HETEROGENEOUS METHANATION:

EFFECTS OF CARBON, SULFUR AND WATER

ON ACTIVITY MEASUREMENTS AT VARIOUS TEMPERATURES

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INTRODUCTION

A wide variety of experimental procedures has been used to measure catalytic activity and to compare catalysts for carbon monoxide hydrogenation. The comparison is generally carried out in flow reactors operating at high conversions. While such conditions are more realistic and may better duplicate catalyst performance in actual use, specific catalyst activities or specific reaction rates are difficult to estimate from such data. This is especially true for highly exothermic reactions such as CO hydrogenation where the temperature as well as concentrations change along the catalyst bed. Sulfur tolerance tests generally took the form of sulfidation capacity measurements with the sulfur being quantitatively taken up by the catalyst bed.

The first publications of this series presented data on initial reaction rates (1) on clean metal surfaces and on steady-state rates (2) on several catalysts both in sulfur-free and sulfur containing streams. In this paper a series of Ni catalysts is compared in several different tests. It will be demonstrated that conclusions derived from steady-state rates at 673 K are markedly different from those drawn at 523 K. Similar contradictions apply to tests designed to assess the activity in the presence of sulfur. Water vapor in the reactant stream is found to have a significant effect on both the high temperature steady-state activity and the final activity in the presence of sulfur.

EXPERIMENTAL

1. Apparatus

Initial rates were measured in a Pyrex glass batch recycle system as described previously (1). The reactor loop was filled with the reactants to the required pressure and mixed by circulating through a bypass. The catalyst sample was reduced in a stream of flowing hydrogen, cooled to the reaction temperature, evacuated and the reactants diverted over the catalyst. Samples of the reactant gas were analyzed by injection into a gas chromatograph equipped with a flame ionization detector. Both methane and total hydrocarbons were determined, steady-state rates were

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measured in an atmospheric pressure single pass flow reactor, also described previously (2). The flow of each reactant was set by controlling the upstream pressure on a stainless steel capillary. The catalyst was contained in a Pyrex reactor supported on a porous glass disc. The reactor effluent was analyzed as described above.

Water was introduced into the reactant stream through a Pyrex tube extending into the glass reactor and connected to a motor driven positive displacement syringe pump. The pump was constructed of stainless steel and had a volume of 500 cc. The inlet portion of the reactor, including a plug of glass wool, was heated resistively to vaporize the water. The pressure of water in the reactant stream was controlled by the pump speed which was set at 0.049 cc/min.

2. Materials

The catalysts have been described in detail in previous publications (1,2). The supported catalysts were prepared by impregnation of the oxide support with aqueous $Ni(NO_3)_2$ solution. The 5% Ni/ZrO_2 (I) (1) and 5% Ni/ZrO_2 (II) (2) were prepared from different batches of ZrO_2 obtained from the TAM Division of National Lead Co. This material was found to be quite impure, containing appreciable amounts of Cl, Ca, Mg, Fe and Hf (3). These batch to batch variations may, possibly explain some of the activity differences observed in the catalysts made with the ZrO_2 support. Raney Ni was prepared by extraction of a 50:50 Ni/Al alloy with NaOH to dissolve 60% of the Al. Hydrogen adsorption isotherms were determined on these catalysts (2) and the results are collected in Table 1.

RESULTS

After reduction of the catalyst at 723 K, initial reaction rates were measured on the clean metal surface using the batch recycle reactor. Reactant composition was $P(H_2)$ 0.5625 atm and P(CO) 0.1875 atm. The rate was calculated from conversion versus time data at short times (1). The system is well-behaved as shown by a typical set of data for 2% Ni/Al_2O_3 presented in Fig. 1. Results for a number of Ni catalysts are collected in Table 2.

Steady-state rates were measured in the single pass flow reactor at atmospheric pressure with a reactant stream composition of $P(H_2)$ 0.5938, P(CO) 0.1562, and P(He) 0.250 atm, corresponding to an H_2/CO ratio of 3.8. After the catalyst was reduced at 723 K, the temperature was lowered to 523 K and the reactants diverted over the sample. Steady-state was usually attained after 6 to 8 hrs. but 24 hrs. were allowed to elapse before at least four gas samples are analyzed and averaged to determine the catalyst activity. Then, 10 ppm H_2S was introduced into the reactant stream, and after 24 hrs., the activity again determined. In a similar manner, the H_2S flow was stopped and the activity recovery, if any, noted. These results are presented in Fig.2. In Fig.3 the catalyst activities are compared at 673 K. The procedure used in this case was to start the reactants over the samples at 520 to 550 K then slowly heat the samples to 673 K without exceeding a turnover number of 0.2/s. As before, 24 hrs. elapsed at each condition before activity data were taken.

