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[CONTRIBUTION FROM THE HOUDRY PROCESS CORPORATION]

## Effect of Water on the Catalytic Activity of Chromic Oxide

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Both reduced and oxidized chromic oxide, after evacuation at 500°, are able to absorb considerable amounts of water at very low pressures at 30°. The catalytic activity of reduced chromic oxide for hydrogen-deuterium exchange at -78 and -124° is completely inhibited by adsorbed water corresponding to about 15% of surface coverage. At -195° only about one-half of this amount is required for complete deactivation. A much smaller quantity of water is necessary to poison the oxidized than the reduced catalyst; at -78° complete deactivation results from the adsorption of water sufficient to cover only 2% of the surface.

### Introduction

Previous work<sup>1</sup> in this Laboratory has established that the electrical conductivity is low and the catalytic activity for low temperature hydrogen-deuterium exchange is high for reduced chromic oxide, while the reverse behavior is shown by oxidized chromic oxide.

Since water is formed in the oxidation of reduced chromic oxide or the reduction of oxidized chromic oxide, it is important to determine any effect which adsorbed water may have on the catalytic activity of the chromic oxide. This is especially true in view of the possibility that different amounts of water may remain on oxidized or reduced chromic oxide.

The adsorption of water vapor on chromic oxide has been studied by Harbard and King.<sup>2</sup> Their results showed that the initial adsorption of the water vapor was complete at about 0.1 relative humidity, beyond which point the amount of water vapor adsorbed increased slowly with increasing pressure. Salley, Fehrer and Taylor<sup>3</sup> have shown that 0.35 mole of water per mole of chromic oxide can be removed between 300 to 550° from a chromia gel, even after previous evacuation at 300°. Practically all of the water is desorbed below 500°. They also showed that the addition of as little as one mole per cent. water to a heptane charge stock sharply decreased the extent to which dehydrocyclization proceeded over a chromia catalyst.

In this work water adsorption isotherms at 30° have been determined for oxidized and for reduced chromic oxide. The hydrogen-deuterium exchange reaction has also been studied on oxidized and reduced catalysts as a function of the amount of adsorbed water.

### Experimental

**Materials.**—Tank hydrogen was purified by passage over palladized alumina at 250 to 300° and through a silica gel trap at -195°. Tank oxygen was dried by passage through calcium sulfate. Helium was purified by the use of a charcoal trap at -195°. The deuterium (99.5%) was obtained from the Stuart Oxygen Company and used without further purification.

The distilled water employed in these experiments was degassed by repeated freezing and melting under vacuum.

(1) S. Voltz and S. Weller, *THIS JOURNAL*, **75**, 5227 (1953).

(2) E. H. Harbard and A. King, *J. Chem. Soc.*, 19 (1940).

(3) D. J. Salley, H. Fehrer and H. S. Taylor, *THIS JOURNAL*, **63**, 1131 (1941).

The preparation of the unsupported chromic oxide used in this study has been described elsewhere.<sup>1</sup> Prior to use, this catalyst was stabilized by cycling several times in hydrogen and oxygen at 500°; its specific surface area after this treatment was 35 m.<sup>2</sup>/g.

**Apparatus and Procedure.**—The water adsorption isotherms were determined in a standard adsorption apparatus<sup>4</sup> equipped with a water reservoir and an extra gas buret.

The hydrogen-deuterium exchange experiments were carried out in a high vacuum system. An all-glass circulating pump was employed to circulate the reaction mixture over the catalyst, and the sampling system was so designed that small gas samples could be taken for mass spectrographic analyses at any desired time. In most of the experiments the catalyst was treated with hydrogen (or oxygen) at 500° for three hours, evacuated for one hour, re-treated with hydrogen (or oxygen) for three hours, and then evacuated for at least 16 hours. It was then cooled to room temperature under helium and, after the helium was evacuated, the desired amount of water vapor was admitted to the catalyst. The adsorption of water was essentially complete in less than one minute for amounts of water up to about 150  $\mu$  moles of water per gram. The catalyst was then cooled to a low temperature and a 50-50 mixture of hydrogen and deuterium was admitted to the reactor.

### Results

**Water Adsorption.**—Figure 1 contains the water adsorption isotherms at 30° for chromic oxide after either oxygen or hydrogen treatment at 500° and evacuation at 500°. In both cases there is an initial adsorption of 140 to 180  $\mu$  moles of water per gram catalyst which occurs at very low pressures, after which the adsorption increases gradually with increasing partial pressure. The amount of the initial adsorption corresponds approximately to a third of a monolayer, using 10.8 Å.<sup>2</sup> as the effective cross-sectional area of an adsorbed water molecule. In the absence of confirming data, no significance is attributed to the slightly higher adsorption values shown by the reduced catalyst.

