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The Exchange of $H_2{}^{18}O$ with the Oxygen of Promoters on the Surface of Iron Catalysts

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The oxygen content of promoter oxides or other metallic oxide on the surface of iron synthetic ammonia catalysts has been estimated by a method involving equilibration with a known quantity of $H_2{}^{18}O$ in hydrogen at 450°C. The results indicate a surface coverage by promoters of about 60% for a catalyst containing 1.06% Al_2O_3 and 0.52% K_2O. With reasonable assumptions in regard to the cross sectional area of oxygen ions the coverage agrees with that estimated from the chemisorption of carbon monoxide at −195°C on the same catalyst. A pure iron catalyst revealed only a 1.2% coverage with oxygen after extended reduction at 450°C.

INTRODUCTION

Iron synthetic ammonia catalysts are commonly promoted with small amounts of alkaline oxides or alkaline earth oxides such as K_2O, CaO, or MgO, together with a few percent of an irreducible oxide such as Al_2O_3 or SiO_2. Several approaches have been used in an effort to ascertain the fraction of the surface of the reduced catalysts actually covered by the few percent added promoter. Emmett and Brunauer (*1, 2*) showed that the chemisorption of carbon monoxide at −195 or −183°C will cover the entire surface of a pure iron catalyst but only about 40% of the surface of a catalyst containing 1 or 2% of a K_2O–Al_2O_3 promoter. Furthermore, they showed that the K_2O–Al_2O_3 promoter, itself, was capable of chemisorbing an amount of carbon dioxide at −78° equivalent to about 60% of the surface of the entire catalyst. These facts combined with the inability of a pure iron catalyst to adsorb any carbon dioxide at −78° led to the conclusion that a few percent promoter in these iron catalysts would cover 50–70% of the surface leaving only 30–50% of the surface in the form of iron. Scholten (*3*) discussed the method used by Emmett and Brunauer and pointed out that their procedure for determining the amount of chemisorption by obtaining data for an adsorption isotherm at −195°, evacuating the sample at −78°, and then measuring again the adsorption at −195° might be somewhat in error because of the possibility that some of the chemisorption might pump off at −78°C. As an alternate procedure they measured the exchange of D_2O with the remaining OH groups on the Al_2O_3 of the iron catalyst and compared the amount of exchange with that occurring on a sample of Al_2O_3 of known area pretreated with hydrogen at 450°C, the temperature used for the reduction of the iron catalyst. By assuming that the exchange per unit area covered by Al_2O_3 as a promoter on the surface of the iron would be the same as on the Al_2O_3 sample they were able to estimate the fraction of the surface of the iron catalyst covered by promoter. This method suggested that 1% Al_2O_3 as a promoter covered about 25% of the surface leaving 75% as the free iron surface. For such a catalyst the method of Emmett and Brunauer indicated that 45% of the surface was iron and 55% was covered with aluminum oxide. In the present

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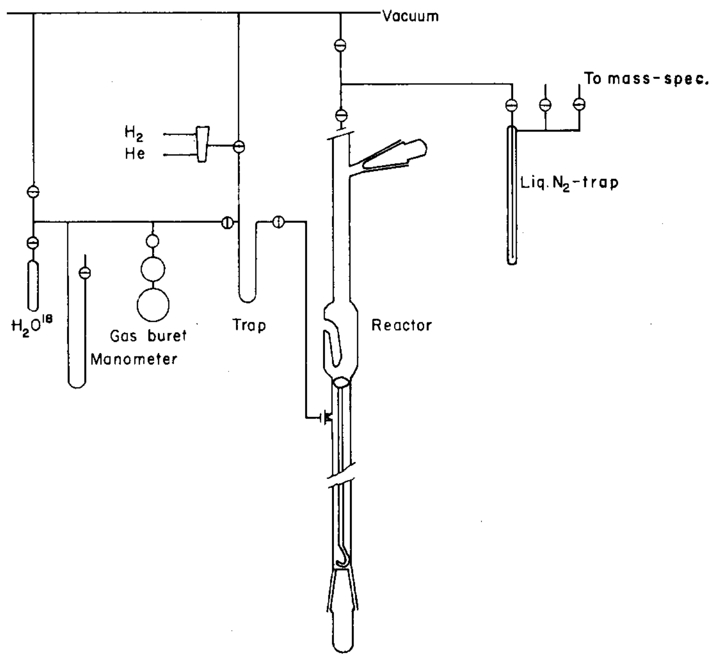

