$$\frac{d(C_n)}{dt} = k'_s(X_n + Z_n + WY_n) = k'_sP_n \quad \text{(II-21)}$$

so that

$$P_n = f'(X_{n-1} + Z_{n-1}) + 2g'f'(X_{n-2} + Z_{n-2}) + h'\left(X_2X_{n-2} + \sum_{i=3}^{n-3}(X_i + Z_i)X_{n-i}\right) \quad \text{(II-22)}$$

The isomer and carbon number distributions may be calculated in terms of the parameters f', g' and h' from (II-22), in the same way as indicated in the text for the more simple stepwise scheme, provided the concentration of one complex is fixed. This has been done choosing the concentration of the C_2 complex as unity. These results have been compared to the experimental isomer distribution data of Bruner[12] and to the results of the stepwise schemes in Table III. The "multiple build-in" scheme appears to agree with the experimental data about as well as (or as badly as) the other schemes; similar results are obtained for cobalt catalysts. Considering the experimental difficulties inherent in obtaining such data, it is probable that all the schemes agree with them within experimental error.

As shown by Anderson,[4] given the isomer distribution, only one additional parameter is required to express the distribution of products by carbon number; the same is true of the present development. Although a detailed study of this problem has not been made, a cursory examination of the situation indicates the following:

(a) When the optimum parameters found for the isomer distribution are carried over and used to calculate the carbon number distribution, none of the schemes fit the data as well as if a new choice of all parameters is made. This may reflect the inaccuracies of the data or the approximations made or both; it may, however, be attributable to secondary processes taking place which are unaccounted for, *e.g.*, C_2H_4 build-in.

(b) All schemes tested adequately represented the data, but under the restriction posed above, the "multiple build-in" scheme did not appear to hold quite as well in the region of low carbon number, but perhaps a little better in the region above about C_{12}.

(c) On the basis of the data examined, it is concluded that the theory of "multiple build-in" presented here represents the true state of affairs to at least as good an approximation as the previous stepwise theory. It therefore tends to support the idea that chain growth occurs by simple condensation reactions involving complexes identical to those formed on adsorption of alcohols.

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[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY]

Chemisorption of Carbon Monoxide, Carbon Dioxide and Nitrogen on Nickel Catalysts

BY R. J. KOKES AND P. H. EMMETT

RECEIVED MARCH 9, 1959

The adsorption of carbon monoxide, carbon dioxide, argon and nitrogen on two types of nickel catalyst have been studied. On one of these catalysts it appears that more than one-third of the nitrogen adsorption at −195° is chemisorption. This complicates the classical procedure for studying carbon monoxide chemisorption. While carbon monoxide chemisorption may still be a useful method of estimating the surface concentration of nickel in promoted catalyst, the surface concentration of alkali promoter cannot be determined simply from carbon dioxide chemisorption.

For two decades the chemisorption of carbon monoxide has been used for estimating the fraction of the surface of iron synthetic ammonia catalyst that is covered with promoter.[1] If the catalyst contained an alkali in the promoter, the surface promoter concentration could be ascertained by measurement of the chemisorption of carbon dioxide at −78°. The carbon monoxide appeared to be chemisorbed on the iron atoms and the carbon dioxide on the alkali promoter molecules. Somewhat later,[2] it was found that similar measurements on nickel catalysts were apparently incapable of measuring the fraction of the surface of a nickel catalyst covered with alkali. The carbon monoxide and the carbon dioxide were each capable of being adsorbed in quantities sufficient to cover nearly the entire surface of the catalyst as measured by nitrogen adsorption at −195°. Very recently,[3] doubt has been thrown on the results for nickel catalysts by the discovery that nitrogen chemisorbs on nickel at −195°. Accordingly, it has seemed worthwhile to reexamine the adsorption of carbon monoxide and carbon dioxide on nickel catalysts.

