

LETTER TO THE EDITOR

On the Reactivity of Hydrogen Chemisorbed on Metal Surfaces

It was recently reported by Wood that hydrogen atoms chemisorbed on metal surfaces were required for the dehydrogenation of cyclohexane (1). Also Wood and Wise have indicated the reactive nature of adsorbed hydrogen for hydrogenation of cyclohexene (2). In the latter case they observed that together with cyclohexane, an appreciable amount of benzene was formed when hydrogen was supplied through metal membrane to cyclohexene. It is interesting that two events we have experienced in entirely different circumstances seem to suggest the enhanced reactivity of hydrogen atoms chemisorbed on metals, in the same way as above.

The first experiment was concerned with the pyrolysis of methane in a nickel thimble. The original intention of this experiment was that hydrogen atoms supplied from one side of a metal membrane and forced to diffuse through the metal might suppress the decomposition of and subsequent carbon deposition from hydrocarbons on the opposite side of the metal surface. The arrangement of the apparatus employed was in principle the same as that used by Wood and Wise (1, 2), but the thimble was made of nickel and had the dimensions of 1 mm in thickness, 26 mm in inner diameter and 20 cm in length. This thimble was placed in a quartz tube. The volumes of the inner side of the thimble (this space is referred to as I) and of the outer side (referred to as II) were 98 and 174 ml respectively.

The rate of hydrogen permeation was measured by admitting 760 mm Hg of hydrogen to II and reading the pressure increase of I, which was evacuated at the

start. At 770°C, the pressure increase of I was 204 mm Hg in 10 min.

The decomposition of methane at 770°C was conducted under the following conditions; (A) methane was introduced into I, and II was evacuated, (B) nearly the same pressure of methane as (A) was introduced to I, and II was filled with 760 mm Hg of hydrogen, so that hydrogen would permeate through nickel and be supplied to the inner surface. The decomposition was continued for 10 min and the composition of gases was analyzed by gas chromatograph. The results are shown in Table 1.

The results indicate that hydrogen permeated through metal is by no means effective for suppression of methane decomposition, rather it accelerated the decomposition. This can be explained by assuming that permeated and chemisorbed hydrogen is reactive for dehydrogenation of hydrocarbon. Thus a methane molecule on the surface is abstracted of its hydrogen and is forced to decompose. The repetition of the experiments in the same thimble yielded essentially the same results, indicating that the trend is not seriously affected by alteration of the nickel surface by carbon deposition.

The second observation which was made in a course of study of ethane pyrolysis seems likewise to be associated with the reactivity of adsorbed hydrogen. In this case, ethane was decomposed in a static system at pressures from 30 to 400 mm Hg and at 700°C, using a quartz reaction vessel packed with a sheet of various metals in turn. The purpose of this investigation was to examine the effects of metallic surfaces on the decomposition rate.

TABLE 1
METHANE DECOMPOSITION ON NICKEL AT 770°C

		I ^a		% decomposed	II ^a	
		CH ₄	H ₂		CH ₄	H ₂
(A)	Initial	151	0	52	0	
	Final	72	66		22	
(B)	Initial	152	0	75	760	
	Final	38	256		760 ^b	
(A)	Initial	153	0	41	0	
	Final	91	49		20	
(B)	Initial	150	0	74	760	
	Final	39	272		760 ^b	

^a Pressures in mm Hg.

^b Space II was connected with a reservoir of 5 liters.

The details of the procedure, comparison of various metals and a kinetic discussion will be reported elsewhere, so are described here briefly.

The volume of the vessel was 8.6 ml and the amounts of ethane decomposed in one run were 0.1 to 1.4 ml STP, and the duration of pyrolysis was 2 to 10 sec. The composition of the products was analyzed by gas chromatograph. The decomposition was repeated several times using the same packing. The metal sheets were 0.1 mm in thickness and were bent and packed into the vessel.

The main reaction, dehydrogenation of ethane, was supposed to take place in the homogeneous gas phase and to be of radical nature under present conditions. The effect of metallic surfaces, including titanium, zirconium, iron and copper, on ethane decomposition was to reduce the rate of ethylene formation. This can be explained as the catalytic action of metals to recombine hydrogen atoms or hydrogen and ethyl radicals and therefore to reduce the radical concentrations in gas phase. The effect was dependent on the nature of the metal and was larger for the larger area of packings.

The observation to be written here is a difference between the effect of titanium sheets with and without hydrogen treatment. Normally, titanium sheets were used without hydrogen pretreatment. The hydrogen treatment was done as follows: After

the reaction vessel, packed with a titanium sheet, was heated to 700°C, about 400 mm Hg of hydrogen was introduced to the vessel and kept for 1 hr, the final pressure being 270 to 300 mm Hg. The amount of hydrogen dissolved was about 110 ml STP/g, i.e., near saturation. Then the vessel was evacuated for 5 min and ethane was introduced and decomposed.

The essential parts of the results are illustrated in Fig. 1. The ordinate of this represents, in logarithmic scale, the ratio of the rate of ethylene formation at the initial stage, r_0 , to the initial pressure of ethane, p_0 , the former being substantially the same as the rate of ethane decomposition.

The pretreatment of titanium with hydrogen resulted in a larger decrease of the decomposition rate, as if the area of the packing was enlarged. On the basis of the above explanation, the absorbed hydrogen in titanium would have accelerated the termination of radical chain reactions. This can be interpreted well by assuming that the hydrogen emerged from bulk solution

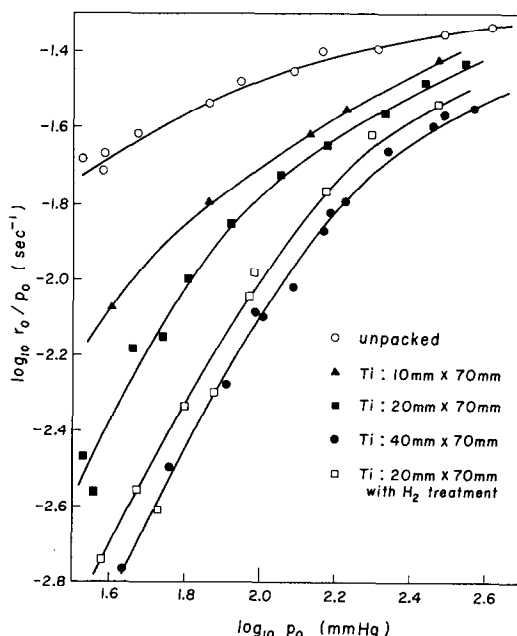


Fig. 1. Rate of dehydrogenation of ethane at 700°C. Areas of the packings are indicated in the figure.

and sorbed on the metal surface have enhanced activity to combine with radicals from the gas phase.

Of course, surface decomposition of ethane would have occurred here, forming titanium carbide, as the effect was diminished by prolonged exposure of titanium to ethane. But the retardation of ethylene formation cannot be explained by secondary decomposition of this on the surface, as the weight increment of titanium was slight and the rate of carbide formation of titanium with ethane is no less than that with ethylene (3). It should be mentioned that the addition of hydrogen to ethane results in the increase of the rate at the temperature and pressures used here, so that evolution of hydrogen into the gas phase cannot itself cause retardation of the decomposition.

The above two cases differ from each other, the former being abstraction of hydrogen from methane, the latter recombination with radicals from the gas phase,

but in any case hydrogen dissolved in or permeated through metals seems to have a particular activity. The results reported by Wood may be another manifestation of the same property at lower temperatures, so the reaction of chemisorbed hydrogen will be an interesting subject to be clarified in a wider point of view.

REFERENCES

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