FIG. 1. The equipment used for the exchange of $H_2{}^{18}O$ with ^{16}O in promoters on the surface of iron catalysts.

work an attempt has been made to obtain a third estimate of the fraction of the surface covered by promoter. This third method entails adding a mixture of $H_2{}^{18}O$ and hydrogen to the reduced catalyst and letting it stand until equilibrium is set up between the oxygen-16 in the promoter and oxygen-18 of the water vapor. The results of these measurements are reported in the present paper.

EXPERIMENTAL

The experimental set-up is illustrated in Fig. 1. The reactor (about 20 cc) was constructed so that it could be filled and emptied without getting air into the system. The catalyst, the amount of which was chosen so that the surface area was 5–7 m^2, was introduced through a standard tapered joint at the top of the reactor while helium was streaming through. It could be emptied through a similar joint in the bottom of the reactor. The plug in the bottom supported a rod with a loosely fitting plunger to keep the catalyst in the reactor zone but to allow gas to stream by. Fitting a plastic bag filled with inert gas around the bottom plug helped in the removal of the highly active catalyst without getting it in contact with air.

A furnace around the reactor was controlled by a thyratron unit to a temperature of 450°C ± 1° during reduction and exchange. The catalyst was reduced with 60 ml/min of hydrogen. During some experiments it was taken directly from the tank (Matheson "zero" gas, "analyzed") but during most of the experiments it was first allowed to diffuse through a palladium–silver alloy tube. The reduction time was usually 18 hr but was extended in some instances for comparison to 42 and 114 hr. Some of the samples were subject to several successive exchanges with $H_2{}^{18}O$ to see whether the sublayers of oxygen also were exchanged. During these experiments the catalyst was always reduced 18 hr between each run. After the reduction, the sample was pumped for 30 min and a measured amount of water enriched with oxygen-18 was introduced into the reactor by first freezing it into a trap from the measuring system, and then melting and evaporating it into the reactor. The trap was flushed with hydrogen so the H_2 pressure in the reactor was about 300 mm Hg during the exchange. The water–hydrogen mixture was kept in contact with the catalyst for 3 hrs. In two experiments, 1 and 5 hr were used to be sure that equilibrium had been reached. The gas was then flushed into a —195°C trap (about 5 cc) with a stream of hydrogen which also reduced off any surface oxide. The reduction was continued for 30 min although times from 10 min to 5 hr were tried without changing the concentration of oxygen-18 in the water product, further evidence that equilibrium had been reached. The trap was connected through a stopcock to a Consolidated 21–611 mass spectrometer as shown in Fig. 1. The memory effect of the mass spectrometer could be overcome by introducing consecutively 10–15 samples (0.025 cc H_2O [S.T.P.] each) of the trapped water vapor. In between each introduction the expansion chamber and connecting tubes were briefly pumped for 3 min; usually five isotope measurements were made for each introduced sample. The values for each of these measurements were statistically treated to find the concentration at zero time. The results were highly reproducible.

The catalysts used in these experiments were the following: No. 418, a doubly promoted iron catalysts containing 1.06% Al_2O_3 and 0.52% K_2O (based on unreduced catalyst); No. 927, with no promoters added, but probably containing up to 0.15% Al_2O_3 as an impurity; and No. 954, a singly promoted catalyst containing 10.2% Al_2O_3. In addition, S(Fe)1 was prepared as a porous pure iron catalyst made from pure chemicals after a method described by Emmett and Gray (*4*). To confirm that the exchange takes place only on the surface of the Al_2O_3 phase, two samples of alpha–alumina with a specific surface of 4.40 m²/g were treated in exactly the same way as the iron catalyst samples and exchanged in the $H_2{}^{18}O$–H_2 mixture.