Experimental

Two types of nickel catalyst were used in the present study. The first of these is designated as SE II and was prepared in the manner described by Emmett and Skau[2] for their Ni II catalyst by precipitation of the hydrous oxide from aqueous $Ni(NO_3)_2$ with NaOH. Two samples of this catalyst were studied, SE II (1) and SE II (2). The other nickel catalyst used in this study was prepared by the method used by Best and Russell.[4] Solid NH_4HCO_3 was added to a solution of $Ni(NO_3)_2$ to precipitate the basic carbonate which was calcined for 6 hr. at about 450° to convert it to NiO. Three samples of this catalyst were studied. These are designated as BR1, BR2 and BR3.

Different reduction procedures were used for the SE II (1) and SE II (2) catalyst. SE II (1) was first reduced with tank hydrogen as the temperature was raised slowly to 340°. Then, the hydrogen was purified by passage through hot copper and through a trap filled with charcoal at −195°. Reduction was continued at a space velocity of about 5000 hr.$^{-1}$ until the amount of water in the effluent gas was less than two parts per million. The catalyst was evacuated for 2 hr. at the reduction temperature prior to the start of an adsorption experiment. After completion of a series of experiments the catalyst was reduced for 2 hr. in the manner described above and evacuated 2 hr. at 340°. This is re-

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[1] P. H. Emmett and S. Brunauer, THIS JOURNAL, **59**, 310, 1553 (1937).

[2] P. H. Emmett and N. Skau, *ibid.*, **65**, 1029 (1943).

[3] R. J. Kokes and P. H. Emmett, *ibid.*, **80**, 2082 (1958).

[4] R. H. Best and W. W. Russell, *ibid.*, **76**, 838 (1954).

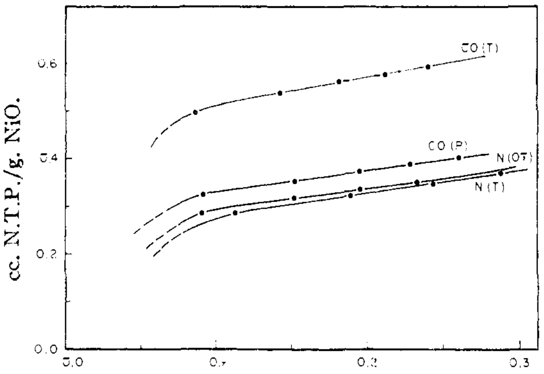

Fig. 1.—Nitrogen and carbon monoxide adsorption on SE II (1) catalyst (runs 9 to 12, Table I).

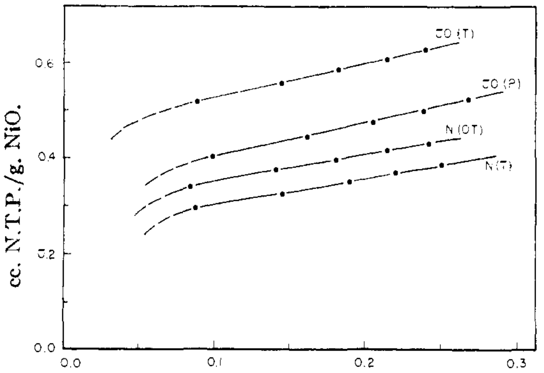

Fig. 2.—Nitrogen and carbon monoxide adsorption on SE II (2) catalyst (runs 16 to 19, Table I).

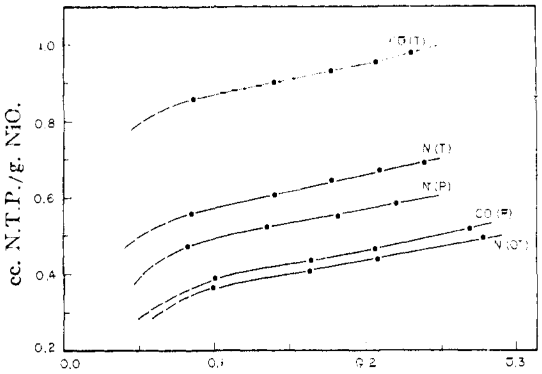

Fig. 3.—Nitrogen and carbon monoxide adsorption on BR2 catalyst (runs 1 to 6, Table II).

