

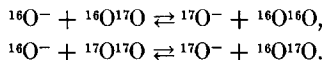
## An EPR Study of the Kinetics of Oxygen Isotopic Exchange Involving O<sup>-</sup> Adsorbed Species on V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> Catalysts

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The kinetics of the oxygen isotopic exchange reaction involving adsorbed O<sup>-</sup> species has been investigated on partially reduced silica-supported vanadium pentoxide. The first low-field line of the EPR spectrum of adsorbed <sup>16</sup>O<sup>-</sup> species has been taken as a measure of their concentration to monitor the following reactions:



It was shown that the exchange proceeds at room temperature with a rate constant  $k \simeq 0.9 \cdot 10^{-10}$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup> and that only about 70% of the adsorbed O<sup>-</sup> species participate in the process, in contrast to reactions with H<sub>2</sub>, CO, and other molecules which have been found earlier to take place even at 77°K.

### INTRODUCTION

In previous work (1), using oxygen enriched with <sup>17</sup>O, we have investigated the structure of a new type of ozonide ion stabilized on a silica-supported vanadium oxide catalyst and found that within the radical two oxygen nuclei are equivalent. This is in sharp contrast with the structure of the ozonide ion adsorbed on MgO with three inequivalent oxygen nuclei (2). While the former ion was suggested to be an intermediate on V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalysts in the oxygen isotopic reaction studied by mass spectrometry (3), the latter was not the case from results obtained by EPR (2).

Using an analysis "at equilibrium," we

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recently reported that, on MgO at room temperature, isotopic exchange was occurring between gas-phase oxygen and adsorbed molecular ions O<sub>2</sub><sup>-</sup> (4).

In the present work, we wish to report the first use of EPR in the study of the kinetics of the isotopic exchange of oxygen between gas-phase oxygen enriched in <sup>17</sup>O and <sup>16</sup>O<sup>-</sup> ions adsorbed on V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalysts.

### EXPERIMENTAL METHODS

Samples of V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalysts containing 2.4% by weight of V<sub>2</sub>O<sub>5</sub> were used in this study. They were prepared by impregnation of SiO<sub>2</sub> (specific surface area ~300 m<sup>2</sup>/g) with a NH<sub>4</sub>VO<sub>3</sub> solution as described in Ref. (5).

The samples were activated for 1 hr at 500°C (in air), reduced in hydrogen (40

Torr) for 0.5 hr at 500°C, and finally evacuated to  $10^{-4}$ – $10^{-5}$  Torr at the same temperature.

The  $O_2^-$  and  $O^-$  species were produced by adsorption of  $^{16}O_2$  onto the sample at a pressure of 50 Torr for 30 min at room temperature through a liquid nitrogen trap.<sup>3</sup> After evacuating the excess oxygen, the paramagnetic oxygen species were characterized by means of their EPR spectra (5).

After natural or isotopically enriched oxygen was admitted onto the catalysts at 77°K, the EPR spectra were measured after various time intervals at room temperature and the exchange kinetics was followed. The first line at low field in the EPR spectra of  $^{16}O^-$  species at room temperature was taken as a measure of their concentration (Fig. 1a). The number of oxygen molecules contacting the samples (0.038 g) at 77°K was  $5 \cdot 10^{17}$ .

EPR measurements were carried out on a Varian V4502 spectrometer (X band) at room temperature. A standard sample of  $CuSO_4 \cdot 5H_2O$  was used in order to measure the spin concentrations.

According to the mass spectrometer analysis the normalized peak heights for the oxygen enriched in  $^{17}O$  (hereafter referred to as "enriched gas") were as follows:

$$C_{32} = 0.056,$$

$$C_{33} = 0.243,$$

$$C_{34} = 0.418,$$

$$C_{35} = 0.241,$$

$$C_{36} = 0.043,$$

totaling 1.001. If  $\alpha$ ,  $\beta$ , and  $\gamma$  are atomic percentages of  $^{16}O$ ,  $^{17}O$ , and  $^{18}O$  in the

<sup>3</sup> It has been found that the oxygen species formed are much more stable if the sample tube is protected with a liquid nitrogen trap to avoid contamination by grease vapor.