Up to this point the activity measurements have been run without the addition of water. Although water is a reaction product, the differential conditions of the flow reactor experiment keep the partial pressure of water over the catalyst low.

In Figs.4 and 5 there are, respectively, collected steady-state results from runs in which water was added to the reactant stream for the 5% Ni/ZrO_2 (II) and 2% Ni/Al_2O_3 catalysts. The conditions at which each of the rate measurements, shown in Figs.4 and 5, were made are given in Table 3. Following a procedure similar to the previous measurements, the catalysts were reduced at 723 K, cooled to 523 K and the flow of CO and H_2 started. Data at condition A were obtained after 24 hrs. Water was then injected and 24 hrs. later the reaction rate was measured. Similarly, each subsequent data point was taken after waiting 24 hrs. for steady-state conditions to be established.

DISCUSSION

1. Steady-State Activity

Comparison of the initial rate data (Table 2) and the steady-state data at 523 K (Fig.2) shows that at this temperature the steady-state surface is similar, or at least has comparable catalytic activity to the clean metal surfaces studied by initial rate measurements. The relative ordering of the activity of the three catalysts is the same from either set of data. When the catalysts are heated to 673 K and again compared (Fig.3), the activity is significantly reduced in comparison to the rate expected from extrapolation according to the measured activation energy (Table 2). The activity is lower by a factor of approximately 30, indicating a surface deactivated by carbonaceous deposits either as a carbon overlayer or by the formation of a carbide-like species (2). Although the results presented here are at 673 K, it should be noted that the deactivation was observable at even lower temperatures and varied in its rate of approach to steady-state from one catalyst to another. A quantitative indication of this phenomenon is presented in Fig.6. After reduction, the catalyst was cooled to the temperature at which the initial rate was expected to be either 0.1 or 0.01 per second, and the reactants were passed over. The temperature was then adjusted to maintain a nearly constant turnover number. The Raney Ni at a specific rate of 0.01/s, corresponding to a temperature of 483 K, shows no apparent deterioration in activity after 5 days. At a temperature of 548 K and an activity of 0.1/s, the activity constantly decreased. To maintain a constant activity it was necessary to continuously raise the temperature. The rate of deactivation was observed to accelerate as the temperature was raised, as seen by the accelerating slope of the curve in Fig.6. The rate of activity deterioration appeared also to be dependent on the support, 5% Ni/ZrO_2 deteriorating much more rapidly than 2% Ni/Al_2O_3 or Raney Ni. The deterioration is not associated with thermal sintering of the Ni, since it was shown earlier that cleaning the catalyst of carbon could restore the higher activity (2).

As a result of this different susceptibility to deactivation by carbon overlayer formation at different temperatures the relative specific activity of a series of catalysts at steady state can be completely reversed at different test temperatures. At 523 K the relative activity is 5% Ni/ZrO_2 (II) > 2% Ni/Al_2O_3 > Raney Ni, while at 673 K the order is Raney Ni > 2% Ni/Al_2O_3 > 5% Ni/ZrO_2 (II).

2. Sulfur Poisoning

The temperature chosen for sulfur poisoning studies is also extremely important. At 523 K the deactivation is a factor of 170 in the best case, Raney Ni, while it is only 2.5 for 5% Ni/ZrO_2 (II) at 673 K. This decreased poisoning at

higher temperatures is consistent with the decreased stability of the sulfide. The ordering of the catalysts is substantially different, 2% Ni/Al_2O_3 showing the greatest susceptibility to poisoning at 523 K, while Raney Ni is most susceptible at 673 K. Such large changes in the ordering of catalyst sensitivity to sulfur, at least in this type of test, implies complex behavior. For example, at low temperatures, the presence of sulfur leads to the formation of a bulk metal sulfide (4) and the effect of the support may be to inhibit the formation of such sulfides. At higher temperatures other compounds may form such as sulfospinels in the case of the Raney Ni which contains elemental Al (2).

The H_2S pressure is too low to form a bulk sulfide at 673 K (4) and a surface sulfur layer may have to compete with the carbon containing layer that apparently forms at this temperature. This is in apparent agreement with the observation that the least active catalysts in sulfur-free environment at 673 K are the most active in the presence of H_2S.