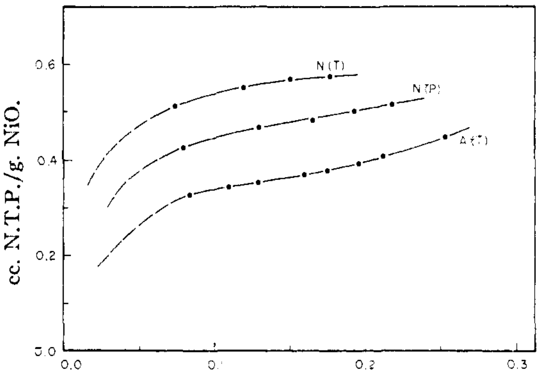

Fig. 4.—Nitrogen and argon adsorption on BR3 catalyst (runs 1 to 4, Table II).

ferred to in the text as regenerative reduction. The second sample of the catalyst SE II (2) was reduced with the same schedule used by Emmett and Skau,[2] namely, 4 hr. reduction at 360° with a hydrogen space velocity of 2000 hr.$^{-1}$; no charcoal trap was used in the hydrogen purification train.

Reduction of the BR1, BR2 and BR3 catalyst was accomplished with hydrogen purified in the aforementioned manner (including a charcoal trap −195°). The reduction was carried out at 325° at a space velocity of 2500–3000 hr.$^{-1}$ until the exit gas contained less than 0.02% water. The catalyst was evacuated for one or two hours at 325° prior to the start of the adsorption experiments. Regenerative reductions, analogous to those for SE II catalysts, were carried out between each set of experiments.

All adsorption runs with carbon monoxide, argon and nitrogen were carried out at −195°. The amount of carbon monoxide or nitrogen chemisorption could be estimated in the standard fashion[1] by first determining the total physical + chemical adsorption at a suitable low temperature, T_1 (−195° for nitrogen or carbon monoxide; −78° for carbon dioxide) then raising the temperature of the samples to T_2, and evacuating it for one hour. The sample then was cooled to T_1 and the isotherm was redetermined. T_2 was arbitrarily selected in earlier work on the CO–Fe system as −78°; this was used both for carbon monoxide and nitrogen in the present work. For carbon dioxide, T_2 was room temperature. Any alterations in this procedure are clearly indicated in the text.

In order to identify these various isotherms the following nomenclature has been adopted: CO(T) refers to the total carbon monoxide adsorption at −195° on a virgin or regenerated catalyst; CO(P) refers to the adsorption of carbon monoxide at −195° (presumably physical) after adsorption at T_1 and a standard one hour evacuation at T_2; N(OT) refers to the adsorption of nitrogen at −195° (presumably on top of a layer of chemisorbed carbon monoxide) after adsorption of carbon monoxide at T_1 and a standard evacuation at T_2. The symbols N(T), N(P), CO_2(T), CO_2(P), A(T) have the same significances, *mutatis mutandis*. If no chemisorption occurs, it should be clear that both N(T) and N(P) refer to physical adsorption. The symbol V^0 followed by one of the above designations refers to the amount adsorbed at P/P_0 = 0.1.

Amounts of adsorption are consistently expressed in cc. S.T.P. adsorbed gas/g. of unreduced catalyst.

Results

All the results obtained with SE II catalyst are summarized in Table I. Illustrative plots of these data are shown in Figs. 1 (SE II 1) and 2 (SE II 2). Results for BR catalysts are summarized in Table II and also in Fig. 3 (BR2) and Fig. 4 (BR3).

Discussion

Detailed examination of these data enables us to make several observations:

1. **Nitrogen Chemisorption.**—Comparison of N(OT) with N(T) isotherms suggests the nitrogen chemisorption does not occur on SE II catalyst.

