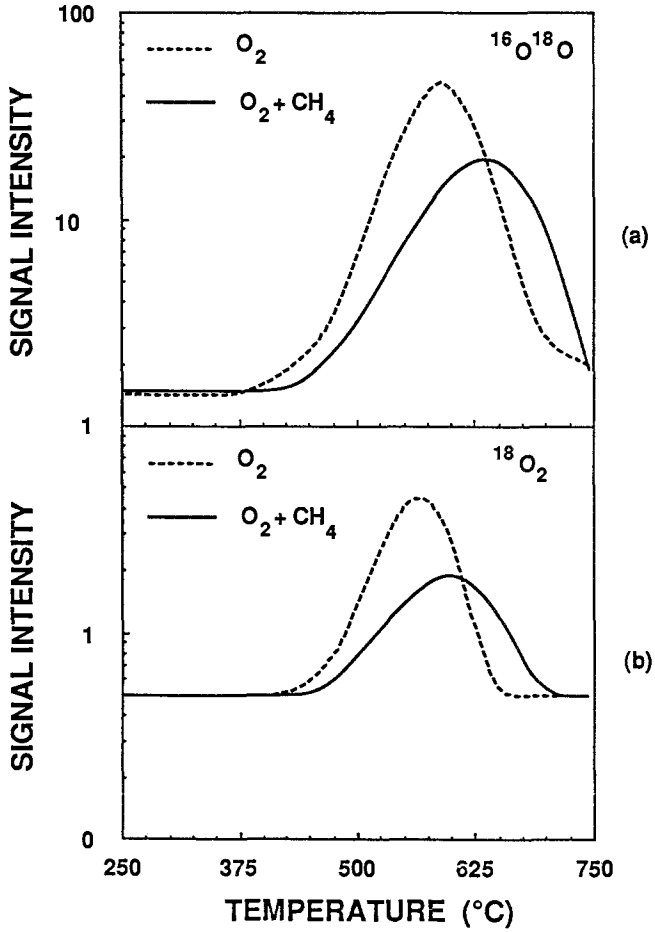

Fig. 3. The effect of methane on the oxygen exchange during TPIE experiments on Sr/La_2O_3 catalyst, (a).–$^{16}O^{18}O$ signal, (b).–$^{18}O_2$ signal. Mass of the catalyst 10 mg, 0.5 cc/min O_2 flow, 2 cc/min CH_4 flow.

In order to determine an influence of carbon dioxide on the SET for the 1% Sr/La_2O_3 catalyst, additional CO_2-TPIE experiments were conducted. The CO_2-TPIE experiment was first performed without gas phase oxygen. As shown in fig. 4 the CO_2 signal decreases significantly throughout the run indicating the uptake of CO_2 to form carbonate. The $C^{16}O^{18}O$ signal appears at about 150 ° C whereas the $C^{18}O_2$ signal starts at 300 ° C. Results of TPD experiments conducted on Sr promoted lanthanum oxide treated overnight with CO_2 (not presented in this paper), showed that lanthanum carbonate decomposition is completed around 750 ° C, and that partial decomposition of the carbonate takes place at temperatures lower to those usually applied during oxidative dimerization of methane. This fact implies that at low temperatures, lanthanum carbonates play an important role during TPIE reactions in the presence of methane, and consequently during steady state oxidative coupling reactions.

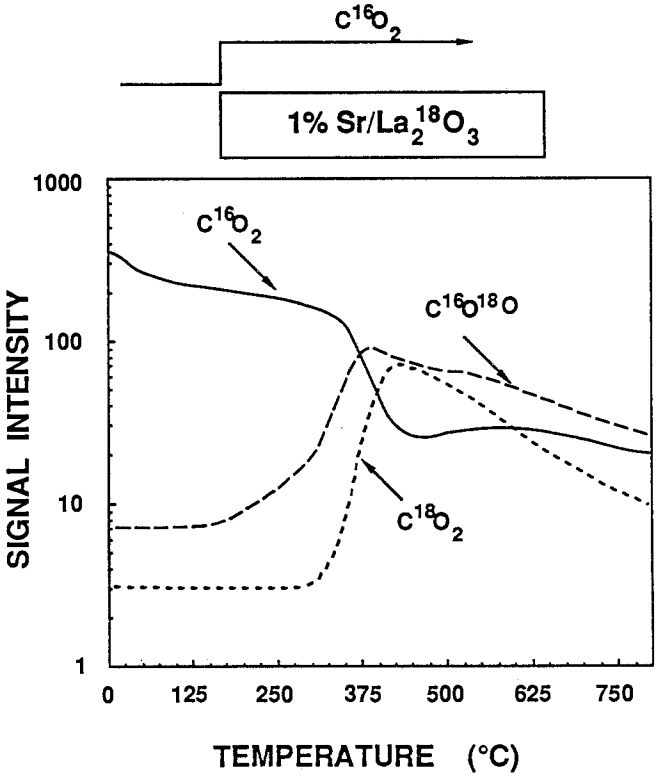

Fig. 4. TPIE experiment for the Sr/La_2O_3 catalyst conducted in the presence of CO_2. Mass of the catalyst 10 mg, 2 cc/min CO_2 flow, 100 cc/min He flow.