3. Effect of H_2O

Yet another measurement procedure to compare catalysts for CO hydrogenation includes H_2O in the reactant stream at the catalyst inlet. Inclusion of a large partial pressure of water would more closely simulate the industrial process since water is purposely added to reduce carbon formation in the reactor and to generate hydrogen by the water gas shift reaction. The data of Figs.4 and 5 show that at 523 K water has an inhibiting effect. At 673 K, however, 5% Ni/ZrO_2 (II) and 2% Ni/Al_2O_3 behave quite differently in the presence of H_2O. The ZrO_2 supported catalyst shows inhibition by water (compare arrow - water free data from Fig.3), while 2% Ni/Al_2O_3 is substantially more active. The latter behavior is expected if it is assumed that the high temperature deactivation is due to carbon and that the presence of water inhibits carbon formation. The thermodynamic inhibition of carbon formation by water is well known (5). The behavior of 5% Ni/ZrO_2 (II) is difficult to explain.

When H_2S is added to the reactant stream, the 2% Ni/Al_2O_3 catalyst becomes totally inactive (Fig.5), the conversion being below the detection limit of the analytical system. The 5% Ni/ZrO_2 (II) is only slightly more active. The comparison of the effect of 10 ppm H_2S in a dry stream and in a reactant stream containing 13 mol% water reveals the significant impact water can have on the measured "sulfur resistance" of a catalyst. Whereas 5% Ni/ZrO_2 (II) appeared to deteriorate by only a factor of two with 10 ppm H_2S, the combination of water and 10 ppm H_2S results in a deterioration greater than 100-fold. When both the water and the H_2S were removed from the reactant stream, the activity recovered but for 5% Ni/ZrO_2 the highest recovery was obtained in a stream containing sulfur. In fact, with the system at reaction conditon D, i.e. both H_2O and H_2S in the reactant stream, removing the H_2O but keeping the H_2S in the reactant stream results in an increase in catalyst activity by two orders of magnitude. This behavior was completely reversible; the catalyst could be cycled between conditions D, E and G of Table 3 repeatedly without adverse effects.

The behavior described above emphasizes the importance of water when searching for sulfur resistant catalysts. But even more significantly it may give clues to the properties desired in a sulfur resistant methanation catalyst. The formation of a material stable toward reaction with H_2S is one route to sulfur resistance if this phase possesses some catalytic activity (6). The carbon containing phase may be such a material. A significant partial pressure of water may reduce its stability, permitting the inactive sulfide phase to form.

The measured specific activity and the relative ordering of CO hydrogenation catalysts can vary markedly depending on the temperature and reactant stream composition chosen for the catalytic test. Low temperature tests employing either initial or steady-state rate measurements, give activity data for a clean metal surface. Results obtained at 673 K apparently are representative of a carbon contaminated surface.

The choice of the test temperature and reactant stream composition is extremely important in designing an experimental test for catalyst resistance to sulfur poisoning. Water should be added to the reactant stream since it has a great effect on the sulfur tolerance of Ni catalysts.

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TABLE 1

Hydrogen Adsorption Results

Catalyst	H_2 Adsorption μmol/g	Dispersion H (ads)/M(tot)
5% Ni/ZrO_2 (I) (*)	33.7	0.079
5% Ni/ZrO_2 (II) (**)	19.2	0.045
2% Ni/Al_2O_3	5.6	0.033
Raney Ni	137	0.031

(*) Sample used in ref (1)
(**) Sample used in ref (2)

TABLE 2

Initial Rates of CO Hydrogenation (*)

Sample	N at 523 K s^{-1} x 100		E_a kcal/mol	
	HC(total)	CH_4	HC(total)	CH_4
5% Ni/ZrO_2 (I)	6.3	2.3	20	28
5% Ni/ZrO_2* (II)	27	9.6	30	33
2% Ni/Al_2O_3	5.1	2.0	30	31
Raney Ni	3.2	1.0	26	31

(*) $P(H_2)$ 0.5625 atm., P(CO) 0.1875 atm.

TABLE 3

Reaction Conditions at Steady-State for Runs in Figures 4 & 5

Reactions Conditions(*)	Temp (K)	Reactant Composition (Atm)				
		H_2O	H_2S	H_2	CO	He
A	523	0	0	0.5938	0.1562	0.250
B	523	0.133	0	0.515	0.135	0.217
C	673	0.133	0	0.515	0.135	0.217
D	673	0.133	10-5	0.515	0.135	0.217
E	673	0.133	0	0.515	0.135	0.217
F	673	0	0	0.5938	0.1562	0.250
G	673	0	10-5	0.5938	0.5938	0.250

(*) The conditions were maintained for 24 hrs before the steady-state reaction rate was determined.

