minimum at 5100 Å. This emission may correspond to the known absorption system ($\tilde{a}^3A_2$–$\tilde{X}^1\Sigma_g^+$),[6,17] but higher intensity and higher resolution spectra are required before this can be definitely proven.

This paper shows the usefulness of our flow system for studying the reactions of $N_2(A^3\Sigma_u^+)$ in the absence of other reactive species. This interesting metastable is important for understanding the chemistry of active nitrogen[5b] and also promises to be a good sensitizing agent for study of high-energy triplet states.

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(18) Phillips Petroleum Research Fellow.
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Catalysis of Addition of Deuterium to Ethylene over Zinc Oxide

Sir:

Addition of deuterium to ethylene is catalyzed by a variety of solids. With transition metals[1] the product (with light ethylene as a reactant) is a mixture represented by the formula $C_2H_{6-x}D_x$ ($0 \leq x \leq 6$), and the yield of $C_2H_4D_2$ is usually less than 50%. Oxides also catalyze hydrogenation reactions.[2] In one case, chromia,[3] it has been shown that addition of deuterium to ethylene yields about 99% $C_2H_4D_2$. Recently, we have found that zinc oxide also catalyzes the addition of deuterium to ethylene with $C_2H_4D_2$ yields of approximately 99%.

Two samples of zinc oxide were used in this work. Sample I was prepared by heating zinc oxalate in oxygen at 500° for 16 hr. Sample II was Kadox-25, a product of the New Jersey Zinc Co. In the standard pretreatment, the catalyst was degassed for 4 hr at 450°, reduced with dried hydrogen at 350° for 40 min, and degassed at 400° for 3 hr.

Analyses of the products by mass spectroscopic techniques are shown in Table I, along with comparable data for a chromia catalyst prepared by the procedure suggested by Burwell.[3] Essentially pure dideuterioethane is formed. Comparison of the fragmentation pattern of the product with that of authentic samples of CH_2DCH_2D and CH_3CHD_2 show that the ethane product is more than 95% 1,2-dideuterioethane.

Table I. Product Distribution

Sample (temp, °C)	Product %		
	C_2H_6	C_2H_5D	$C_2H_4D_2$
ZnO-I (60)	0.0	2.0	97.5
ZnO-II (25)	0.0	0.1	99.9
Cr_2O_3 (−78)	0.0	0.0	100.0

Most of our studies have centered on the zinc oxide II. In a circulating system with a volume of 100 cc, the half-time for ethylene conversion (H_2:C_2H_4 = 130 mm:13 mm) is 15 min at room temperature. Even at −78° conversion is readily observable, *i.e.*, about 20%/hr. Comparison with activities per square meter for ethylene hydrogenation over zinc oxide reported by other workers[4,5] are listed in Table II. It seems clear that this catalyst (prepared by burning zinc in air) is significantly more active than those prepared by decomposition of the hydroxide[4] or oxalate.[5,6]

Table II. Comparison of Activities over ZnO

Ref	Activity,[a] molecules cm^{-2} sec^{-1}	Order H_2	Activation energy, kcal
This work	3.3×10^{11}	0.5	~10
4	2.5×10^{6}	1	22.4
5	1.2×10^{10}	~0	22.4

[a] Computed at 298 and 100 mm of hydrogen.

It has been suggested[2] that the pattern of activity for transition metal oxides can be correlated to the configuration of the d electrons. Clearly, this is not the case with zinc oxide. Indeed, the similarity of zinc oxide and chromia oxide with regard to selectivity suggests the possibility that the selective ethylene hydrogenation activity occurs on similar sites. Since unfilled d shells are not a *sine qua non* for activity, these sites may be anion vacancies.[7] If, on such isolated sites, only one carbon surface bond can be formed, it seems reasonable to suppose[3] that ethyl radicals form irreversibly by an insertion reaction of ethylene into a hydrogen-covered site. Such a pathway would explain the selectivity. Furthermore, if these are the sites of catalytic activity on oxides, all active oxides in contrast to metals should show selective 1,2 addition of deuterium to ethylene at moderate temperatures.[8]

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(6) Activities for ref 4 and 5 were extrapolated from 150 and 56° and corrected to the same pressure with the use of indicated activities, energies, and orders. It was assumed that the volume of the system in ref 4 was the same as in this work, and an area of 10 m^2/g was assigned to the catalyst in ref 5. Activity estimates were also made for the data of E. H. Taylor and J. A. Wethington, *ibid.*, **76**, 971 (1954). These estimates suggested the activity of their preparation was a factor of 2–3 higher than that for ref 5, but, since orders were not reported, the estimates are more approximate than those listed.
(7) The "strained" sites of S. W. Weller and S. E. Voltz, *ibid.*, **76**, 4695 (1954), may be interpreted as surface anion vacancies.
(8) NOTE ADDED IN PROOF. Dr. Atsumu Ozaki of Tokyo Institute of Technology has informed me that addition of deuterium to ethylene over Co_3O_4 also leads to $C_2H_4D_2$ with C_2H_6.

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