The N(P) isotherms for BR catalysts are always significantly less than the N(T) isotherms (*cf.* Figs. 3 and 4). According to our criteria this clearly suggests nitrogen chemisorption. Since the catalyst is restored to its initial state by evacuation at room temperature (runs 1, 2, 3 for BR2 catalyst) this chemisorbed nitrogen is removed readily and, hence, must be weakly held. Evidence that some chemisorbed nitrogen is removed by evacuation even at −78° is given on comparison of V_m values for N(P) and N(OT) in Table I, column 5. The former is always definitely greater than the latter (see also Fig. 3) and since one would expect N(OT) to be a valid measure of physically adsorbed nitrogen, it appears that N(P) isotherms include some

TABLE I

ADSORPTION ON SE II Ni CATALYST

Run no.	Isotherm[g]	Temp., °C.	Pretreatment[h]	V_m, cc./g.	$V°(T)$,[a] cc./g.	$V°(T) - V°(P)$, cc./g.	$V°(T) - V°N(T)$, cc./g.	$\frac{V°CO(T) - V°CO(P)}{V_mN_2{}^b}$	$\frac{V°CO(T) - V°N(T)}{V_mN_2{}^b}$
SE II (1) (23 g. NiO)									
1	N(T)	−195	Initial reduction	0.261					
2	CO(T)	−195	16 hr. evacuation at rm. temp.		0.555		0.291[d]		1.11[d]
3	CO(P)	−195	1 hr. evacuation at −195°	.273					
4	N(OT)	−195	1 hr. evacuation at −195°	.222					
5	N(T)	−195	Regenerative reduction	.243					
6	CO(T)	−195	16 hr. evacuation at rm. temp.		.435		.191[d]		0.79[d]
7	CO(P)	−195	1 hr. evacuation at −78°	.304		.122[c]		0.50[c]	
8	N(OT)	−195	1 hr. evacuation at −78°	.270					
9	N(T)	−195	Regenerative reduction	.270					
10	CO(T)	−195	16 hr. evacuation at rm. temp.		.515		.235[d]		.87[d]
11	CO(P)	−195	1 hr. evacuation at −78°	.300		.187[c]		.69[c]	
12	N(OT)	−195	1 hr. evacuation at −78°	.278					
13	N(T)	−195	Regenerative reduction	.218					
14	CO_2(T)	− 78	1 hr. evacuation at room temp.		.400		.174[e]		.80[e]
15	CO_2(P)	− 78	1 hr. evacuation at rm. temp.	.215		.192[e]		.88[e]	
SE II (2) (20.0 g. NiO)[f]									
16	N(T)	−195	Initial reduction	.310					
17	CO(T)	−195	16 hr. evacuation at room temp.		.530		.225[d]		
18	CO(P)	−195	1 hr. evacuation at −78°	.395		.125[c]		.40[c]	.73[d]
19	N(OT)	−195	1 hr. evacuation at −78°	.330					

[a] This is the amount of $CO(CO_2)$ adsorbed on a clean catalyst at $P/P_0 = 0.10$. [b] This is the V_m value for the first N(T) isotherm in the cycle. [c] The amount of CO chemisorbed was assumed to be the difference between the total amount CO adsorption on a clean catalyst and that adsorbed in the succeeding experiment after a 1 hr. evacuation at −78°. [d] The amount of CO chemisorbed was assumed to be the difference between the amount of N_2 adsorbed on a clean catalyst and the amount of CO adsorbed on a clean catalyst at $P/P_0 = 0.10$. [e] These values were calculated in a fashion analogous to that used with CO. [f] The reduction procedure for this sample was identical to that used by Emmett and Skau.[2] [g] See Experimental section for the meaning of these symbols. [h] This is the treatment prior to the indicated run immediately after the preceding run.

very weak chemisorbed nitrogen. (This last conclusion includes the tacit assumption that chemisorbed carbon monoxide does not greatly inhibit physical adsorption of nitrogen.) If chemisorbed carbon monoxide blocks out chemisorbed nitrogen without influencing the volume of physically adsorbed nitrogen, then N(T) − N(OT)(*cf.* Fig. 3) is the best measure of the amount of chemisorbed nitrogen and V_mN(OT) is the best measure of a monolayer of adsorbed nitrogen. If we take the cross-sectional area of the chemisorbed nitrogen as 16.2 Å.,[2] then we would conclude that about 57% of the surface will chemisorb nitrogen at −195°.