**Effect of Water on Activity of Reduced Chromic Oxide.**—In Table I are summarized data showing the influence of water, adsorbed at room temperature, on the catalytic activity of reduced chromic oxide for hydrogen-deuterium exchange at -78, -124 and -195°. Within the limitation of the experimental procedure, adsorbed water exerted no influence on the activity at -78° up to an amount of 35 micromoles per gram; equilibrium was achieved

(4) W. E. Barr and V. J. Anhorn, "Scientific and Industrial Glass Blowing and Laboratory Techniques," Instruments Publishing Co., Pittsburgh, 1949, Chapter XII.

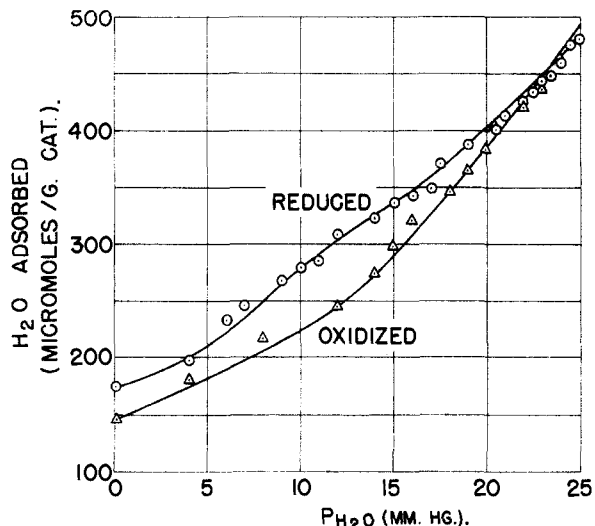


Fig. 1.—Adsorption of water vapor at 30° on oxidized and reduced chromic oxide.

in less than five minutes. It should be noted, however, that since no gas sample was taken before five minutes, the possibility exists that some poisoning effect occurred even at this level. The adsorption of 75  $\mu$  moles of water per gram resulted in a marked inhibiting effect; in this experiment, the computed first-order rate constant was 0.62 hr.<sup>-1</sup>. Complete deactivation resulted from the adsorption of 92  $\mu$  moles of water per gram, an amount which corresponds to a surface coverage of approximately 15%.

TABLE I  
EFFECT OF WATER ON ACTIVITY OF REDUCED CHROMIC OXIDE

Temperature of H <sub>2</sub> -D <sub>2</sub> exchange, °C.	Water adsorbed, $\mu$ moles/g.	Activity
-78	0	Equil. within five min.
	14	Equil. within five min.
	35	Equil. within five min.
	75	Equil. in seven hours
	92	Inactive
-124	0	Equil. within five min.
	16	Equil. within five min.
	41	Equil. within five min.
	87	Inactive
-195	0	4.8% HD in six hours
	16	4.1% HD in six hours
	49	Inactive

The data for exchange at -124° are similar to those at -78°. At this temperature no observable effect resulted from the adsorption of 41  $\mu$  moles of water per gram, while 87  $\mu$  moles of water per

gram caused complete poisoning. The rate at -195° was quite low even in the absence of water, and the adsorption of as little as 49  $\mu$  moles of water per gram resulted in an inactive catalyst.

**Effect of Water on Activity of Oxidized Chromic Oxide.**—The poisoning effect of water on oxidized chromic oxide was studied only for hydrogen-deuterium exchange at -78°. A much smaller quantity of water was necessary to poison the oxidized catalyst than the reduced catalyst. As little as 3  $\mu$  moles of water per gram resulted in decreased activity (the first-order rate constant was 0.094 hr.<sup>-1</sup>) and 12  $\mu$  moles of water per gram caused complete deactivation.

### Discussion

The chromic oxide sample studied, which has a surface area of 35 m.<sup>2</sup>/g., is able to adsorb about 150  $\mu$  moles water per gram catalyst at room temperature and very low water vapor pressures. The steepness of the adsorption isotherm in this region indicates that this water is chemisorbed, with a relatively high heat of adsorption. The adsorption of a fraction of this amount of water is sufficient to severely deactivate the chromic oxide as a catalyst for low temperature hydrogen-deuterium exchange. Reduced and evacuated chromic oxide becomes completely inactive for the exchange when 80 to 90  $\mu$  moles water per gram catalyst are adsorbed. A much smaller amount of water is necessary to poison the oxidized and evacuated chromic oxide; the catalyst is completely poisoned by the adsorption of 12  $\mu$  moles water per gram, and a marked decrease in activity is caused by as little as 3  $\mu$  moles water per gram. If one assumes that the amount of water required for complete poisoning is a measure of the "active surface" of the catalyst, and that the effective cross-sectional area of a water molecule is 10.8 Å.<sup>2</sup>, it is possible to compute that not more than 15% of the surface of the reduced and evacuated catalyst is catalytically active and not more than 2% of the surface of the oxidized and evacuated catalyst is active. Moreover, these figures should represent maximum values, since it is unlikely that water adsorbed at room temperature goes only to catalytically active adsorption sites. Further discussion of the general relation between water adsorption and the surface chemistry of chromic oxide will be deferred to a subsequent paper.

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