The surface area (*5*) and the CO chemisorption values were measured on a McBain type balance with a sensitivity such that the quartz spiral increased in length 1 mm for each 2 mg added weight. Samples weighing approximately 1 g were used. The extension of the spiral was read with a travelling microscope with a sensitivity of about 0.002 mm. The CO was adsorbed at —195.8°C at a few millimeters pressure and then pumped at the same temperature with an effective diffusion pump with large diameter tubes. A steady state was reached after 2.5–3 hr while pumping down to 10^{-6} mm Hg. The CO which did not come off after 4 hr pumping was assumed to be chemisorbed. Experiment M86 on catalyst No. 418 illustrated in Fig. 4 made it evident that this final value attained by pumping at —195°C was substantially the same as that obtained by a short pumping at —78°C.

RESULTS AND DISCUSSION

Figure 2 shows how the mass spectrometer readings came to a steady state after some 10–15 introductions of sample with a 3-min pumping in between. The last values were usually within a few tenths of a percent of each other. The scale on the left gives the percentage ^{18}O measured

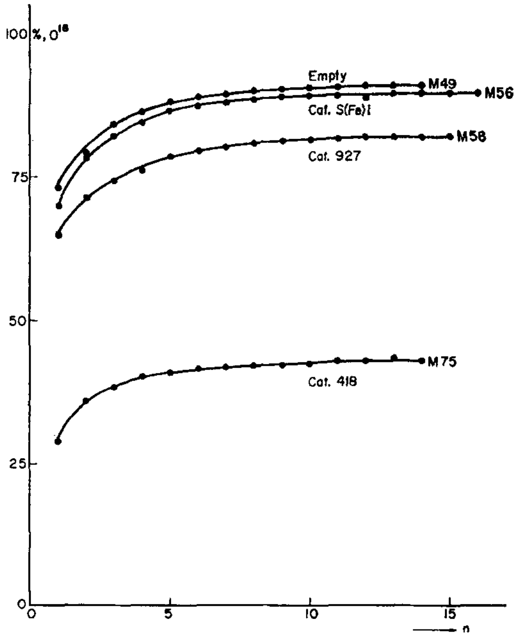

FIG. 2. Representative plots of the measured concentration of ^{18}O in the sample as a function of n, the number of introductions of the sample into the mass spectrometer.

