JOURNAL OF CATALYSIS 40, 173–183 (1975)

Heterogeneous Methanation: Steady-State Rate of CO Hydrogenation on Supported Ruthenium, Nickel and Rhenium

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Received March 25, 1975

A study has been made of initial activity, steady-state activity and activity in the presence of H_2S for CO hydrogenation on a number of supported catalysts. Initial rates of CO hydrogenation were found to be similar on Ni/Al_2O_3, Ni/ZrO_2 and Raney Ni catalysts when corrected for metal surface area. Under steady-state conditions, the specific reaction rate was a factor of 25 lower and the activities were in the order Raney Ni > Ni/Al_2O_3 > Ni/ZrO_2. In the presence of 10 ppm of H_2S the activity decreased by an additional factor of 10 and the order was Ni/ZrO_2 Ni/Al_2O_3 >> Raney Ni. The support has an appreciable effect on the extent of deactivation at steady state and the activity in the presence of sulfur-containing compounds.

In addition, a comparison was made of the specific activity of supported Ni, Ru and Re catalysts at steady state and in sulfur-containing streams.

INTRODUCTION

The first publication of this series presented data on the initial activity for CO hydrogenation on several supported Ru catalysts of varying metal content and particle size (*1*). A comparison of the specific activity of Ru and Ni was also made. However, the initial activity of a clean metal surface in many instances bears little relation to the activity under steady-state reaction conditions. In the hydrogenation of CO, the disproportionation of CO to CO_2 and C or the formation of partially hydrogenated carbonaceous deposits may lead to significant deactivation of the catalyst. The extent of the activity loss will depend on the catalyst, the H_2/CO ratio, and the total pressure. As discussed in the review of Mills and Steffgen (*2*), the normal operating conditions of a methanation catalyst, and an H_2/CO ratio of 3 and a temperature of 250–400°C are very close to the region in which carbon deposition is favored.

Much of the previous testing of catalyst activity and sulfur resistance reported in the literature for the hydrogenation of CO was done in flow reactor systems under integral reactor conditions. The conversion was generally high, making the calculation of catalyst activity difficult if not impossible. This is especially true for the hydrogenation of CO to methane since the reaction is highly exothermic and the heat generated can cause local overheating in the initial part of the catalyst bed. Also, the effect of sulfur compounds in the feed stream was measured by noting the change in useful catalyst life as defined by a minimum conversion and a maximum operating temperature. Such a test would be dependent mainly on the ability of the initial part of the catalyst bed to retain sulfur and would have little to do with the resistance of the catalyst to sulfur poisoning if the poisoned activity resulted in a conversion below the specified minimum conversion.

Part of the data presented herein were obtained at differential reactor conditions in a flow reactor at steady state. The catalyst had reached equilibrium with the reactant stream and the measured activity was that of the steady-state surface. Also, the reactor is operated at low conversion, thus minimizing the possibility of heat or mass transfer limitations. Similarly, in the presence of sulfur the small catalyst sample is equilibrated with a reactant stream containing sulfur and the measured activity is that of the sulfur-poisoned catalyst.

If steady-state rates are significantly different from initial rates or if the relative steady-state activities of various catalyst systems are ranked differently than the order of initial rates, the steady-state activity has to be measured and will be a more useful indication than initial activities of catalyst performance in practice. The operation of a catalyst in a sulfur-containing environment is also of practical importance. In general the sulfur over industrial methanation catalysts is maintained at a sufficiently low level (<0.1 ppm by volume) to prevent significant accumulation on the catalyst. The removal of sulfur to such a low level represents a significant fraction of the methanation cost and a catalyst capable of operation at a higher level of sulfur will be useful. A level of 10 ppm sulfur (by volume), which can be readily attained by hot carbonate scrubbing, was chosen for use in this work. The measurement of differential steady-state rates in a sulfur-containing stream would provide information on the activity of such sulfur-saturated catalysts.

The work presented here includes initial activities for CO hydrogenation on several Ni catalysts including oxide-supported samples and a Raney Ni catalyst to complement the data of the first paper (*1*). Steady-state activities and the activity in the presence of H_2S were measured for Ru, Ni and Re catalysts in a continuous flow reactor. The interpretation of the data gives insight into the relative roles in catalyst deactivation played by carbon deposition, the formation of carbonaceous deposits or bulk carbides and sulfur poisoning for the systems under consideration and the possible effects on the product distribution.