2. Carbon Monoxide Chemisorption.—Classical studies of carbon monoxide chemisorption generally include the assumption that only physically adsorbed carbon monoxide is removed by evacuation at −78°. Three situations can be imagined which would require different interpretations: (a) If this is true and there is no N_2 chemisorption, then since carbon monoxide and nitrogen have comparable cross-sections $V(T)N = V(P)CO$. (b) If this is true and there is nitrogen chemisorption but this is "blocked-out" by carbon monoxide chemisorption and the latter does not significantly enhance physically adsorbed nitrogen, then $V(T)N > V(P)CO = V(OT)N$. (c) Lastly, if chemisorbed carbon monoxide is partly removed by standard evacuation and there is no chemisorbed nitrogen, then $V(T)N < V(P)CO$ and the former is the best measure of the amount of physically adsorbed nitrogen. For these three cases the best estimates of the amount of chemisorbed carbon monoxide are: (a) $V°(T)CO - V°(P)CO \approx V°(T)CO - V°(T)N$; (b) $V°(T)CO - V°(P)CO$ or $V°(T)CO - V°N(OT)$; and (c) $V(T)CO - V(T)N$.

Clearly, there is no nitrogen chemisorption on the SE II catalysts. (Compare N(T) and N(OT) in Fig. 1 and 2.) We have calculated the amounts of chemisorbed carbon monoxide for cases a and c in columns 7 and 8 respectively in Table I. We have also calculated the fraction of the surface covered with carbon monoxide (assuming it has a cross section of 16.2 Å.[2]) in columns 9 and 10. Clearly, (Figs. 1 and 2, Table I, column 5) these catalysts conform to case c and the values in columns 8 and 10 of Table I are the best estimates. On this basis roughly 90% of the surface of SE II-1 will chemisorb CO. If we assume the cross sectional area of chemisorbed carbon monoxide is 12Å.[2], while that of physically adsorbed carbon monoxide is 16.2 A.[2], we find that 70% of the surface will chemisorb carbon monoxide. These results are at variance with those of Emmett and Skau[2] who found that the amount of chemisorbed carbon monoxide was 1.78 V_mN(T).

The BR catalysts conform to case b. The ratio of chemisorbed carbon monoxide (at −195°) to V_mN(OT) ranges from 1.24 to 1.3 (Table II runs 10 through 17 BR1, and 1 through 6, BR2). If part of this carbon monoxide is chemisorbed at or above −78°, this ratio may be as high as 1.6. This latter observation is similar to that reported in earlier work on iron catalysts.[6] If N(OT) constitutes the best basis for determining V_m, the cross-sectional area of a chemisorbed carbon monoxide molecule (at −195°) is 13 Å.[2], the same as the value observed for iron catalysts.

TABLE II

ADSORPTION ON BR Ni CATALYSTS AT −195°

Run no.	Isotherm[i]	Pretreatment[j]	$V^0(T)$[a]	$V_m$cc./g.	V_{chem},[b] cc./g.
		Sample BR (1) (40 g. NiO[c])			
1[d]	N(T)	Initial reduction		0.552	
2[d]	N(T)	Regenerative reduction		.530	
3[d]	CO(T)	16 hr. evacuation at 25°	0.930		
4[d]	CO(P)	1 hr. evacuation at −78°		.378	0.554
5[d]	N(OT)	1 hr. evacuation at −78°		.347	
6[d]	N(T)	Regenerative reduction		.495	
7[d]	CO(T)	16 hr. evacuation at 25°	.880		
8[d]	CO(P)	1 hr. evacuation at −78°		.358	.520
9[d]	N(OT)	1 hr. evacuation at −78°		.328	
10[e]	N(T)	Regenerative reduction		.497	
11[e]	CO(T)	16 hr. evacuation at 25°	.785		
12[e]	CO(P)	1 hr. evacuation at −195°		(.253)[g]	(.553)[g]
13[e]	N(OT)	1 hr. evacuation at −195°		(.263)[g]	
14[e]	N(T)	Regenerative reduction		.470	
15[e]	CO(T)	16 hr. evacuation at 25°	.763		
16[e]	CO(P)	1 hr. evacuation at −195°		(.280)	(.545)[g]
17[e]	N(OT)	1 hr. evacuation at −195°		(.258)[g]	
18[e]	N(T)	Regenerative reduction		.480	
19[f]	CO(T)	16 hr. evacuation at 25°	.849		
20[e]	CO(P)	1 hr. evacuation at −195°		(.252)[g]	(.615)[g]
21[e]	N(OT)	1 hr. evacuation at −195°		(.244)[g]	
		Sample BR (2) (21.4 g. NiO[c])			
1[e]	N(T)	Initial reduction		0.547	
2[e]	N(P)	1 hr. evacuation at −78°		.481	0.080
3[e]	N(T)	1 hr. evacuation at 35°		.547	
4[e]	CO(T)	16 hr. evacuation at 30°	0.864		
5[e]	CO(P)	1 hr. evacuation at −78°		.388	.481
6[e]	N(OT)	1 hr. evacuation at −78°		.369	
7[eh]	N(T)	Regenerative reduction		.533	
8[eh]	N(P)	1 hr. evacuation at −78°		.467	.093
		Sample BR (3) (23.2 g. NiO)			
1[e]	A(T)	Initial reduction		0.324	
2[e]	N(T)	16 hr. evacuation at 30°		.490	
3[e]	N(P)	1 hr. evacuation at −78°		.410	0.085
4[e]	A(T)	1 hr. evacuation at 30°		.336	