mixture, respectively, one can write:

$$\alpha = C_{32} + \frac{1}{2}C_{33} + \frac{1}{2}(^{16}O^{18}O), \quad (1)$$

$$\beta = (^{17}O^{17}O) + \frac{1}{2}C_{33} + \frac{1}{2}C_{35}, \quad (2)$$

$$\gamma = C_{36} + \frac{1}{2}(^{16}O^{18}O) + \frac{1}{2}C_{35}, \quad (3)$$

where

$$(^{17}O^{17}O) + (^{16}O^{18}O) = C_{34}. \quad (4)$$

Assuming that the mixture is at equi-

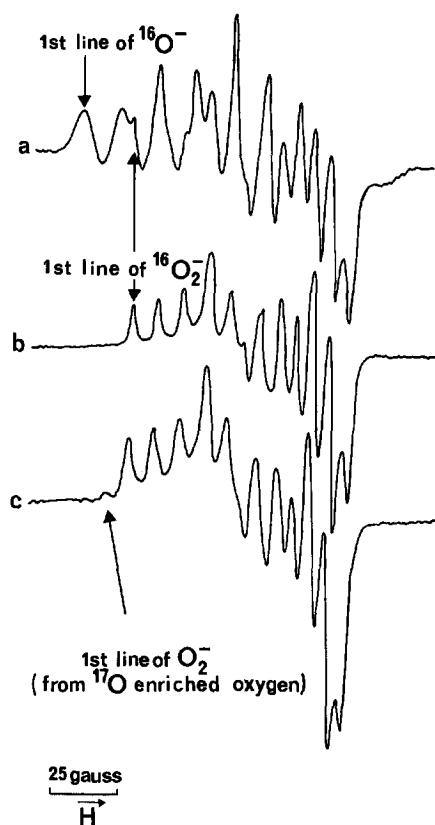


FIG. 1. (a) EPR spectrum obtained at room temperature of  $^{16}O^-$  and  $^{16}O_2^-$  species produced by adsorption of  $^{16}O_2$  on reduced  $V_2O_5/SiO_2$  samples. The arrows indicate the first low-field lines of  $^{16}O^-$  and  $^{16}O_2^-$  species. (b) EPR spectrum obtained at room temperature of  $^{16}O_2^-$  species produced by adsorption of oxygen on reduced  $V_2O_5/SiO_2$  samples and further contact with CO to eliminate  $^{16}O^-$  species. (c) EPR spectrum obtained at room temperature of  $^{16}O_2^-$ ,  $^{16}O^{17}O^-$ , and  $^{17}O_2^-$  species produced by adsorption of  $^{17}O$ -enriched oxygen on reduced  $V_2O_5/SiO_2$  samples and further contact with CO to eliminate  $^{16}O^-$  and  $^{17}O^-$  species.

librium, that is,

$$\frac{({}^{16}\text{O}^{18}\text{O})^2}{({}^{16}\text{O}^{16}\text{O})({}^{18}\text{O}^{18}\text{O})} = 4 \quad \text{or}$$

$$({}^{16}\text{O}^{18}\text{O})^2 = 4C_{32}C_{36}, \quad (5)$$

we find

$$({}^{16}\text{O}^{18}\text{O}) = 0.098 \quad \text{and} \quad ({}^{17}\text{O}^{17}\text{O}) = 0.32.$$

Putting these values into Eqs. (1)–(3) we find that  $\alpha = 22.65\%$ ,  $\beta = 56.2\%$ , and  $\gamma = 21.25\%$ .

### RESULTS AND DISCUSSION

The first line at low field of the  ${}^{16}\text{O}^-$  EPR spectra being taken as a measure of the concentration of  ${}^{16}\text{O}^-$  species, it is therefore important to comment on whether this line can overlap with lines due to other oxygen species. From Fig. 1a, it is clear that the first line of  ${}^{16}\text{O}^-$  species does not overlap with the first line due to  ${}^{16}\text{O}_2^-$  ions (Fig. 1b). Figure 1c shows the spectrum obtained when reduced  $\text{V}_2\text{O}_5/\text{SiO}_2$  catalysts are contacted with  ${}^{17}\text{O}$ -enriched gas to produce  $\text{O}_2^-$  and  $\text{O}^-$  species and then with CO to elimi-

nate the  $\text{O}^-$  species. Thus, only  ${}^{16}\text{O}_2^-$ ,  ${}^{16}\text{O}^{17}\text{O}^-$ , and  ${}^{17}\text{O}_2^-$  species are left and it is seen that the first line at low field in this case occurs at a higher field than that taken to measure the  ${}^{16}\text{O}^-$  concentration in Fig. 1a.