EXPERIMENTAL METHODS

Apparatus

Adsorption measurements were performed with a conventional Pyrex glass constant-volume adsorption system equipped with greased high-vacuum stopcocks (*3*). The pumping system consisted of an oil diffusion pump and a rotary mechanical pump isolated from the adsorption system by liquid-nitrogen cooled traps. The pressure was measured with a Texas Instruments quartz spiral Bourdon gage. The catalyst sample was placed in a flow-through cell to permit reduction in a flowing hydrogen stream prior to the adsorption measurement.

Initial reaction rates were measured in a Pyrex batch recycle reactor operated at very low conversion per pass as described previously (*1*). The reacting gases were sampled by a gastight small-volume injection valve and analyzed by a gas chromatograph equipped with a flame ionization detector. The gas sample was analyzed for total hydrocarbons and methane.

Steady-state rates were measured in an atmospheric pressure single pass flow reactor. The flow of each reactant was controlled using a two-stage metal diaphragm regulator to set the upstream pressure of the gas on a length of stainless steel capillary with an internal diameter of 0.1–0.3 mm. The pressure was measured with a stainless steel Bourdon gage of 0.25% accuracy and the flow was calibrated with a bubble flow meter. The mixed gases passed through the Pyrex reactor contained in a tube furnace then through a gas sampling valve connected to a gas chromatograph. The analysis was identical to that performed for the batch recycle reactor except that the gas chromatograph response was calibrated with a dilute methane in nitrogen mixture.

Materials

The supported catalysts were prepared by impregnating Dispal M alumina (Continental Oil Co.) or colloidal zirconia (TAM Division of N. L. Industries) with sufficient ruthenium trichloride, nickel nitrate, or perrhenic acid solution to just fill the support pore system. A small amount of nitric acid was added to the ruthenium chloride solution to prevent hydrolysis and precipitation of the ruthenium. After impregnation, the samples were dried in air at 80°C.

The Raney nickel catalyst was prepared by extracting a 50/50 Ni/Al alloy (Alfa Products, Ventron Inc.) with 2% NaOH until 60% of the aluminum had been reacted as measured by hydrogen evolution. The catalyst was washed repeatedly and then dried in air at 80°C. After reduction at 450°C, the Raney nickel sample had a BET surface area of 17.3 m^2 g^{-1}.

Helium (99.995% purity) and H_2 (99.95% purity) were used as received in the flow reactor experiments. Matheson ultrahigh purity CO (99.8%) was passed over activated carbon to remove metal carbonyl impurities. The measured hydrocarbon level of this gas was less than 15 ppm. A mixture of 91 ppm H_2S in He was used in the poisoning experiments and was analyzed periodically to check the H_2S concentration.

In the batch recycle reactor, the hydrogen was passed through an Engelhard palladium Deoxo catalytic purifier and dehydrated over 5A molecular sieve at −195°C before use.

RESULTS

Adsorption Measurements

Prior to adsorption measurements, the samples were first reduced in hydrogen, flowing at 100 cc min^{-1}, for 2 hr at 450°C and then evacuated at 450°C for another 2 hr. Hydrogen adsorption isotherms were measured at 21°C over a pressure range from 50 to 250 Torr (1 Torr = 133.3 N m^{-2}) and the linear portion, generally above 120 Torr, extrapolated to zero pressure to obtain the hydrogen adsorption on the metal. These data are presented in Table 1. For each metal examined in this study, the adsorption stoichiometry was assumed to be H − M (surface). This was shown to be the case for Ru (*3*) and was used for Ni and Re by a number of authors (*4–6*).

TABLE 1

HYDROGEN ADSORPTION ON Ni, Ru AND Re CATALYSTS

Sample	H_2 adsorption (μmoles g^{-1})	Dispersion (H_{ads}/M_{total})	*d* (Å)
Ni Catalysts			
5% Ni/ZrO_2	33.7	0.079	
2% Ni/Al_2O_3	5.6	0.033	
Raney Ni	137	0.031	
Ru Catalysts			
0.5% Ru/Al_2O_3	15.1	0.61	14
1.5% Ru/Al_2O_3	25.6	0.35	24
5% Ru/Al_2O_3 (heat treated)	21.7	0.088	96
Re Catalyst			
1% Re/Al_2O_3	2.27	0.085	

