lakes. The lakes formed by adding a drop of a solution containing at least 0.2 mg./ml. of the respective dyes to a little solid palladium(II) cyanide on a piece of filter paper are dark blue and red-pink, respectively. Hence it is easy to differentiate between drops of solutions which contain at least approximately 0.2 mg. of dye per milliliter.

Palladium(II) cyanide also forms adsorption complexes with many alkaloids. Dilute hydrochloric acid solutions of caffeine, theobromine, quinine, ephedrine and berberine were prepared which gave a turbidity on the addition of phosphomolybdic acid. About 5 ml. of these solutions was shaken with palladium(II) cyanide and filtered. On the addition of phosphomolybdic acid, the solution remained clear, showing that the alkaloids were completely adsorbed by the palladium(II) cyanide. Some of the caffeine adsorption complex with palladium(II) cyanide was prepared by heating a suspension of the cyanide in an aqueous solution of caffeine. After drying the residue at 110° the palladium content was found to be 52.5%. Thus in spite of its large molecular volume, caffeine forms the same type of adsorption complex as do the amines which have a smaller molecular volume. It is thus possible to concentrate alkaloids by forming adsorption complexes with palladium(II) cyanide and decomposing the complex in a suitable manner.

Acknowledgment.—One of us, G.B.H., wishes to express his appreciation to the Ministry of Agricultura do Brazil for permission to work in the laboratories of the Departamento da Producão Mineral, to the University of Minnesota for the sabbatical leave, and to Messrs. W. Cummings and H. Turner for nitrogen, carbon and hydrogen analyses.

Minneapolis, Minn. Received November 24, 1950

[Contribution from the Research and Development Division of Humble Oil and Refining Co.]

In Situ X-Ray Diffraction Studies of Heterogeneous Reactions[1]

By M. A. Mosesman

An apparatus embodying a metallic microreactor of approximately 0.002-ml. capacity, fabricated from high purity, machinable beryllium rod, has been developed and utilized for the investigation of the changes that occur in solid materials through chemical interaction with gaseous reactants in a flow system as revealed by *in situ* X-ray powder diffraction patterns. The construction of the apparatus is such as to permit operations at pressures and temperatures as high as 11 atmospheres and 650°, respectively, and flow rates as low as 1.0 ml./hr. The X-ray diffraction data obtained in the application of this apparatus to the determination of the stable oxidation states of iron in an ammonia synthesis catalyst and of molybdenum in bulk and alumina-supported molybdenum trioxide in reducing and oxidizing atmospheres identify Fe_3O_4, FeO and Fe in the former instance and MoO_3 and MoO_2 in the latter instances during the course of the reactions observed under the imposed operating conditions.

Introduction

The reliability and accuracy, as well as the limitations, of the X-ray powder diffraction technique for the examination and identification of solids and solid mixtures are well established,[2] but the application of this method in a conventional manner to the investigation of the changes that occur in solid materials participating in heterogeneous chemical reactions is generally time-consuming and laborious. Moreover, X-ray diffraction data obtained on samples necessarily removed from a reaction zone under reaction conditions frequently may be ambiguous unless adequate precautions are taken to insure that the atmospheres to which the sample is subjected subsequent to its removal are nonreactive. As a consequence, it is extremely desirable to have available for optimum results a means of obtaining *in situ* diffraction patterns under reaction conditions. A number of recent investigators[3–7] have developed X-ray cameras for obtaining diffraction data at elevated temperatures, under controlled atmospheres in some instances, or elevated pressures, but, in general, these apparatus are not readily adaptable to the study of solids in heterogeneous, dynamic reaction systems. The first report of an apparatus especially designed for obtaining X-ray diffraction patterns of powders in contact with a flowing gas under varying conditions of pressure and temperature was disclosed by Long.[8] The present research reports some further applications of this apparatus in the investigation of gas–solid reactions between ammonia synthesis catalyst, bulk molybdenum trioxide, and alumina-supported molybdenum trioxide and reducing or oxidizing atmospheres. In view of the generally limited dissemination of the foregoing reference, a brief description of the apparatus as currently constituted is also included.

