

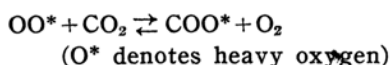
SHORT COMMUNICATIONS

Isotopic Exchange Reaction Between Heavy Oxygen and Carbon Dioxide on Silver Catalyst

By Hisashi MORI, Kozo HIROTA
and Yasushi KOBAYASHI

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As reduced silver can catalyze the oxidation reaction of carbon monoxide even at such a low temperature as 80°C¹, it is of interest to study the behavior of oxygen and carbon dioxide on this metal. It was attempted, therefore, to ascertain whether or not the catalytic isotopic exchange reaction:



was measurable by the static method, as done with platinum by use of slightly shifted oxygen². The heavy oxygen was obtained

by thermal diffusion column constructed in our laboratory by Mr. Y. Horibe³ (total column length=15 m.).

The catalyst was prepared by the reduction of precipitated silver oxide at 120–240°C using the hydrogen gas, followed by repeated activation at 240°C. Throughout this research one and the same catalyst was used, but it was reduced again before each run. The original gas consisted of heavy oxygen (OO* being 2.12% of total O₂) and carbon dioxide in nearly equal molar amount. Its total pressure was 127–148 mmHg, the partial pressure of O₂ being less than the decomposition pressure⁴ of Ag₂O at 175–250°C. In the measurement of chemisorption of O₂ and CO₂, their initial pressure was taken to be 76–78 mmHg. As the volume of reaction tube was about 120 cc. (STP), the volume of oxygen in the original gas was about 7 cc. (STP), which was fairly little as compared with the catalyst quantity (74 g.). Such a proportion was adopted, so as to make the amount

TABLE I

Run No.	React. temp. °C	React. time min.	OO ¹⁸ %	COO ¹⁸ %	CO ₂ /O ₂	Initial pres. mmHg	Adsorb. gas amount mmHg	Remark
1	175	90	2.1 ₄	1.0 ₄	0.99	141	19	b
		270	2.1 ₁	1.1 ₁			25	
2	188	20	—	—	0.97	142	17	b
		60	2.0 ₄	0.9 ₉			22	
		210	1.8 ₈	1.1 ₀			26	
3	200	15	2.0 ₇	0.8 ₉	1.08	127	15	a
		90	2.0 ₃	1.1 ₁			21	
		270	1.4 ₃	1.1 ₈			21	
4	200	15	1.5 ₄	1.0 ₅	1.28	130	0	c CO ₂ after O ₂
		60	1.5 ₇	1.0 ₅			0	
		180	1.2 ₆	1.1 ₄			0	
5	200	15	2.0 ₇	1.1 ₄	1.15	133	21	c, O ₂ after CO ₂
		60	1.9 ₅	1.2 ₀			22	
		180	1.5 ₃	1.2 ₁			22	
6	200	15	1.7 ₇	—	—	78	16.5	c, O ₂ only
		180	1.6 ₄	—			16.5	
7	200	180	—	0.4 ₁	—	76	0	c, CO ₂ only
8	220	60	1.8 ₀	0.8 ₀	1.03	137	16	a
		180	1.0 ₂	0.8 ₇			—	
9	220	10	2.0 ₀	1.0 ₁	0.93	148	16	b
		50	1.3 ₄	1.0 ₉			18	
		180	1.2 ₀	1.1 ₂			18	
10	250	15	1.6 ₂	—	—	76	6	b, O ₂ only
		210	1.4 ₀	—			7	

of gaseous oxygen comparable to that chemisorbed.

Besides the continuous manometric reading, the progress of the reaction was investigated intermittently by mass-spectrometric analyses of the samples (about one cc. STP) taken out from the reaction tube at recorded times. Abundance ratios of O^{18}/O^{16} in O_2 and CO_2 contained in them were determined by the same mass-spectrogram (Type of the mass-spectrometer: Hitachi-RMB-1). The ratio could be determined within the accuracy of $\pm 0.05\%$ for O_2 and $\pm 0.03\%$ for CO_2 .

Summarized results are shown in Table I, where a, b, and c in the last column denote the reducing temperatures 220, 250, and 300°C, respectively. In runs 1, 2, 3, and 5 there is this curious result that the increase of O^{18} in CO_2 from its natural abundance, 0.40% as COO^{18} , is greater than the corresponding decrease of O^{18} in O_2 . This tendency becomes more marked as the reaction temperature decreases. It can be explained, however, if we assume that, following the rapid adsorption of O_2 and CO_2 , the exchange reaction and desorption of CO_2 soon occur before the desorption of a considerable amount of oxygen takes place. This assumption is plausible, because the chemisorbed amount of oxygen cannot be neglected in reference to the initial gas volume.

Though the data are not yet reproducible, due to the gradual increase of catalytic activity, the following conclusion can be derived.

i) Even when the catalyst is reduced at 300°C for five hours, some chemical species containing oxygen atoms remain in the sub-surface or bulkphase of the catalyst; see runs 10, 6, 7, and 8.

ii) The exchange reaction proceeds evidently at 175–220°C, though the desorption of O_2 is very slow at 175–188°C; thus the rate-determining step is the desorption of oxygen atoms; see runs 1, 2, 3, 4, 5, 7, 8 and 9.

Detailed studies are now going on.

1) A.F. Benton and R.P. Bell, *J. Am. Chem. Soc.*, **56**, 501 (1934). T. Titani et al., *J. Chem. Soc. Japan*, **55**, 13, 224, 305 (1934). N. Yamada, *This Bulletin*, **27**, 36, (1954).

2) N. Morita and T. Titani, *This Bulletin*, **12**, 104 (1937); **13**, 357 (1938).

3) Y. Horibe and S. Nishizawa, *J. Chem. Soc. Japan*, **76**, 26 (1955).

4) E.g., A.F. Benton and L.C. Drake, *J. Am. Chem. Soc.*, **54**, 2186 (1932); **56**, 255 (1934).