Kinetic Measurements

Initial reaction rates were measured as described previously (*1*). Approximately 100 mg of catalyst was reduced at 450°C in flowing H_2 for at least 2 hr then cooled to the reaction temperature and the H_2 was removed by a short evacuation. The initial reaction rate was determined from conversion vs time data for times less than 1000 s. The specific rates are expressed as turnover numbers, *N*, in units of reciprocal seconds (s^{-1}), i.e., molecules of product

TABLE 2
INITIAL RATES OF CO HYDROGENATION[a]

Sample	N at 250°C ($s^{-1} \times 10^2$)		E_a (kcal $mole^{-1}$)	
	HC_{total}	CH_4	HC_{total}	CH_4
5% Ni/ZrO_2 (*1*)	6.3	2.3	20	28
2% Ni/Al_2O_3	5.1	2.0	30	31
Raney Ni	3.2	1.0	26	31
1.5% Ru/Al_2O_3(*1*)	2.1	0.52	17	24
1% Re/Al_2O_3	0.68	0.32	20	23

[a] $P_{H_2} = 0.5625$ atm; $P_{CO} = 0.1875$ atm.

formed for each surface metal atom per second.

The initial rates measured on 5% Ni/ZrO_2, 2% Ni/Al_2O_3, Raney Ni, and 1.5% Ru/Al_2O_3 are presented in Table 2. These data have been discussed in part in a previous publication (*1*).

Steady-state reaction rates were measured after the catalyst sample was reduced for 2 hr at 450°C in flowing hydrogen. The reactor was cooled to 280°C, the flow rate of each reactant was adjusted to the desired value and then the mixture was diverted over the catalyst. The total flow rate was 400 cc min^{-1} with standard reaction conditions of H_2/CO ratio equal to 3.8 and $P_{H_2} + P_{CO} = 0.75$ atm. The diluent was helium. As the reaction slowed, the temperature was raised to 400°C without exceeding a turnover number of 2×10^{-1} s^{-1}. The reaction was continued over the catalyst at 400°C for at least 24 hr before four or more product samples were analyzed and the results averaged. After measurement of the steady-state activity, 10 ppm H_2S (by volume) was added to the reactant stream. After 24 hr, the reaction products were again analyzed. Subsequently the H_2S was discontinued, and the recovery of the catalyst activity after 24 hr in the original sulfur-free reaction mixture was determined.

The results of the rate measurements are presented in comparative bargraphs on four separate figures. Each figure compares the effect of one variable. Figure 1 shows the effect of varying the H_2/CO ratio using the 1.5% Ru/Al_2O_3 catalyst. The reactant partial pressures expressed in atmospheres of $H_2/CO/He$ were: at $H_2/CO = 3.0$, 0.5625:0.1875:0.250; at $H_2/CO = 3.8$, 0.5938:0.1562:0.250; and at $H_2/CO = 6.0$, 0.6429:0.1071:0.250. Also shown in Fig. 1 is the estimated initial rate obtained by the extrapolation of the Arrhenius plot for this catalyst to 400°C [see Ref. (*1*)]. Each bar in Fig. 1 (and the subsequent figures) is composed of two parts: the lower part gives the turnover number for methane only and the upper part for all hydrocarbons.

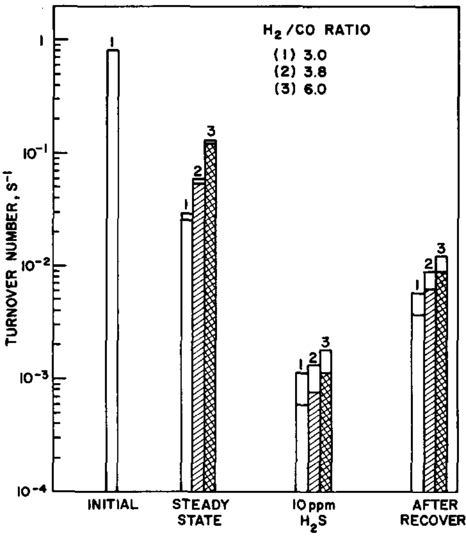

FIG. 1. CO hydrogenation at 400°C on 1.5% Ru/Al_2O_3. Initial rate by extrapolation from data of Ref. (*1*). H_2/CO ratio: (1) 3.0; (2) 3.8; (3) 6.0.