Experimental

Apparatus.—The essential feature of the apparatus is the metallic microreactor of approximately 0.002-ml. capacity fabricated from high purity, machinable beryllium rod;[9] the selection of beryllium for construction of the microreactor was dictated by the need for a material possessing a low X-ray absorption coefficient[10] and a simple X-ray diffraction pattern and capable of withstanding operations at elevated pressures and temperatures. The design of the beryllium microreactor assembly is shown in Fig. 1. The microreactor A is mounted in a hollow steel housing B threaded internally at each end and provided with entrance and exit openings for the respective collimated and diffracted X-ray beams. Steel unions C exerting compressive force against specially made copper ferrules D on each end of the microreactor maintain the latter gas-tight and rigid within the housing. These unions also provide the means of attaching charge and exit gas lines. The microreactor-housing-union assembly is surrounded by a well-insulated resistance heater E wound upon a Pyrex tube containing openings that coincide with those of the housing. Appropriately sized openings are also provided through the insulating material for

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[1] Presented at the 119th Meeting of the American Chemical Society at Cleveland, Ohio, April, 1951.

[2] See, for example, W. T. Sproull, "X-Rays in Practice," McGraw-Hill Book Company, Inc., New York, N. Y., 1946.

[3] M. J. Buerger, N. W. Buerger and F. G. Chesley, *Am. Mineral.*, **28**, 285 (1943).

[4] J. J. Lander, *Rev. Sci. Instruments*, **20**, 82 (1949).

[5] J. W. Edwards, R. Speiser and H. L. Johnston, *ibid.*, **20**, 343 (1949).

[6] A. N. Lawson and N. A. Riley, *ibid.*, **20**, 763 (1949).

[7] P. Gordon, *J. Applied Phys.*, **20**, 908 (1949).

[8] R. W. Long, U. S. Patent 2,483,500.

[9] Obtained from Brush Beryllium Company, 3714 Chester Avenue, Cleveland, Ohio.

[10] H. Brackney and Z. J. Atlee, *Rev. Sci. Instruments*, **14**, 59 (1943).

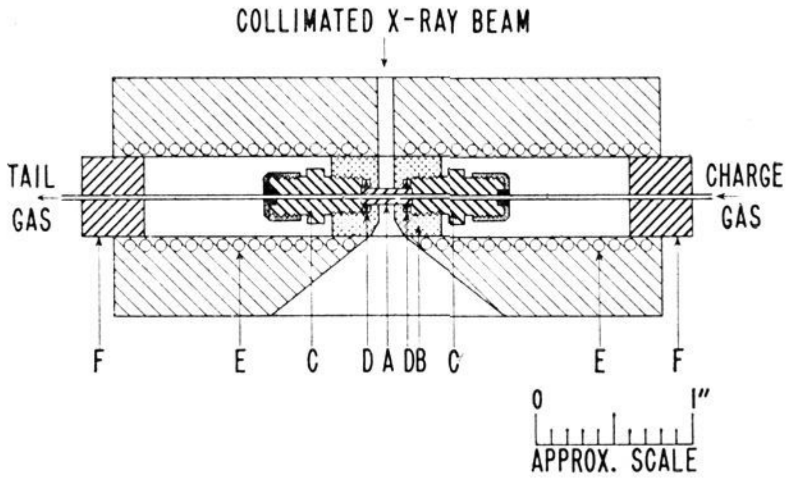

Fig. 1.—Beryllium microreactor assembly.

the collimated and diffracted X-ray beams; the considerably larger size opening on the diffracted beam side is covered with aluminum foil in order to keep radiation heat losses small. Transite supports F that fit into the heater tube and through which pass the charge and exit gas lines support the entire assembly and minimize heat losses. A molybdenum target X-ray tube with a zirconium filter is employed in order to take advantage of the penetrating MoKα X-radiation, thereby minimizing exposure time; in general, satisfactory diffraction patterns are recorded with a film cassette during exposures of 2–3 hours. Although the construction of the microreactor assembly limits the maximum diffraction angle that can be recorded to approximately 30°, this limitation is not critical since the strong, identifying reflections of all the materials studied are within the observable range.