TABLE 1
EXCHANGE WITH ^{18}O ENRICHED WATER (91.1% $H_2{}^{18}O$) ON IRON CATALYSTS AND α-ALUMINA

Run M No.	Cat.	Red. cat. (g)	Red. (hr)	Exch. (hr)	a_0 mmole enriched H_2O added	x_1 % $H_2{}^{18}O$ in water after equil.	a_1 Oxygen on surf. (matom)	Spec. surf. area (m^2/g)	No. of O atoms per cm^2 $\times 10^{-15}$
43	418	1.00	18	3	0.0659	45.5	0.0659	(7.04)[a]	0.563
44	Same		18	3	0.0661	63.5	(0.0835)		
45	Same		18	3	0.0658	68.7	(0.1038)		
46	Empty		18	3	0.0674	91.1			
47	S(Fe)1	5.11	42	3	0.0655	82.5	0.0067	(1.98)[a]	0.040
48	Same		18	3	0.0652	83.3	(0.0185)	(1.98)[a]	
49	Empty		18	3	0.0649	90.8			
50	418	1.00	18	5	0.0652	44.8	0.0672	(7.04)[a]	0.574
51	418	1.00	18	1	0.0631	43.0	0.0704	(7.04)[a]	0.602
52	Same		18	3	0.0613	61.9	(0.0830)	6.54	
54	418	1.00	42	3	0.0667	47.9	0.0600	6.40	0.564
55	Empty		18	3	0.0648	90.4			
56	S(Fe)1	2.16	42	3	0.0653	89.7	0.0009	(1.98)[a]	0.012
57	Same		18	3	0.0648	91.2	(0.0000)	1.98	
58	927	7.43	42	3	0.0647	82.3	0.0068	(0.66)[a]	0.083
59	Same		18	3	0.0651	87.2		0.58	
67	418	1.00	18	3	0.0554	40.1	0.0703	6.98	0.606
69	Empty		18	3	0.0612	91.6			
70	418	1.00	18	3	0.0411	34.8	0.0663	(7.04)[a]	0.566
71	Same		18	3	0.0610	60.9	(0.0700)	6.42	
74	Empty		18	3	0.0607	90.5			
75	418	1.00	42	3	0.0553	43.1	0.0614	6.55	0.564
76	418	1.00	114	3	0.0648	49.3	0.0548	6.29	0.524
77	Empty		18	3	0.0653	90.5			
78	418	1.00	42	3	0.0659	47.7	0.0602	(6.40)[a]	0.566
79	Same		18	3	0.0654	68.6	(0.0647)		
80	Same		18	3	0.0656	79.6	(0.0644)		
81	Same		18	3	0.0656	83.9	(0.0669)	5.86	
82	418	1.00	18	3	0.0655	45.6	0.0653	7.04	0.558
83	927	7.43	42	3	0.0655	73.8	0.0156	0.66	0.186
88	α-Alumina	0.610	18	3	0.0652	54.1	0.0444	4.39	1.00
89	α-Alumina	0.498	18	5	0.0652	59.1	0.0352	(4.39)	0.97
90	Same		18	3	0.0650	71.8	(0.0573)	4.30	(1.60)
92	954	1.07	18	3	0.0640[b]	23.9	0.123	8.81	0.780[b]

[a] These surface area values are assumed to be the same as those taken under identical conditions for Runs 83, 82, 57, and 54, respectively.

[b] Due to an accident during this run, the $H_2{}^{18}O$ concentration, a_0, was 70.3%. The figures for this catalyst are less certain, but as no more catalyst was available, the authors decided to report the values as shown.

by the mass spectrometer. As we know the amount, a_0, and the ^{18}O concentrations, x_0, of the water added (^{18}O concentration taken as that for a sample added to the empty reactor), we can calculate the amount of water, a_1, exchangeable on the surface in the following way:

$$\frac{a_0 x_0}{a_0 + a_1} = x_1, \tag{1}$$

where x_1 is the concentration of ^{18}O in the product out of the reactor.

The results of the experiments are shown in Table 1, together with a calculation from them of the number of O atoms/cm^2. Table 1 also gives the exchange on α-alumina (M88 and M89) of known surface area. For these, with exchange times of 3 and 5 hrs we found no significant difference in the exchangeable part of the sample, which came out close to 10^{15} atoms O/cm^2.

The question immediately arises as to whether the exchange carried out as described may reach oxygen atoms in the second and deeper layers of the alumina or the promoter molecules. Whalley and Winter (*6*) were able to show that $H_2{}^{18}O$ exchanged with the surface of Al_2O_3 at a very high rate whereas further exchange with interior oxygen was extremely slow even at 400°C. The first step in checking the depth of penetration of the exchange was to extend some of the equilibration times to 5 hr instead of the usual 3 hr. The results obtained as shown, for example, by Runs 50 and 89 in Table 1 indicated that the exchange was not appreciably greater in 5 hr than in 3 hr and was not, therefore, extending to lower layers of the promoters.