Figure 2 compares the reaction rates for three Ru/Al_2O_3 catalysts with metal particle sizes of 14, 24 and 96 Å. The three catalysts, as shown in Table 1, had similar specific uptakes of hydrogen and therefore also similar Ru surface areas. The differences in the Ru content were compensated by the differences in dispersion.

Figure 3 compares the results on three Ni catalysts. It is worth noting that in this

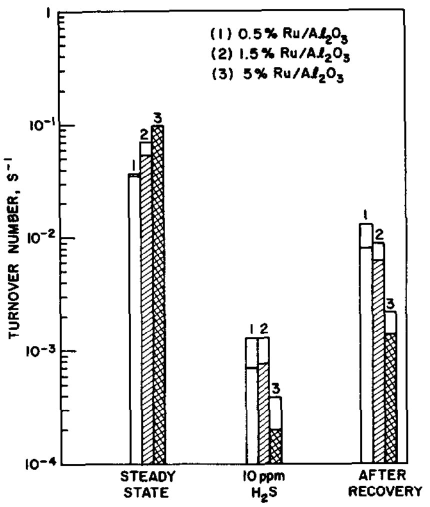

FIG. 2. CO hydrogenation at 400°C on (1) 0.5% Ru/Al_2O_3; (2) 1.5% Ru/Al_2O_3; (3) 5% Ru/Al_2O_3.

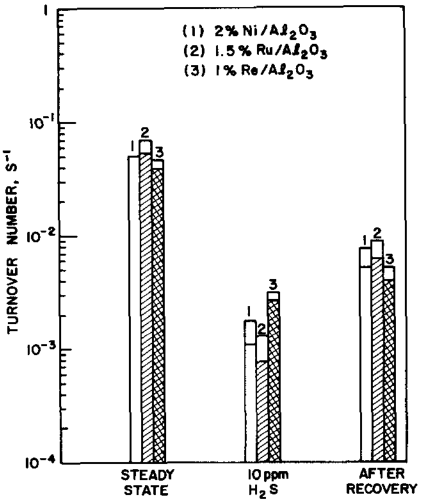

FIG. 4. CO hydrogenation at 400°C on (1) 2% Ni/Al_2O_3; (2) 1.5% Ru/Al_2O_3; (3) 1% Re/Al_2O_3.

case we also have large differences in dispersion. Also, the dispersion on the supported samples appears to be less than on the Ru samples, with the particles in both cases being larger than 100 Å. It must be mentioned that the evaluation of the degree of dispersion on the Al_2O_3-supported Ni catalyst is probably complicated by the possible formation of a surface spinel. It is plausible to assume that Ni atoms associated with such a spinel are active neither for H_2 chemisorption nor for the methanation reaction and therefore the specific rate, based on the hydrogen adsorption measurement is valid. However, the particle size deduced from the adsorption measurement might not be, since this calculation includes the total Ni content, part of which may be present as a spinel.

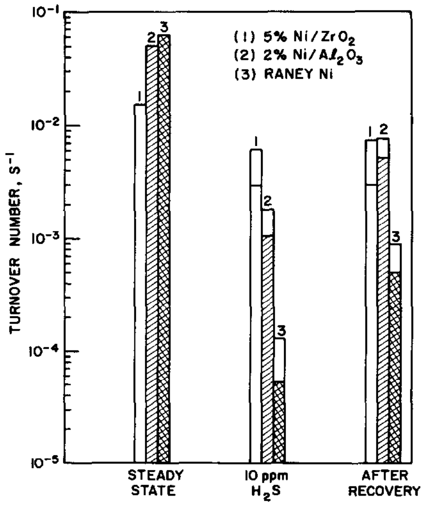

FIG. 3. CO hydrogenation at 400°C on (1) 5% Ni/ZrO_2; (2) 2% Ni/Al_2O_3; (3) Raney Ni.

Figure 4 compares the steady-state rates of the supported catalysts of Ni, Ru and Re under standard conditions. For easy reference the main results of the figures are condensed into Table 3.

Table 4 compares the activity of 1.5% Ru/Al_2O_3 and 2% Ni/Al_2O_3 at three levels of H_2S. The 1 ppm sulfur level was equilibrated over the catalyst for 48 hr and the 5 and 10 ppm concentration for 24 hr before the steady-state rate was measured. At all H_2S levels including the lowest level, the catalyst appeared to be at steady state since the reaction rate was observed to be constant over a period of 8 hr. Comparison of the steady-state rate, the rate in 10 ppm H_2S and the rate after recovery with the data in Table 3 show the rates of Fig. 4 to be slightly high but within the expected experimental reproducibility.