Temperature calibration of the apparatus is accomplished primarily by means of an end-to-end (butt-weld) iron–constantan thermocouple with the junction directly in the X-ray beam as evidenced by observation of the fluorescent radiograph. Figure 2 shows a plot of microreactor temperature as a function of power input to the resistance heater for temperatures as high as 575°. In order to provide an independent check on the accuracy of the temperature calibration by thermocouple measurements, the method described by Buerger, Buerger and Chesley[3] involving the X-ray detection of sharp and readily reversible transition points of salts exhibiting polymorphism was employed. The results obtained on NH_4Cl, NH_4ClO_4 and $KClO_4$ with this technique, also shown in Fig. 2, were in good agreement with those obtained from thermocouple measurements in the temperature range of comparison. For temperatures above 575°, recourse was had to linear extrapolation of the calibration curve in the 300–575° range. It is estimated that the calibration data are accurate to better than ±5°.

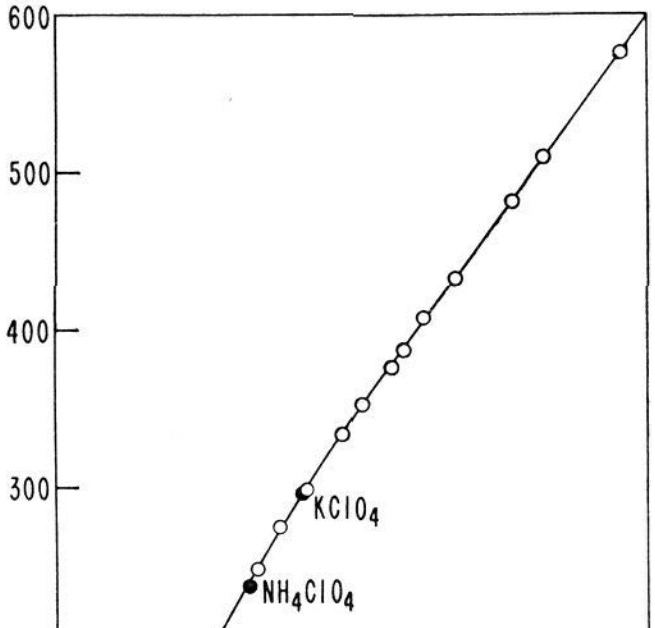

Fig. 2.—Temperature calibration curve for microreactor.

The X-ray microreactor apparatus exclusive of the components described above and the usual items required for X-ray diffraction work consists essentially of the piping, valves and other equipment required for maintaining the system under vacuum, for contacting the solid material in the microreactor with a gas or gas mixture at a desired pressure and flow rate, and for collecting the tail gas by liquid displacement for subsequent analysis.

Operation of the apparatus after charging the microreactor with the solid, assembling the components, and pressure-testing may be classified as either "intermittent" or "continuous." The former category comprises operation under desired conditions for relatively short periods (15 minutes to 2 hours), after which the gas flow is interrupted, the system evacuated, and an exposure obtained. This procedure is effective in minimizing a possible failure to detect any rapid changes in the sample under study. The latter category embraces operation under desired conditions for lengthy periods (several days to weeks) in which the gas flow is not interrupted during exposures.

Materials.—The solid materials employed in this research, with the exceptions noted below, were of standard C.P. quality. Cylinder gases from The Matheson Company, East Rutherford, New Jersey, were used without further purification except in the case of hydrogen; the electrolytic hydrogen, containing 0.2% H_2O as the only impurity, was charged to the apparatus through a $Mg(ClO_4)_2$ drier.

Ammonia Synthesis Catalyst.—This material is a commercial catalyst manufactured by Consolidated Mining and Smelting Company, Trail, British Columbia. Analysis of the catalyst indicated 65.5% Fe, 25.5% O, 3.5% Al_2O_3, and 1.5% K_2O.