Therefore, the only possible overlap concerns  ${}^{17}\text{O}^-$  species and this can occur only if the perpendicular component of the superhyperfine tensor due to the interaction of the unpaired electron of  $\text{O}^-$  with  ${}^{51}\text{V}$  nuclei is equal to the perpendicular or parallel component of the hyperfine tensor due to the interaction of the unpaired electron of  $\text{O}^-$  with  ${}^{17}\text{O}$  nuclei. For  $\text{MgO}$ , the hyperfine tensor has been found to be  $A_{\perp} = 19.5$  gauss and  $A_{\parallel} = 103$  gauss (6), and for  $\text{Mo}/\text{SiO}_2$  catalysts  $A_{\perp} \approx 0$  gauss and  $A_{\parallel} = 96$  gauss (7). These values can be compared to the perpendicular component of the superhyperfine tensor of 14 gauss obtained with  $\text{V}_2\text{O}_5/\text{SiO}_2$  and this suggests that the overlap is probably not significant with the latter system. Despite these considerations it is nevertheless possible to compute, from the mass spectrometric results, the hypothetical con-

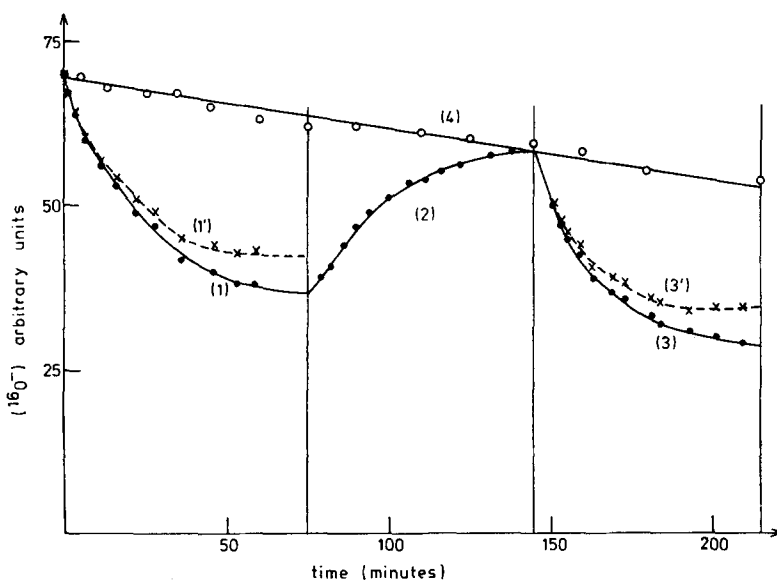


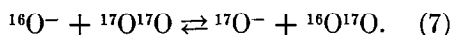
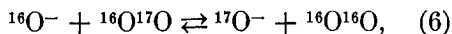
Fig. 2. Variations in  $({}^{16}\text{O}^-)$  concentrations as a function of time during isotopic exchange under various conditions (see text).

tribution of  $^{17}\text{O}^-$  species should an overlap occur.  $^{17}\text{O}^-$  species ( $I = \frac{5}{2}$ ) interacting with  $^{51}\text{V}$  nuclei ( $I = \frac{7}{2}$ ) would lead to EPR spectra with  $6 \times 8$  perpendicular components for a 56.2% abundance ( $\beta = 56.2\%$ ), while  $^{16}\text{O}^- + ^{18}\text{O}^-$  species with six perpendicular components are only 43.90% abundant ( $\alpha + \gamma = 43.9\%$ ). Therefore, assuming full exchange, the  $^{17}\text{O}^-$  would only contribute to 16% in the  $^{16}\text{O}^- + ^{18}\text{O}^-$  EPR spectra and this represents both a maximum and hypothetical value [16% is obtained from the ratio  $100 \times \{56.2/(6 \times 8)\}/\{43.9/6\}$ ]. Furthermore, the results show that the measure of the  $^{16}\text{O}^-$  concentration with the first line at low field is justified (vide infra).

The data obtained for isotopic exchange between  $\text{O}^-$  species and gas-phase oxygen are given in Fig. 2.