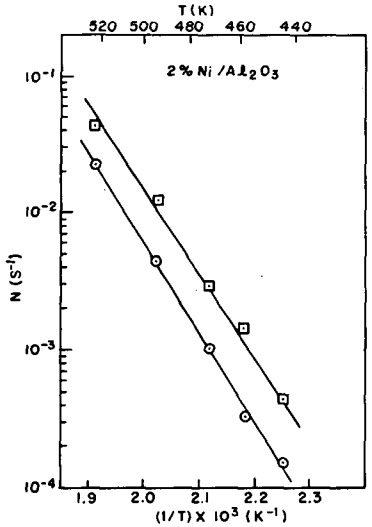

FIG. 1

Initial rate of CO hydrogenation on 2% Ni/Al_2O_3. □ - Total hydrocarbon synthesis rate; O - CH_4 synthesis rate.

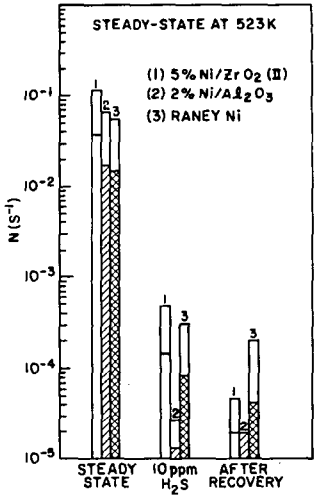

FIG. 2

CO hydrogenation at 523K on (1) 5% Ni/ZrO_2(II); (2) 2% Ni/Al_2O_3; (3) Raney Ni.

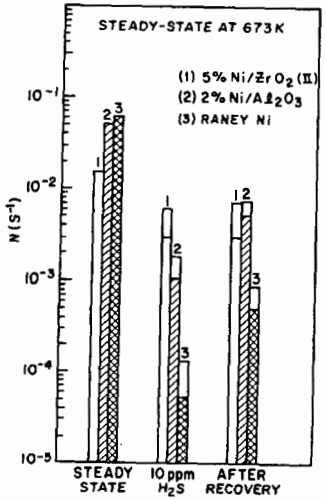

FIG. 3

CO hydrogenation at 673K on (1) 5% Ni/ZrO_2(II); (2) 2% Ni/Al_2O_3; (3) Raney Ni.

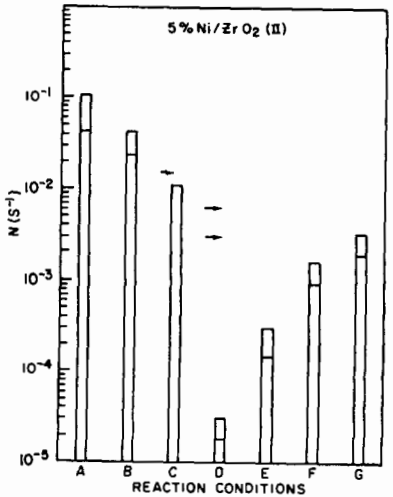

FIG. 4

CO hydrogenation at 673K on 5% Ni/ZrO_2(II), with H_2O in the reactant stream. See Table 3 for description of conditions. Arrows give rate in water-free system.

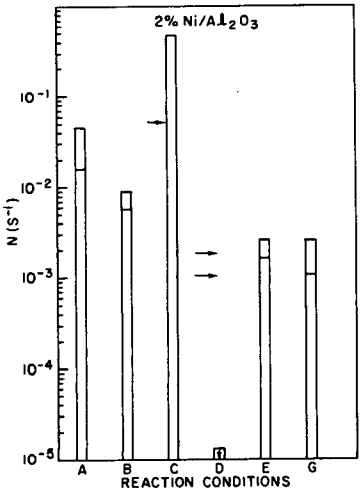

FIG. 5

CO hydrogenation at 673K on 2% Ni/Al_2O_3 with H_2O in the reactant stream. See Table 3 for description of conditions. Arrows give rate in water-free system.

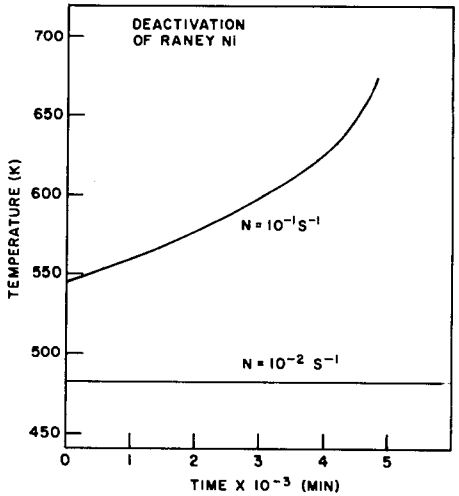

FIG. 6

Deactivation of Raney Ni for CO hydrogenation with reaction time.