20% MoO_3 on γ-Al_2O_3.—The preparation of this material was carried out by slurrying a solution containing the required amount of MoO_3 with the appropriate quantity of Aluminum Company of America H-40 Grade Alumina, ball-milling the resulting mixture for 20 hours, and then drying for 20 hours at 105°. The dried product was heated for 30 minutes at 150° and then subjected to a calcination treatment in which the temperature was increased at the rate of 50° per 15 minutes until a temperature of 370° was reached, after which the temperature was increased rapidly to 650° and maintained at that level for 6 hours. The calcined material was then cooled to 105° and formed into pills to yield the final product.

Data and Discussion

I. Ammonia Synthesis Catalyst.—The reaction conditions and results obtained in the investigation of this catalyst are summarized in Table I. The diffraction pattern of the fresh material showed only the presence of Fe_3O_4. Following the initiation of continuous hydrogen flow at 371°, 1.34 atmospheres, and 1.5 ml./hr., essentially no reduction occurred during the first 60 hours of operation. The first evidence of reduction was observed soon after hr. 60 with the appearance of the strongest iron reflection, 2.01 Å. Continued operation at the initially imposed conditions produced a gradual increase in the intensity of the 2.01 Å. line, but at hr. 135 the presence of Fe_3O_4 was still clearly evident in the diffraction pattern. Accordingly, the temperature was increased to 413° in an effort to accelerate reduction; this higher temperature in conjunction with the installation of a $Mg(ClO_4)_2$ drier in the hydrogen charge line markedly increased the rate of reduction. In addition to the diminishing intensity and essentially complete disappearance of the Fe_3O_4 pattern observed during the period 135-343 hours, the presence of FeO was detected after hr. 262. Moreover, when reduction was finally terminated after 444 hours of operation,

TABLE I

In situ X-RAY DIFFRACTION STUDY OF AMMONIA SYNTHESIS CATALYST[a]

Reaction	Hours	Reaction conditions			Type of operation[b]	Substances identified[c]	No. of X-ray patterns
		T, °C.	P., atm.	Flow rate, ml./hr.			
I. Reduction with H_2	0–60	371	1.34	1.5	C	Fe_3O_4, Be	6
	60–135	371	1.34	1.5	C	Fe_3O_4, Fe, Be[d]	8
	135–343	413	1.61	1.5	C	Fe_3O_4, FeO, Fe, Be[e]	17
	343–444	413	1.61	1.5	C	FeO, Fe, Be[f]	9
II. Oxidation with 40.0% H_2, 35.4% CO_2, 24.6% CO	0.0–0.25	343	11.20	1.0	I	Fe_3O_4, FeO, Fe, Be[g]	1
	0.25–2.0	343	11.20	1.0	I	Fe_3O_4, Fe, Be[h]	10
	2.0–8.5	343	11.20	1.0	I	Fe_3O_4, FeO, Fe, Be[i]	15
	8.5–48.5	343	11.20	1.0	I	Fe_3O_4, FeO, Be	9
	48.5–75	343	11.20	1.0	C	Fe_3O_4, FeO, Be[j]	3
	75–247	357	11.20	1.0	C	Fe_3O_4, Be[k]	12

[a] Consolidated Mining & Smelting Co. Ammonia Synthesis Catalyst. [b] C, continuous; I, intermittent. [c] Diffraction patterns obtained with MoKα X-radiation. [d] Strongest Fe line, first observed after hr. 60, increasing in intensity. [e] Weak Fe_3O_4 reflections; FeO observed after hr. 262. [f] Weak FeO reflections; reduction terminated. [g] Strongest Fe line decreasing in intensity; few weak, unidentified lines. [h] Fe_3O_4 reflections increasing in intensity; few weak, unidentified lines. [i] FeO observed after hr. 2; Fe essentially absent after hr. 8. [j] Weak FeO reflections. [k] Oxidation terminated.

the pattern of FeO, although weak, was still discernible in the presence of the strong pattern of iron. The detection of FeO during this phase of the study is convincing evidence that all of the reduction of this particular material does not proceed directly from Fe_3O_4 to iron, especially since Gulbransen and Ruka[11] have shown that the solid phase reaction between elemental iron and Fe_3O_4 to yield FeO is thermodynamically unfeasible below 570°. Further, despite the greater thermodynamic stability of iron with respect to FeO under the imposed reaction conditions, the rate at which the latter was reduced to the former was quite slow.