A more satisfactory way of ascertaining the penetration of the exchange to lower layers entailed exposing the samples to a stream of hydrogen for a period of 18 hr immediately after the first $H_2{}^{18}O$ exchange experiment. It is then possible to calculate from a second exchange experiment the amount of ^{16}O from the second layer that has equilibrated with ^{18}O atoms in the first layer from the exchange run. If such further exchange occurs, the ^{18}O content of the surface layer will decrease from the value given for the equilibrated water from the first exchange down to a value, x'_1. One can then calculate the value of x'_1 from the new exchange data by the equation

$$\frac{a_1x'_1 + a_0x_0}{a_0 + a_1} = x_2, \qquad (2)$$

where a_1 is the number of milliatoms of oxygen calculated from the first exchange run as being present on the surface of the promoter, a_0 is the number of millimoles of ^{18}O in the sample of $H_2{}^{18}O$ added for the second run, and x_2 is the fraction of ^{18}O in the product from the second equilibration. By this equation, calculations were made for a number of repeat runs as shown in Table 2. Runs 43–52 appeared to indicate that during the 18-hr exposure to a stream of hydrogen considerable oxygen-16 accumulated in the surface layer. This was found to be due, however, to water vapor contained to the extent of 4–8 ppm in the stream of hydrogen. The Δa_1 increments decreased to a very small value when, as in runs 56–81, the hydrogen passing over the iron catalysts came from the palladium–silver alloy diffusion tube. Apparently the oxygen diffusing into the first layer during these runs was only in the range 5–7% of the amount of oxygen in the surface of the iron or the promoters.

The experiments with aluminum oxide, however, indicated that in 18 hr considerable ^{16}O diffused into and exchanged with ^{18}O that was already in the first layer from the first exchange run. Thus, a comparison of Run 90 with Run 89 in Table 1 or Table 2 showed that additional oxygen-16 from the second layer equal to 60% of that originally in the first layer had equilibrated with the ^{18}O from the first exchange experiment. In other words, during the 18-hr reduction 60% of the oxygen atoms from the second layer were equilibrated with the first layer of the alumina whereas only 5–7% of the lower lying oxygen atoms from the promoter on the iron catalysts so exchanged. This is consistent with the idea that the promoter molecules are present as single layers for the most part and do not therefore have many oxygen atoms in lower lying layers. Incidentally, it should be pointed out that the a_1 values for the iron catalysts in runs 43–52 indicate that most of the 4–8 ppm of water in the stream of hydrogen undergoes exchange with the ^{18}O left on the promoter molecules during the first exchange run.

It is interesting to compare the results for different reduction times with respect to the total coverage of the surface with promoter oxygen, on the doubly promoted catalyst No. 418. Eighteen-hour reductions (Runs 43, 50, 51, 67, 70, and 82 in Table

TABLE 2
RESULTS OF CONSECUTIVE EXCHANGES OF $H_2{}^{18}O$ ENRICHED WATER ON IRON CATALYSTS AND α-ALUMINA

M. No.[b]	Cat.	a_1 mAtom O on surface	Δa_1[a] mAtom of oxygen	O/cm² × 10^{-15}
43	418	0.0659		0.563
44	Same	(0.0835)	0.0177	
45	Same	(0.1038)	0.0203	
47	S(Fe)1	0.0067		0.040
48	Same	(0.0185)	0.0118	
51	418	0.0704		0.602
52	Same	(0.0830)	0.0126	
56	S(Fe)1	0.0009		0.012
57	Same	(0.0000)	0.0000	
70	418	0.0663		0.566
71	Same	0.0696	0.0033	
78	418	0.0602		0.566
79	Same	(0.0447)	0.0041	
80	Same	(0.0644)	−0.0003	
81	Same	(0.0667)	0.0025	
89	α-Alumina	0.0352		0.97
90	Same	(0.0573)	0.0221	

[a] Δa_1 is additional oxygen which seems to have equilibrated with surface oxygens during the 18-hr lapse between experiments.

[b] In runs 43–52 tank hydrogen was used for reduction. It contained 4–8 ppm water vapor. For runs 56–90, the hydrogen was all diffused through a palladium-silver tube.