Finally, in Table 5 are given the mea-

TABLE 3

STEADY-STATE RATES AT 400°C AND H_2/CO RATIO OF 3.8 (EXCEPT AS INDICATED)

	Steady-state rate, N (s^{-1}) × 10^4					
	Steady-state		10 ppm H_2S		After recovery	
Sample	CH_4	C_{2+}	CH_4	C_{2+}	CH_4	C_{2+}
1.5% Ru/Al_2O_3						
H_2/CO = 3.0	259	32	6.0	5.2	37.3	21.1
	(89)[a]		(54)		(64)	
3.8	550	63	8.23	6.60	58.4	29.6
	(90)		(56)		(66)	
6.0	1260	50	11.6	6.4	90.6	33.0
	(96)		(64)		(73)	
0.5% Ru/Al_2O_3	348	21	7.01	5.80	80.9	46.0
	(94)		(55)		(64)	
5% Ru/Al_2O_3	987	0	1.99	1.90	14.1	7.4
(heat treated)	(100)		(51)		(66)	
5% Ni/ZrO_2	156	0	30.0	32.3	30.5	45.3
	(100)		(48)		(40)	
2% Ni/Al_2O_3	519	0	10.6	7.7	52.1	24.1
	(100)		(58)		(68)	
Raney Ni	629	9	0.538	0.78	5.12	3.90
	(99)		(41)		(57)	

[a] Percent methane.

sured steady-state rates at 250°C on several of the catalyst samples. Standard conditions of H_2/CO ratio equal to 3.8, $P_{CO} + P_{H_2} = 0.75$ atm and a total flow rate of 400 cc min^{-1} were employed. These data are compared with the rates at 400°C in Fig. 5. Each pair of bars presents data at 250°C (left) and 400°C (right) for each catalyst and steady-state condition.

DISCUSSION

Steady-State Rates

As a general rule the reaction rate at steady state and 400°C is 25 times lower than the initial rate obtained from the extrapolation of the Arrhenius data, such as given in Ref. (*1*). Obviously the only process leading to such a drop in activity, in streams free of sulfur-containing contaminants, is the formation of carbonaceous deposits in the form of elemental carbon, unsaturated hydrocarbon species or the formation of bulk or surface metal carbide. No change in the catalyst surface area is expected since the deactivated catalyst can be regenerated by treatment to remove the carbonaceous deposits. For example, a sample of 5% Ni/ZrO_2 showed a steady-state rate at 250°C of 8.75×10^{-2} s^{-1} (very near the expected initial rate) and a rate of 1.70×10^{-2} s^{-1} at 400°C. After cleaning the catalyst of carbonaceous deposits with pure hydrogen at 450°C, a rate of 5.48×10^{-2} s^{-1} was measured at 250°C. Since some hydrocarbons were still being produced after hydrogen treatment of the Ni catalyst for 12 hr, an additional cleaning in air at 350°C for 30 min gave a measured reaction rate of 10.0×10^{-2} s^{-1} at 250°C. This final activity is above the steady-state rate measured initially, probably representing some surface roughening

TABLE 4

EFFECT OF H_2S CONCENTRATION ON ACTIVITY OF 1.5% Ru/Al_2O_3 AND 2% Ni/Al_2O_3[a]

	Steady-state rate, N (s^{-1}) × 10^2			
	1.5% Ru/Al_2O_2		2% Ni/Al_2O_3	
Condition	CH_4	C_{2+}	CH_4	C_{2+}
Steady-state	7.59 (92)[b]	0.62	7.96 (100)	0
H_2S, 1 ppm	0.210 (57)	0.157	0.115 (37)	0.198
5 ppm	0.108 (54)	0.093	0.0874 (50)	0.089
10 ppm	0.096 (51)	0.089	0.0816 (50)	0.081
After recovery	0.659 (67)	0.331	0.184 (53)	0.163

[a] 400°C; H_2/CO = 3.8.

[b] Percent methane.