Oxidation of the reduced ammonia synthesis catalyst was carried out with a gaseous mixture comprised of 40.0% H_2, 35.4% CO_2 and 24.6% CO flowing initially at 343°, 11.20 atmospheres and 1.0 ml./hr. In view of the high oxidizing potential of the feed mixture ($CO_2/CO = 1.4$) and in order to establish the first changes that occurred in the reduced catalyst, the early stages of operation were intermittent. The diffraction pattern obtained after only 15 minutes of oxidation revealed a pronounced decrease in the intensity of the strongest iron line and the appearance of several lines identifying Fe_3O_4; no significant change in the FeO pattern was noted. Several unidentified lines, possibly attributable to carbide formation, also were observed, but their scarcity and weak intensity did not permit positive identification. Additional short periods of oxidation through hr. 2 resulted in a continued increase in the intensity of the Fe_3O_4 pattern with a corresponding diminution in the intensity of that of iron; in fact, the latter intensity had decreased to such an extent after an aggregate 75 minutes of oxidation that only the strongest iron line was discernible. The FeO which persisted during the first 15 minutes of oxidation was no longer present at the end of a second equivalent period. However, subsequent to hr. 2 FeO was again detected in the diffraction patterns and its presence in decreasing concentrations was noted through hr. 75; iron, on the other hand, was essentially absent after hr. 8. Although complete oxidation of the catalyst was not achieved at 343° during 75 hours of operation, an increase in operating temperature to 357° was sufficient to effect the conversion of the remaining FeO to Fe_3O_4 in a relatively short time. Since additional lengthy operations at this temperature produced no further change in the Fe_3O_4 diffraction pattern, oxidation was terminated at hr. 247.

The identification of FeO as a definite intermediate in both the reduction and oxidation phases of this study proves that at least a portion of the reduced material is oxidized by retracing the reduction path involving FeO. If the principle of microscopic reversibility is indeed operative in these reactions, the H_2O necessary for oxidation must originate with reversal of the water gas shift reaction. Inasmuch as the ammonia synthesis catalyst is active in the water gas shift equilibrium, an acceptable explanation for the formation of H_2O in the reaction zone is available, especially in view of the high CO_2/CO ratio in the feed gas. On the basis of water gas shift equilibrium, calculations indicate that the equilibrated feed would contain approximately 2.7% H_2O; this relatively low concentration of oxidizing agent presumably could account for the observed slow oxidation rate. Such a gross mechanism for the oxidation reaction obviously is oversimplified in that it neglects the role of CO_2 as an oxidizing agent; however, since the extent of oxidation by CO_2 and by H_2O could not be determined with the available data, the latter possibility should not be completely ignored.

II. **Bulk Molybdenum Trioxide.**—In order to establish a reference case for determining the identity and stability of alumina-supported oxides of molybdenum in reducing and oxidizing atmospheres, an investigation of bulk MoO_3 was first undertaken; Table II presents a summary of this study. The X-ray diffraction data obtained during the first 33 hours of intermittent operation with hydrogen flowing at 1.34 atmospheres and 1.0–4.0 ml./hr. showed that no reduction was achieved at temperatures below 493° (the initial operating temperature was 423°); at this temperature and at an increased pressure, 2.77 atmospheres, reduction proceeded completely to the +4 oxidation state, MoO_2, with no indication that the +5 oxidation state or a complex constituted an intermediate in the reduction. Reduction of the MoO_3 to MoO_2

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(11) E. A. Gulbransen and R. Ruka, *Ind. Eng. Chem.*, **43**, 697 (1951).