It is seen that the  $^{16}\text{O}^-$  concentration decreases in the presence of enriched gas (curve 1) and then increases when the latter is replaced by  $^{16}\text{O}_2$  (curve 2). Again, in the presence of enriched gas the  $^{16}\text{O}^-$  concentration decreases (curve 3). Curve 4 represents the thermal stability of  $\text{O}^-$  species at room temperature in the presence of  $^{18}\text{O}_2$  only. In the present work, no exchange between  $\text{O}^-$  and lattice oxygen was found to occur since the  $^{16}\text{O}^-$  concentration does not change when the sample was kept *in vacuo* after contact with enriched gas.

The data in Fig. 1 can be explained by the isotopic exchange reactions:



These reactions have recently been suggested to occur on  $\text{V}_2\text{O}_5/\text{SiO}_2$ -supported catalysts on the basis of mass spectrometric analysis (3).

Taking into account the thermal stability of  $\text{O}^-$  species (curve 4), corrected curves (1') and (3') were obtained (Fig. 2), which represent the variations in  $^{16}\text{O}^-$  concentration due to reactions (6) and (7) only.

For reactions (1) and (2) one can write, assuming a three-center model:

$$\begin{aligned} -\frac{d(^{16}\text{O}^-)}{dt} &= \frac{1}{3}k(^{16}\text{O}^-)(^{16}\text{O}^{17}\text{O}) \\ &\quad - \frac{2}{3}k(^{17}\text{O}^-)(^{16}\text{O}^{16}\text{O}) + \frac{2}{3}k(^{16}\text{O}^-)(^{17}\text{O}^{17}\text{O}) \\ &\quad - \frac{1}{3}k(^{17}\text{O}^-)(^{16}\text{O}^{17}\text{O}), \quad (8) \end{aligned}$$

where  $k$  is the rate constant of the isotopic exchange reaction and  $\frac{1}{3}$  and  $\frac{2}{3}$  are the probabilities of the forward and back reactions, respectively. For kinetics considerations, we may ignore the presence of  $^{18}\text{O}$  in the enriched gas since  $^{16}\text{O}^-$  and  $^{18}\text{O}^-$  species are indistinguishable in EPR spectra.

Taking into account that

$$(^{17}\text{O}^-) = (^{16}\text{O}^-)_0 - (^{16}\text{O}^-), \quad (9)$$

where  $(^{16}\text{O}^-)_0$  is the initial  $^{16}\text{O}^-$  concentration, we obtain:

$$\begin{aligned} -\frac{d(^{16}\text{O}^-)}{dt} &= \frac{2}{3}k(^{16}\text{O}^-) \\ &\quad \times [(^{16}\text{O}^{16}\text{O}) + (^{16}\text{O}^{17}\text{O}) + (^{17}\text{O}^{17}\text{O})] \\ &\quad - \frac{1}{3}k(^{16}\text{O}^-)_0 [2(^{16}\text{O}^{16}\text{O}) + (^{16}\text{O}^{17}\text{O})]. \quad (10) \end{aligned}$$

Putting

$$\begin{aligned} A &= \frac{2}{3}k[(^{16}\text{O}^{16}\text{O}) + (^{16}\text{O}^{17}\text{O}) + (^{17}\text{O}^{17}\text{O})] \\ &= \frac{2}{3}k \frac{N}{V}, \quad (11) \end{aligned}$$

where  $N$  is the total number of oxygen molecules in the gas phase in the volume  $V$ , and

$$\begin{aligned} B &= \frac{1}{3}k(^{16}\text{O}^-)_0 [2(^{16}\text{O}^{16}\text{O}) + (^{16}\text{O}^{17}\text{O})] \\ &= \frac{1}{3}k(^{16}\text{O}^-)_0 \frac{N}{V} [2(1 - \beta)^2 + 2\beta(1 - \beta)] \\ &= \frac{2}{3}k(^{16}\text{O}^-)_0 (1 - \beta) \frac{N}{V}, \quad (12) \end{aligned}$$

with

$$(^{16}\text{O}^{16}\text{O}) = \frac{N}{V} (1 - \beta)^2 \quad (13)$$

and

$$({}^{16}\text{O}^{17}\text{O}) = 2\beta \frac{N}{V} (1 - \beta) \quad (14)$$

obtained at equilibrium (8), we obtain the following equation:

$$-\frac{d({}^{16}\text{O}^-)}{dt} = A({}^{16}\text{O}^-) - B. \quad (15)$$

If  $N \gg ({}^{16}\text{O}^-)$ , we can consider  $A$  and  $B$  as constants and thus solve this equation to obtain:

$$\frac{1}{A} \ln [A({}^{16}\text{O}^-) - B] = -t + C, \quad (16)$$

where  $C$  is the constant of integration at  $t = 0$ ,  $({}^{16}\text{O}^-) = ({}^{16}\text{O}^-)_0$ , and therefore

$$C = \frac{1}{A} \ln [A({}^{16}\text{O}^-)_0 - B], \quad (17)$$

which combined with Eq. (16), gives (3)

$$\ln \frac{A({}^{16}\text{O}^-) - B}{A({}^{16}\text{O}^-)_0 - B} = -At. \quad (18)$$