1) yield a value of 0.58×10^{15} oxygen atoms per cm². Forty-two-hour reductions (Runs 54 and 75) yield an average of 0.56×10^{15} atoms of O per cm² and 114-hour, yield (Run 76) 0.52×10^{15}. The percentage coverage with promoters thus decreases about 10%. Simultaneously, the total surface area changes from 7 m²/g down to 6.3. Normally one would expect an increase in coverage of the surface with promoters as the iron crystals grow. Possibly, the observed effect is due to a partial clustering of the promoter molecules during the longer reduction period to form a multilayer of promoters in a few places. The same effect would be produced if there are a few low area crystallites of promoters present to which some of the disperse phase can gradually diffuse during longer periods of reduction.

Two other minor items should be noted in connection with the data in Table 1. For the pure iron catalyst S(Fe)1, 4% surface coverage with oxygen atoms was noted in Run 47 when hydrogen gas was being used with 4–8 ppm of water vapor, whereas for hydrogen that had been allowed to diffuse through the Pd tube, the final coverage was only 1.2% (Run 56). The result is clearly in the expected direction even though the exact numerical values for the coverage are subject to considerable error. The final observation that may be worth noting is that the surface area for the sample of No. 418 reduced 114 hr (Run 76) was 6.3 m²/g, whereas the area of the sample reduced 96 hr in Runs 79, 80, 81, and 82 with intervening exchange experiments with $H_2{}^{18}O$ had an area of only 5.86 m²/g. This is in line with the usual expectation that exposing metallic iron to water vapor causes the iron crystals to grow.

In Table 3 are gathered the CO chemisorption data for some of the samples. The last column, "CO-coverage," is calculated using 16.2 Å² per CO molecule. The value given is, therefore, equal to V_{CO}/V_{N_2} where

TABLE 3

CO CHEMISORPTION MEASUREMENTS ON IRON CATALYSTS

M No.	Cat.	Cat. (g)	CO (mg)	m²/g	Number of CO molecules per cm² × 10^{-15}	CO-cov.[a]
52	418	0.652	0.54	6.54	0.27	0.44
54	418	0.705	0.52	6.40	0.25	0.40
57	S(Fe)1	0.713	0.46	1.98	0.70	1.13
59	927	0.703	0.12	0.58	0.65	1.05
75	418	0.643	0.50	6.55	0.25	0.41
76	418	0.644	0.52	6.29	0.28	0.45
81	418	0.651	0.46	5.86	0.26	0.42
82	418	0.647	0.56	7.04	0.26	0.43
83	927	0.671	0.11	0.66	0.53	0.86
87	954	0.653	0.68	8.81	0.25	0.41
87[b]	Same		0.63[b]			

[a] Assuming 16.2 Å²/CO, the coverage is equal to V_{CO}/V_{N_2}, where V_{N_2} is monolayer coverage of N_2 at −195.8°C and V_{CO} is the volume of adsorbed carbon monoxide.

[b] After 1 hr pumping at −78°C.

Note: The sensitivity of the balance system used is about ±5 μg, giving an accuracy of about ±5% for M59 and M83, and about ±1% for the rest of the experiments.

V_{CO} is the volume of carbon monoxide chemisorbed, and V_{N_2} is the volume of physically adsorbed nitrogen required to form a monolayer at —195.8°C. In accordance with the theory that CO is chemisorbed only on the free iron of the surface, the area covered with CO and the one covered with oxygen containing species should give the total surface area. The values are certainly in the right direction even before one assumes specific sizes for the molecules involved. The values of V_{CO}/V_{N_2} on a doubly promoted catalyst surface is, as we see, .400–.445 the highest