TABLE II

In situ X-RAY DIFFRACTION STUDY OF BULK MOLYBDENUM TRIOXIDE

Reaction	Reaction conditions Hours	T, °C.	P., atm.	Flow rate, ml./hr.	Type of operation[a]	Substances identified[b]	No. of X-ray patterns
I. Reduction with H_2	0–33	423–485	1.34	1.0–4.0	I	MoO_3, Be[c]	15
	33–68	493	2.77	1.0	C-I	MoO_3, MoO_2, Be[d]	8
	68–213	493–640	2.77	1.0–2.4	I-C	MoO_2, Be[e]	27
II. Oxidation with air	0–163	24–291	1.34	2.2–4.0	C	MoO_2, Be[f]	15
	163–307	376–427	1.34	1.2–1.8	C	MoO_3, MoO_2, Be	16
	307–355	427	1.34	1.2	C	MoO_3, Be[g]	5
III. Reduction with H_2	0–8	454	1.34	3.0	I	MoO_3, Be	5
	8–33.5	454	1.34	3.0	C	MoO_3, MoO_2, Be[h]	4
	33.5–57.5	454	1.34	5.0	C	MoO_2, Be[i]	4

[a] C, continuous; I, intermittent. [b] Diffraction patterns obtained with MoKα X-radiation. [c] "Spotty" MoO_3 pattern. [d] MoO_2 observed after hr. 56. [e] "Smooth" MoO_2 pattern; reduction terminated. [f] Very faint indication of MoO_3. [g] "Smooth" MoO_3 pattern; oxidation terminated. [h] MoO_2 observed after hr. 31. [i] Reduction terminated.

was accomplished in about 24 hours. Once formed, the MoO_2 proved resistant to further reduction; despite lengthy operations at temperatures increasing to 640°, no change in the MoO_2 diffraction pattern was evident. One point of interest observed during the course of the reduction was the definite change in crystal size concomitant with the conversion of MoO_3 to MoO_2. In marked contrast to the "spotty" diffraction pattern of the MoO_3, that of the MoO_2 was uniform and homogeneous. This observed decrease in crystal size apparently resulted from fracture of the MoO_3 crystals with production of the lower oxidation state material since oxidation of the MoO_2 to MoO_3, as described below, effected no change in the uniform character of the reflections.

Following termination of the above reduction phase, attempts to oxidize the MoO_2 with air at 1.34 atmospheres were initiated. The high stability of this oxide with respect to such oxidation is indicated by the fact that no evidence of reaction was discerned in the diffraction patterns during approximately 160 hours of operation in which the temperature was increased progressively from room temperature to 291°. The presence of MoO_3 was established definitely only after operation at 376°. Inasmuch as the rate of oxidation proved very slow at this temperature, complete conversion of the MoO_2 to MoO_3 was effected at 425°.

In order to ascertain whether a single reduction–oxidation cycle would render the MoO_3 more susceptible to reduction, the reoxidized material was subjected to treatment with hydrogen. In contrast to the temperature of 493° required for reduction of the original MoO_3, the regenerated MoO_3 was reduced at 454° with approximately the same time requirement. The greater ease of reduction observed in the case of the reoxidized material is indicative of the effect of a single reduction–oxidation cycle with respect to "surface clean-up"; in addition, it may also reflect the increased surface that accompanied the decrease in crystal size during the initial reduction.