One can find further, by means of Eqs. (11)

and (12), that

$$\begin{aligned} & A({}^{16}\text{O}^-) - B \\ &= \frac{2}{3}k \frac{N}{V} ({}^{16}\text{O}^-) - \frac{2}{3}k \frac{N}{V} ({}^{16}\text{O}^-)_0(1 - \beta) \\ &= \frac{2}{3}k \frac{N}{V} [({}^{16}\text{O}^-) - ({}^{16}\text{O}^-)_0(1 - \beta)], \quad (19) \\ & A({}^{16}\text{O}^-)_0 - B \\ &= \frac{2}{3}k \frac{N}{V} \beta ({}^{16}\text{O}^-)_0, \quad (20) \end{aligned}$$

so that (18) becomes

$$\begin{aligned} & \ln \frac{({}^{16}\text{O}^-) - ({}^{16}\text{O}^-)_0(1 - \beta)}{({}^{16}\text{O}^-)_0\beta} \\ &= -\frac{2}{3}k \frac{N}{V} t, \quad (21) \end{aligned}$$

$$\begin{aligned} & ({}^{16}\text{O}^-) - (1 - \beta)({}^{16}\text{O}^-)_0 \\ &= \beta ({}^{16}\text{O}^-)_0 \exp \left[ -\frac{2}{3}k \frac{N}{V} t \right] \\ & ({}^{16}\text{O}^-) = ({}^{16}\text{O}^-)_0 \\ & \quad \times \left( 1 - \beta + \beta \exp \left[ -\frac{2}{3}k \frac{N}{V} t \right] \right). \quad (22) \end{aligned}$$

TABLE 1  
Curve 1, Fig. 2 ( $\beta = 0.56$ )

Time (min)	( ${}^{16}\text{O}^-$ ) (arbitrary units)	( ${}^{16}\text{O}^-$ ) after correction for thermal instability (curve 1')	Exchangeable ( ${}^{16}\text{O}^-$ ) (arbitrary units)	$k \cdot 10^{19}$ (cm <sup>3</sup> mole <sup>-1</sup> sec <sup>-1</sup> )
0	70	70	48.2	
1	67	67.1	45.3	
3	64	64.2	42.4	1.14
6	60	60.5	38.7	0.98
11	56	56.9	35.1	0.82
16	53	54.3	32.5	0.76
22	49	50.9	29.1	0.76
29	47	49.4	27.6	0.68
36	42	45.0	23.2	0.92
46	40	43.9	22.1	1.03
53	38	42.5	20.7	
59	38	43	21.2	

TABLE 2  
Curve 3, Fig. 2 ( $\beta = 0.56$ )

Time (min)	$(^{16}\text{O}^-)$ (arbitrary units)	$(^{16}\text{O}^-)$ after correction for thermal instability (curve 3')	Exchangeable $(^{16}\text{O}^-)$ (arbitrary units)	$k \cdot 10^{19} (\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1})$
0	58	58	42	
6	50	50.3	34.3	0.88
8	47	47.7	31.7	0.97
10	45	45.9	29.9	0.99
14	43	44.2	28.2	0.86
18	39	40.5	24.5	1.03
24	37	39.1	23.1	0.93
29	36	38.5	22.5	0.82
36	33	36.1	20.1	1.02
39	32	35.3	19.3	1.21
48	31	33.6	17.6	
56	30	34.8	18.8	
64	29	34.5	18.5	

For  $t = \infty$ , at equilibrium, one gets:

$$(^{16}\text{O}^-)_{\text{eq}} = (^{16}\text{O}^-)_0(1 - \beta). \quad (23)$$

Putting  $\beta = 0.562$  (see Experimental

Methods) into Eq. (23) and taking  $(^{16}\text{O}^-)_0$  from curves (1') and (3') of Fig. 1, we can calculate  $(^{16}\text{O}^-)_{\text{eq}}$ . Comparison of the calculated values with the experimental ones