[a] This is the total volume of CO adsorbed at $P/P_0 = 0.10$. [b] This is the difference between the isotherm on a clean catalyst and the isotherm obtained after the catalyst was exposed to the gas at −195° and evacuated for 1 hr. at −78°. [c] The weight of sample I was not accurately known. The sample tube was accidentally broken before the weight could be obtained. For the purposes of the discussion in the text only the relative values of the adsorption are important but in order to be consistent throughout we have expressed these values in cc./g. on the basis of a weight estimated by the volume of the sample (*i.e.*, 40 g.). [d] In this run the sample was cooled from room temperature *in vacuo* to −195°. [e] In this run the sample was cooled in He to −195°. [f] In this run the sample was cooled in He to −78° and exposed to CO at this temperature for 5 minutes. The sample then was cooled from −78 to −195° with the CO. [g] The meaning of these values is subject to some question. See text. [h] These values were previously reported and are included here for the sake of completeness. See the experimental section for the meaning of these symbols. [i] This is the treatment prior to the run indicated immediately after the preceding run.

3. Reproducibility.—Duplicate sets of runs on the same sample of SE II catalyst with intervening regenerative reduction yielded V_mN(T) values differing as much as 20% (*cf.* Table I—column 5). This variation probably was not due to sintering. Data for V°CO(T) isotherms in the same sequence also showed similar variations (Table I—column 6), and these variations appeared to be uncorrelated to those of V_mN(T). It appears that the surface chemistry of the SE II catalysts is a sensitive function of its previous history.

Duplicate runs on the same sample of BR catalyst were reproducible and such variations as did occur in V_mN(T) could be ascribed to sintering (Table II—column 5). Variations in the value of $V^\circ T$(CO) (Table II—column 4) can be associated with the fact that carbon monoxide adsorption is more extensive at about −78° than at −195°; consequently, all samples cooled to −195° in helium have smaller CO(T) adsorption than those cooled in a vacuum or from −78° in CO.

Reasons for the different behavior of SE II and BR catalyst are not known. It is possible that small amounts of residual alkali are present in the SE II catalyst which are not present in BR catalysts[5]; this might be a partial cause of the difference in sensitivity to pretreatment.

4. Synergetic Adsorptions.—In all significant runs on the SE II catalysts the N(OT) isotherm is higher than the N(T) isotherm (Table I—column 5). This difference is again a function of pretreatment and ranges from a few % (Fig. 1) to about

20% (Fig. 2). Clearly, chemisorbed carbon monoxide enhances the physical nitrogen adsorption; no cogent explanation for this can be given.

On BR catalysts the N(OT) is definitely not greater than N(T); it may or may not be greater than the true physical adsorption of nitrogen. The presence of weak chemisorbed nitrogen makes the true value of the physical adsorption uncertain.