TABLE 4

COVERAGE OF CATALYST SURFACE BY PROMOTERS AS JUDGED BY EXCHANGE WITH $H_2{}^{18}O$ AND BY CO CHEMISORPTION

Run M No.	Catalyst	O Coverage by exch. Area per Oatom		$1 - \theta_{CO}$ Area per CO molecule	
		12 Å²	10 Å²	16.2 Å²	14.3 Å²
67	418	0.73	0.61		
70	418	0.69	0.57		
75	418	0.67	0.56	0.59	0.64
70	418	0.62	0.52	0.55	0.60
78	418	0.68	0.57		
81	418			0.58	0.63
82	418	0.67	0.56	0.57	0.62
58	927	0.099	0.083	−0.05	0.07
83	927	0.23	0.186	0.14	0.24
56	S(Fe)1		0.012	−0.13	0.00
92	954		0.78(0.62)[a]	0.59	0.64
88	Al_2O_3		1.00		
89			0.97		

[a] The value in parenthesis is for an area of 8 Å² per oxygen atom.

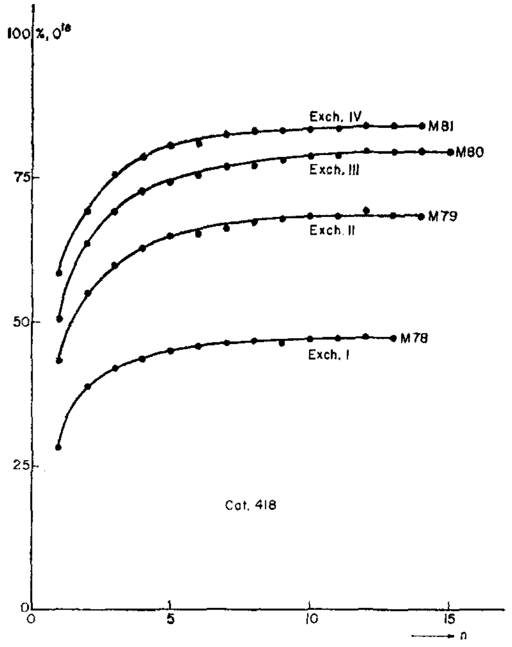

FIG. 3. The change in equilibrium concentrations in a sample exchanged four times with intervening reduction for 18 hr at 450°C with hydrogen, as a function of n, the number of introductions of the sample into the mass spectrometer.

value measured being the sample of 418 having the lowest oxygen number found (M76). The pure iron catalyst S(Fe)1 which has only 0.012×10^{15} O/cm^2 has a value of $V_{CO}/V_{N_2} = 1.13$. Catalyst 927, which is unpromoted but assumed to contain about .15% Al_2O_3, seems to contain some inhomogeneities as M58 gave $.083 \times 10^{15}$ O/cm^2, while the sample for M83 gave $.186 \times 10^{15}$ O/cm^2. The CO chemisorption values, however, are in line with this as M59 (M58 exchanged with H_2O^{18} a second time) gave $V_{CO}/V_{N_2} = 1.05$ and M83 gave 0.86.

In the above discussion and in Table 3 we have assumed that each oxygen atom on the promoter would occupy about 10 Å^2 and each CO molecule, 16.2 Å^2. Perhaps a little discussion and a few additional cross comparisons are in order.

The radius for oxygen ions in univalent crystals is, according to Pauling, 1.76 Å. This would correspond to a closest packing value of about 10.7 Å^2 per ion. For a promoter consisting of equal moles of K_2O and Al_2O_3 possibly as $KAlO_2$ a value of