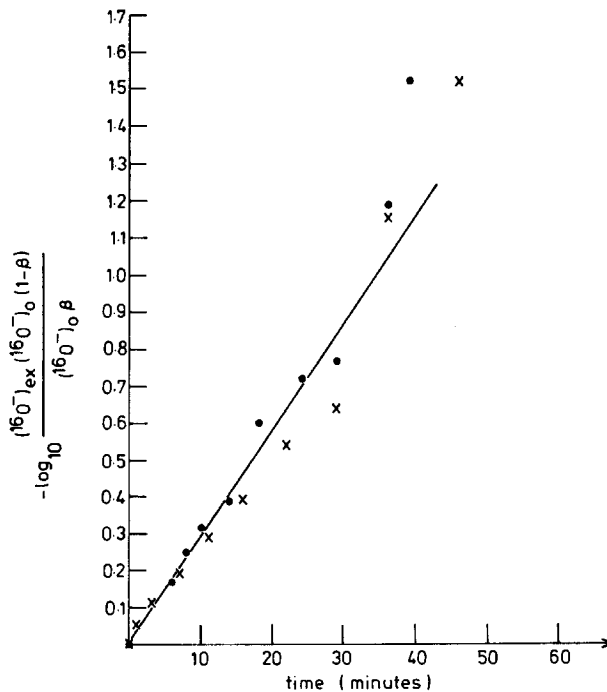


Fig. 3. Linear transformations of Eq. (21) obtained from experimental data. The points and crosses correspond to the data in Tables 1 and 2, respectively.

taken from curves (1') and (3') shows that only a certain part of  $O^-$  species can be exchanged with gas-phase oxygen.

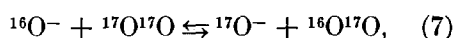
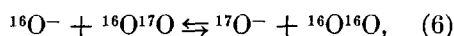
From the experimental data (see Tables 1 and 2), it is found that only about 70% of  $O^-$  species are exchangeable. If we label the exchangeable  $O^-$  species as  $(O^-)^e$  we can apply Eq. (21) for these species to obtain a linear transform for curves 1' and 3' of Fig. 2. The corresponding data are given in Fig. 3 (see also Tables 1 and 2). The linear transformation obtained applying Eq. (21) to the experimental data justifies the choice of the first line of the  $O^-$  spectrum as a measure of the  $(^{16}O^-)$  concentration. An interesting feature of Eq. (21) is that absolute spin concentrations (always tedious and delicate to measure) are not necessary to determine the rate constant of the oxygen isotopic exchange reaction. Using this linear transformation and putting into Eq. (21)  $N = 5 \cdot 10^{17}$  moles and  $V = 27 \text{ cm}^3$ , we can find the rate constant,  $k$ , for the isotopic exchange reaction. At room temperature,  $k$  was found to be  $0.9 \cdot 10^{-19} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ .

From the preceding results, it is thus concluded that:

(i) only a certain part ( $\sim 70\%$ ) of the  $O^-$  ions adsorbed on  $V_2O_5/SiO_2$  catalysts can be exchanged with gas-phase oxygen at room temperature. This means that these species are not uniform as far as their reactivity is concerned, which probably reflects the existence of a number of adsorption sites.

(ii) The oxygen isotopic exchange reaction occurs at a slow rate at room temperature, in contrast to reactions of  $O^-$  ions with  $H_2$ ,  $CO$ , and other molecules which take place already at  $77^\circ K$ .

(iii) The reactions



do proceed, and therefore  $O_3^-$  species might be regarded as intermediates. Unfortunately, we cannot conclude whether those correspond to the ones whose structure has been reported earlier (1). The absence of any detectable EPR signal at room temperature for  $O_3^-$  might be due to a too-low steady-state concentration. In a similar work we were also unable to detect  $O_4^-$  species suggested as intermediates in isotopic exchange reaction involving  $O_2^-$  species (4). It is difficult to conclude whether reactions (6) and (7) are the only pathways bringing the  $^{16}O_2 + ^{17}O_2$  mixture to equilibrium. For showing this, it would be necessary to compare the rates of isotopic exchange using both EPR and mass spectrometric techniques.

#### ACKNOWLEDGMENTS

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