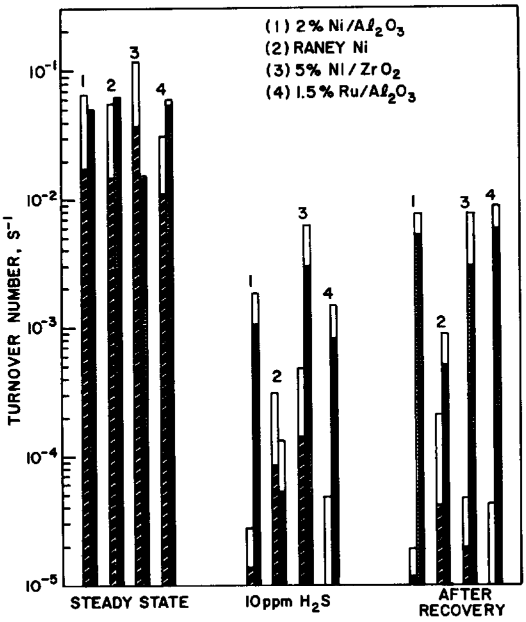

FIG. 5. CO hydrogenation at 250°C (left) and 400°C (right). (1) 2% Ni/Al_2O_3, (2) Raney Ni, (3) 5% Ni/ZrO_2; (4) 1.5% Ru/Al_2O_3.

by the oxygen treatment, and demonstrating that the deactivation at 400°C is reversible.

Since at a constant overall pressure the extent of the formation of elemental carbon deposits is dependent chiefly on the H_2/CO ratio (*2*), it was important to establish the effect of this variable on the extent of the rate decrease from its initial value to its steady-state value. Figure 1 shows that there is a slight effect of the H_2/CO ratio, in the range from 3.0 to 6.0 at all three levels of activity for the 1.5% Ru/Al_2O_3 catalyst. From the kinetic data of Ref (*1*) it is possible to estimate the relative ratios of the rates at different H_2/CO

TABLE 5

STEADY-STATE RATE AT 250°C AND H_2/CO RATIO OF 3.8

	Steady-state rate, N (s^{-1}) × 10^4					
	Steady-state		10 ppm H_2S		After recovery	
Sample	CH_4	C_{2+}	CH_4	C_{2+}	CH_4	C_{2+}
2% Ni/Al_2O_3	173 (26)[a]	495	0.138 (50)	0.136	0.117 (61)	0.076
Raney Ni	149 (27)	410	0.844 (27)	2.27	0.436 (21)	1.66
5% Ni/ZrO_2	373 (32)	807	1.42 (29)	3.42	0.196 (41)	0.278
1.5% Ru/Al_2O_3	110 (35)	202	0.005 (1)	0.483	0.071 (17)	0.359

[a] Percent methane.

ratios expected from the simple power law $r = r_0 P_{H_2}{}^n P_{CO}{}^m$. The values of n and m are temperature dependent but they appear to be approaching the values of 2 and −1, respectively, as the temperature increases and these exponents were adopted to calculate the expected values at 400°C. The expected ratio for the overall reaction rates at H_2/CO ratios of 3.0, 3.8 and 6.0 are 1:1.3:2.3, while those observed at steady state are 1:2.1:4.5. Although the assumed reaction orders may be substantially in error, this is an indication that some carbonaceous material is affecting the reaction rate and the decrease in carbonaceous deposits at higher H_2/CO ratios contributes to the larger differences in the rate than those that could be expected from the simple power law derived for clean surfaces (i.e., initial rates). However, the small size of the effect of H_2/CO ratio on the rate indicates that massive carbon deposition via the disproportionation of carbon monoxide,

$$2CO \longrightarrow C + CO_2,$$

is not occurring at a significant rate. This is consistent with the instability of elemental carbon at equilibrium for the gas compositions used in this work (*2*). The measured rates are assumed to be representative rates on a steady-state surface.

In the presence of 10 ppm H_2S and after recovery, the rate ratios at H_2/CO ratios of 3.0, 3.8 and 6.0 are 1:1.3:1.6 and 1:1.5:2.1, respectively. The values are very near those expected from the clean surface power rate law. Even through the available ruthenium surface must increase as the H_2/CO is increased, the presence of H_2S nullifies this effect. Either the deactivation by H_2S is so severe that the prior contamination by carbonaceous deposits is of no consequence or the sulfur acts independently of the previous deactivation.