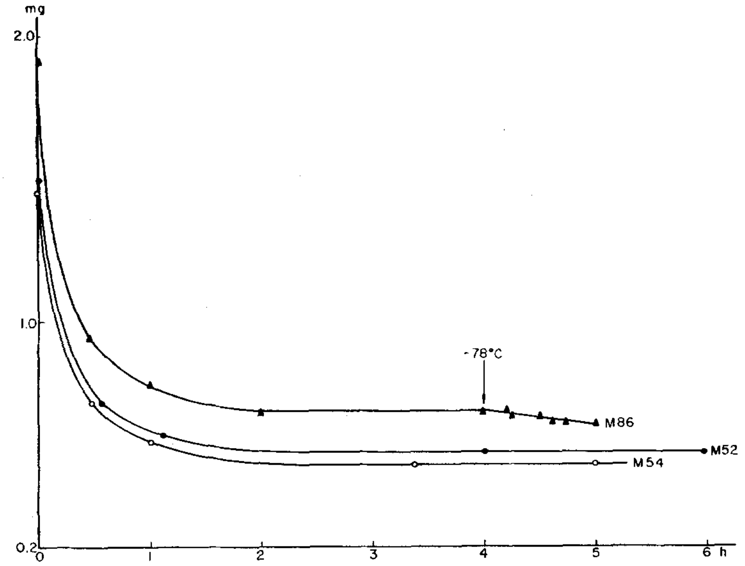

FIG. 4. The change in adsorbed CO measured in a McBain balance on three different samples with pumping at −195.8°C as a function of time. At arrow, the surrounding temperature on M86 for catalyst No. 418 was increased to −78°C.

about 12 Å^2 per oxygen seems realistic. For CO the value 16.2 Å^2 is almost certainly too large.

Probably a better value for the area covered by a molecule of carbon monoxide would be one deduced from the ratio of 1.13 volume of carbon monoxide as a monolayer compared to the volume of a monolayer of physically adsorbed nitrogen. This would correspond to a figure of 14.3 Å^2 per CO. In Table 4, for comparison, the fraction of the surface covered by the promoter on the assumption of 10 Å^2 per oxygen ion and also 12 Å^2 are shown. Also are included the surface equivalent to $1\text{-}\theta_{CO}$ where the coverage by carbon monoxide, θ_{CO} is calculated both from a value of 16.2 and a value of 14.3 Å^2 per CO molecule. It is evident that with a CO cross section of 14.3 Å^2 per molecule and an oxygen cross section of somewhere between 10 and 12 Å^2 excellent agreement is obtained for the fraction of the surface covered by promoters as judged by the oxygen-18 exchange work on the one hand and CO chemisorption on the other.

The result of catalyst 954, which is singly promoted with 10.2% Al_2O_3, is a bit uncertain because of an accident which occurred during the run (see footnote, Table 1) but the figure $.78 \times 10^{15}$ O/cm^2 is probably right within a few percent. Considering the V_{CO}/V_{N_2} value of .41 found for this catalyst, one has to assign a smaller figure for each oxygen atom to obtain a coverage for the promoter on the surface agreeing with that deduced from the carbon monoxide chemisorption. In fact, a value of 8.2 Å^2 per oxygen atom would give a perfect fit.*

The amount of carbon monoxide chemisorbed needs to be discussed a bit further. As shown in Fig. 4, the amount adsorbed was essentially constant after about 2.5–3 hr pumping at −195.8°C. The pumping system was open and very effective such that the pressure reached after about 2.5 hr was about 10^{-6} mm Hg. If we now at this constant value change the temperature to −78°C, as done on M86, we get a steady decrease in the amount adsorbed of about 5–8% per hr. This is in agreement with Scholten's experiments (*3*). Scholten is obviously right when he stresses the importance of the design of the pumping system, the diameter of the tubes, etc. on the rate of desorption of chemisorbed CO at −78°C, and the difficulty in determining the time at which the pumping should be stopped. However, the suggestions made by Brunauer and Emmett (*2*) about using the value obtained after about 0.5 hr. pumping at −78°C probably in most cases will give a value for the volume of carbon monoxide chemisorbed within 5% of the right one. It seems, however, reasonable after these experiments that adsorption and pumping at −195.8°C gives a good value for the amount of chemisorbed CO provided one has a good pumping system with large diameter tubes. Pumping for 3–4 hr at −195°C should give a steady-state value for carbon monoxide chemisorption.

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* Since only about 0.4% Al_2O_3 would be needed to cover 60% of the surface of catalyst 954, a considerable amount of the actual 10.2% Al_2O_3 must be located either on the inside of the crystallites or else in large crystals of Al_2O_3. The exact disposition of the large excess of the promoters is not, as yet, definitely known.