The results of an experiment in which a step of a mixture of O_2 and CO_2 was introduced over a catalyst sample previously exchanged with $^{18}O_2$ are shown in fig. 5. The CO_2 signal shown, decreases steadily but not as pronounced as when no O_2 was present in the system. Furthermore, under these experimental conditions, the reaction of CO_2 with the surface starts slightly above room temperature. CO_2 undergoes exchange leading to the formation of $C^{16}O^{18}O$ at 50 °C, and later to a $C^{18}O_2$ at about 300 °C. The exchange between lattice and gas phase oxygen starts at about 550 °C, i.e. at much higher temperature than the one observed during the experiment with O_2 (fig. 1). The different temperatures at which CO_2 and O_2 start exchanging with lattice oxygen can also be explained by the presence of lanthanum carbonates which cover the surface of the Sr/La_2O_3. Figs. 4a and 4b, indicate that at temperatures around 500 °C a significant fraction of carbonates decomposes, leaving open sites for the exchange between gas phase and lattice oxygen. These results also suggest that during oxidative coupling experiments, the exchange between CO_2 (reaction product), and lattice oxygen is more likely to occur than the similar reaction involving lattice and gas phase oxygen. This type of interaction could be

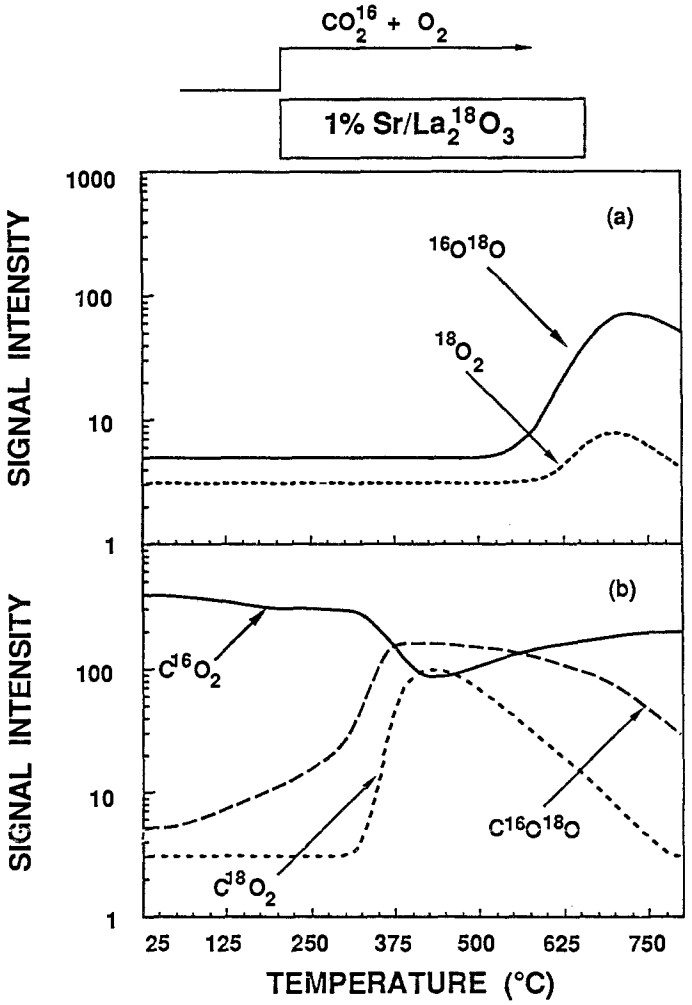

Fig. 5. TPIE experiment for the Sr/La_2O_3 catalyst conducted in the presence of O_2 and CO_2. Mass of the catalyst 10 mg, 0.5 cc/mix O_2 flow, 2 cc/min CO_2 flow, and 100 cc/min He flow.

responsible for the relatively low selectivities of lanthanum oxide as an oxidative coupling catalyst.

The experiments presented in this letter clearly indicate that the TPIE method is a useful tool in detecting the pathways of gaseous oxygen interactions with its lattice counterpart. Many other reactants combinations can be studied for determining how the lattice oxygen interaction affects the overall reaction mechanism. In the case of methane coupling experiments involving the use of mixtures of methane and oxygen, the TPIE technique provides an interesting link between the role of gas phase and lattice oxygen. The purpose of this letter is to demonstrate the usefulness of this method, so that it can be quickly

adopted by those researchers involved in the study of oxidation reactions by similar isotopic techniques.

Acknowledgments

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