In the first publication of this series it was concluded that there is no particle size effect in supported Ru catalysts with respect to the initial rate or the product distribution (*1*). The results in Fig. 2 indicate that the turnover number increases as the particle size increases. The same may be true for Ni (see Fig. 3). However, one must remember that the steady-state deactivation comes about through the formation of carbonaceous deposits of some form and if the finely dispersed particles were more active in the formation of these deposits, we would expect such behavior. This observation fits into a more general pattern concerning the formation of heavier hydrocarbons which is discussed below.

Effect of Sulfur

The actual sulfur level is found to have a minimal effect as shown in Table 4. On the 1.5% Ru/Al_2O_3, a level of 1 ppm reduces the activity by a factor of 36 while an increase to 10 ppm results in only a further 2-fold decrease in activity. Since the formation of bulk sulfide is dependent mainly on the H_2S/H_2 ratio in the case of Ni (and probably Ru), and this ratio varies from 2×10^{-6} to 2×10^{-5} for levels of 1 ppm and 10 ppm H_2S, the small effect of sulfur concentration in the range above 1 ppm is reasonable (*7*).

Of the three nickel catalysts studied, the Raney Ni catalyst showed the highest steady-state activity. This was also observed by Dirksen and Linden (*8*) in a comparison of Raney Ni and Ni on kieselguhr. However, in testing sulfur tolerance, they observed similar behavior for these two catalyst systems but the tests were integral reactor breakthrough tests and did not include measurement of differential activity in equilibrium with the sulfur-containing feed. The very low activity observed here for the sulfur-saturated Raney Ni catalyst may be due to the presence of elemental aluminum and the formation of sulfospinel type compounds, $NiAl_2S_4$, at the surface or in the bulk (*9*). The formation of surface sulfospinels as a possible deactivation path of alumina-containing Ni catalysts is at present only a plausible conjecture. It is worth mentioning that on ZrO_2-supported Ni catalysts, which are least susceptible to sulfur poisoning, the formation of sulfospinels is precluded.

Selectivity

It is worth noting that in the absence of sulfur poisoning the highest steady-state activity for both the Ru and Ni catalysts is also associated with lowest formation of heavier hydrocarbons. This is what one would expect, since the production of carbonaceous deposits, which probably consist of hydrocarbons which are nonvolatile at the reaction conditions, requires the formation of carbon–carbon bonds. Such bonds are necessary also for the formation of the more volatile hydrocarbons with the exception of methane itself. The introduction of H_2S into the system has, besides the obvious effect of sharply reducing the overall activity, another very consistent effect: it alters the product distribution to increase the relative content of heavier hydrocarbons. As Table 3 shows, this is true for *all* the catalysts, irrespective of the identity of the active metal, support or state of aggregation. In other words, *sulfur poisons the ability of the surface to hydrogenate the carbon atom much more severely than the ability to form carbon–carbon bonds.* Moreover, catalysts which in absence of sulfur did not produce any hydrocarbons larger than methane (to the limit of our sensitivity), begin to produce measurable amounts upon the addition of sulfur. The analogous behavior is also observed upon the removal of sulfur from the gas stream. In this instance the recovery of the methanation activity is steeper than that of the activity to make heavier hydrocarbons. The data in Table 3 show that the product distribution changes so as to increase the relative proportion of methane in all cases, save one. Another concomitant observation, true both for Ru (Fig. 2) and for Ni (Fig. 3), is that catalysts which produce only methane and have also the highest specific activity under steady-state conditions in the absence of sulfur are the ones most susceptible to sulfur poisoning. Similar effects were observed by Herington and Woodward (*10*) who proposed that H_2S adsorbed at sites where H_2 adsorbed otherwise, thus reducing the hydrogenation activity more than the rate of chain growth.

Effect of Temperature

At 250°C the steady-state rate of hydrocarbon synthesis is very near that observed at 400°C for each of the Ni and Ru catalysts (Fig. 5). In fact, the 2% Ni/Al_2O_3 and 5% Ni/ZrO_2 samples show higher activity at 250°C while the Raney Ni and 1.5% Ru/Al_2O_3 are more active at 400°C. Such small and negative temperature coefficients are the result of increased deactivation at the higher temperature due to carbonaceous deposits or carbide formation. Of course the implied activation energies are meaningless and caution must be used when interpreting temperature-rate data for rates other than initial rates. The behavior of the 5% Ni/ZrO_2 catalyst is an extreme example in that the total synthesis rate at 250°C is almost an order of magnitude higher than that at 400°C.