5. Carbon Dioxide Chemisorption.—The volume of chemisorbed carbon dioxide is about 80% of the volume of nitrogen required to form a physically adsorbed monolayer. Either carbon dioxide is chemisorbed on both alkali and nickel atoms or else each alkali molecule holds two rather than one carbon dioxide molecule. In any event for the SE II catalyst the sum of the area covered by chemisorbed carbon monoxide plus that covered by chemisorbed carbon dioxide is about 50% larger than the area as measured by a BET plot of the physically adsorbed nitrogen.

6. Argon Adsorption.—If N(OT) does represent the best measure of physically adsorbed nitrogen this value should be comparable to that found from A(T) when the argon is assigned a cross-sectional area of 15.2 Å.[2,5,6] Comparison of the runs for the BR3 catalyst with those for BR2 and BR1 catalyst (Table I, Fig. 3 and 4) shows that the data are consistent with this interpretation. Agreement of the surface area determined by argon with surface area determined from N(OT) is almost exact if the latter value is scaled up to bring the N(T) values for BR2 and BR3 into agreement.

In summary, the present work suggests that the fraction of the surface of a nickel catalyst containing nickel atoms probably can be estimated by carbon monoxide chemisorption. The total area of the catalyst should preferably be measured with argon. If nitrogen is used great care has to be taken to make sure that the volume of nitrogen calculated for a monolayer does not include a considerable amount of chemisorbed nitrogen.

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[CONTRIBUTION FROM THE ESSO RESEARCH LABORATORIES]

The Structures of Synthetic Molecular Sieves

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The crystal structures of synthetic molecular sieves commonly identified as 4A ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot xH_2O$), 5A (1/3 $Na_2O \cdot$ 2/3 $CaO \cdot Al_2O_3 \cdot 2\ SiO_2 \cdot xH_2O$) and 13X ($Na_2O \cdot Al_2O_3 \cdot 2.8\ SiO_2 \cdot xH_2O$) have been determined in their hydrated forms (containing 25–35 wt. % H_2O). These studies show that all three sieves have a common building block called a "sodalite" unit, containing 24 (Si,Al) ions interconnected with 36 oxygen ions. In the 4A and 5A sieves these sodalite units are arranged in a simple cubic array, with each sodalite unit connected to its neighbor by four bridge oxygen ions. In 13X, sodalite units are in tetrahedral coördination (diamond array) with each sodalite unit connected to its neighbor by six bridge oxygen ions. Three-dimensional Fourier analyses were employed to refine atomic positions of the framework and to locate cations. Most of the cations were found near the centers of six-membered rings of oxygen ions in the soda.

Introduction

Synthetic molecular sieves are crystalline zeolitic aluminosilicates that are of general interest because of their selective adsorptive properties.[2] These selective adsorptive properties are due to a crystal structure incorporating interconnecting channels and cavities of definite and uniform size. Molecules having appropriate dimensions with respect to these channels can enter and be adsorbed in the internal cavities.

The molecular sieves commonly identified as 4A, 5A and 13X are crystalline alumino-silicates precipitated from an alkaline mixture of silica and alumina. The 4A sieve is a sodium alumino-silicate which adsorbs only molecules smaller than propane. The 5A sieve results from exchanging replaceable Na ions in 4A with Ca ions. It adsorbs molecules smaller in cross section than *iso*-paraffins or aromatics. The 13X sieve has even larger channels and adsorbs most ordinary hydrocarbons.

The crystal structure of 4A and 5A type sieves has been discussed by Reed and Breck[3] and by Barrer.[4] The crystal structure of 13X sieves is known from its powder diagram to be essentially the same as that of the naturally occurring mineral faujasite. The structure of natural faujasite has been described by Nowacki and Bergerhoff.[5]

The crystal structures of the hydrated form of the two major types of synthetic sieves, 4A-5A and 13X, were deduced independently in this Laboratory. Our development of these structures was based on our early recognition of a cubo-octahedral structural unit, similar to that in the mineral sodalite, as being the fundamental building block of both types of sieves; this was independently recognized by Barrer.[6] An alternative structural unit, a small alumino-silicate cube, has been cited as the fundamental unit in the description of 4A-5A.[3]

This report outlines our parallel work in elucidating the fundamental structural framework of these materials, and in addition describes more extensive studies of them, in particular the appli-

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