In addition there is even a slight disagreement between the initial turnover numbers of Table 2 at 250°C and the steady-state turnover numbers at the same temperature of Table 5 such that the latter are 30% higher than the former. This incongruity is probably associated with the insufficient rate of heat dissipation in the steady-state apparatus at this temperature. A surface temperature difference of approximately 10°C would be sufficient to account for this discrepancy. Even in the initial rate measurements, where the heat dissipation is better due to higher flow rates in the recirculation apparatus, catalyst overheating is observed at 280°C [see Fig. 4 in Ref. (*1*)]. The absence of deactivation at 250°C and the severe deactivation at 400°C implies that the mode of deactivation by carbonaceous materials changes radically over this temperature range. The predominant surface phase may be Ni at 250°C, as indicated by a catalytic activity very near that expected for a clean metallic nickel surface, while at 400°C other phases, such as carbide, or the deposition of elemental carbon may cause the lower activity (*11*). This aspect will be investigated in more detail in the future.

At 250°C under steady-state conditions, approximately 30% of the products are methane for all of the samples (Table 5). This is similar to the selectivity exhibited during initial rate measurements at 250°C by supported Ni and Ru. The selectivity to methane was also found to increase with temperature on a clean surface such that methane is the only product at 400°C which is consistent with the steady-state data at 400°C.

In the presence of 10 ppm of H_2S, the steady-state rates at 250°C are substantially below the rates observed at 400°C for 2% Ni/Al_2O_3, 5% Ni/ZrO_2 and 1.5% Ru/Al_2O_3. These results are consistent with the increased stability of nickel and ruthenium sulfides at lower temperatures. However, the behavior of Raney Ni is unusual, exhibiting as it does a decreased sulfur poisoning at lower temperature. The formation of sulfospinels, a temperature dependent process which would be inhibited at low temperatures, may be responsible for the unusual behavior of Raney Ni. A second notable difference for all samples is the lack of recovery at 250°C when H_2S is removed from the reactant stream. Three of the samples, 2% Ni/Al_2O_3, Raney Ni and 1.5% Ru/Al_2O_3 showed slight losses in activity while the activity of the Ni/ZrO_2 sample decreased by a factor of 10. As sulfur is removed from the reactant stream the surface composition of the catalyst should change to lower sulfur concentrations, albeit slowly, and the resulting surface may have a lower catalytic activity. In fact, results to be published in the future show the activity of some catalysts in equilibrium with a given concentration of H_2S at 400°C decrease as the sulfur level was decreased. The behavior at 250°C can be contrasted to the behavior at 400°C where in every case removal of the H_2S resulted in an increase in catalytic activity, some of which were quite substantial. These trends are a direct result of the decreased stability on the metal sulfides at higher temperatures and the resulting rapid removal of S from the Ni catalyst.

Comparison of Ni, Ru and Re

Finally, the comparison between the steady-state turnover number on the three different metals (Fig. 4), indicates that the differences are less important, at least with Ni, Ru and Re on alumina, than one could, perhaps, anticipate. The highest steady-state activity in the absence of sulfur is exhibited by Ru and in the presence of sulfur by Re. The differences are not large enough, however, to be able to indicate preference for practical application. Moreover, to indicate such preference, steady-state and sulfur-poisoned activities have to be measured and compared under the high pressure conditions prevalent in industrial applications. Such comparisons will be pursued in this laboratory. Recently, Kreindel and co-workers (*12*) have concluded that the specific rate of high pressure (30 atm) hydrogenation of CO over Ni catalysts is independent of catalyst composition, support, calcination temperature, reduction temperature, etc., and therefore efforts to maximize the catalyst activity should be directed towards the preservation of the Ni surface area only. This extremely important behavior, which is not observed at low pressures, requires further confirmation.

To summarize, the main observations of this work are: (a) a large and temperature dependent decrease in activity when initial rates are compared to rates obtained at steady-state conditions, even if high H_2/CO ratios are used; (b) a large decrease in activity when low concentrations of sulfur are added to the reactant stream; (c) a large temperature dependence of sulfur poisoning and the lack of recovery of the catalytic activity when sulfur is discontinued at a temperature of 250°C; (d) an increase in selectivity to higher hydrocarbons upon carbon deposition and sulfur poisoning; and (e) the effect of the support on the behavior of the active metal especially when comparing Ni/Al_2O_3 and Ni/ZrO_2 catalysts. Several of these points will be pursued in more detail in the future.

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