III. γ-Alumina-Supported Molybdenum Trioxide.—Although the interpretation of the diffraction patterns obtained in the study of 20% MoO_3 on γ-Al_2O_3, the results of which are summarized in Table III, is complicated by a number of coincidences in the reflections of MoO_3, MoO_2, γ-Al_2O_3 and Be, this difficulty is adequately resolved by careful consideration of the character and intensity of the respective coincidences. Since it would be anticipated that dispersion of a reducible oxide upon an inactive support would enhance the ease of reduction of the former, intermittent contacting of the supported MoO_3 with hydrogen was initiated at a temperature somewhat below those at which reduction of fresh and regenerated MoO_3 occurred. At the initial operating temperature of 421° evidence of reduction was noted at hr. 11 with the appearance of the strongest MoO_2 reflection; by hr. 50 the reflections of MoO_3 were completely absent while those of MoO_2 were well established in the diffraction pattern. In subsequent continuous operation at temperatures increasing from 421 to 596° no further change in the diffraction pattern was observed, and, accordingly, the reduction phase was terminated at hr. 318. The course of the reduction observed for Al_2O_3–supported MoO_3 was, in general, similar to that noted for bulk MoO_3; the first identifiable product was MoO_2 and there was no indication of an intermediate +5 oxidation state or complex in each instance. In contrast to the bulk MoO_3 results, however, reduction of supported MoO_3 was initiated and completed at an appreciably lower temperature.

The determination of the stability of the above reduction product with respect to air oxidation, as in the case of bulk MoO_2, reflected the high stability of the +4 oxidation state. During an aggregate 216 hours of continuous operation at temperatures increasing from room temperature to 366° the diffraction pattern of MoO_2 underwent no change. Some indication of oxidation was observed at 410°, but the rate of reaction at this temperature level as well as in the range of 410 to 471° was very slow; complete regeneration of the supported MoO_3 ultimately required a temperature of 510°. The slow rate of oxidation exhibited by Al_2O_3–supported MoO_2 at temperatures considerably above those found necessary for the oxidation of bulk MoO_2 suggests that the alumina functions as a stabilizing agent in addition to its role as a surface extender. This hypothesis of an interaction between the alumina support and the +4 oxidation state of molybdenum receives further support from the fact that the MoO_3 reflections in the regenerated product were definitely less intense than those of the original material.

In connection with this hypothesis, it is of interest

TABLE III

In situ X-RAY DIFFRACTION STUDY OF ALUMINA-SUPPORTED MOLYBDENUM TRIOXIDE[a]

Reaction	Reaction conditions Hours	T, °C.	P., atm.	Flow rate, ml./hr.	Type of operation[b]	Substances identified[c]	No. of X-ray patterns
I. Reduction with H_2	0–59	421	1.34	1.6	I	MoO_3, MoO_2, γ-Al_2O_3, Be[d]	23
	59–318	421–596	1.48	1.8–2.6	C	MoO_2, γ-Al_2O_3, Be[e]	26
II. Oxidation with air	0–216	24–366	1.34	1.6–3.6	C	MoO_2, γ-Al_2O_3, Be	14
	216–505	410–471	1.34	1.2–2.0	C	MoO_3, MoO_2, γ-Al_2O_3, Be[f]	18
	505–550	510	1.34	1.2	C	MoO_3, γ-Al_2O_3, Be[g]	4
III. Reduction with H_2	0–23	374	1.27	1.7	C	MoO_3, γ-Al_2O_3, Be	3
	23–40	430	1.27	1.4	C	MoO_3, MoO_2, γ-Al_2O_3, Be[h]	4
	40–86	430	1.27	1.6	C	MoO_2, γ-Al_2O_3, Be[i]	5

[a] 20% MoO_3 on γ-Al_2O_3 (Aluminum Co. of America H-40 Grade alumina). [b] C, continuous; I, intermittent. [c] Diffraction patterns obtained with MoKα X-radiation. [d] MoO_2 observed after hr. 11; MoO_3 absent after hr. 50. [e] Reduction terminated. [f] Very weak MoO_2 reflections. [g] Oxidation terminated. [h] MoO_2 observed after hr. 26. [i] Reduction terminated.

to note that Griffith, Chapman and Lindars[12] report the formation of small quantities of molybdenum metal on reduction with hydrogen at 450° of MoO_3–SiO_2 preparations in which the Si atoms/100 Mo atoms ratio varied from 4.4 to 9.4. Although the Al_2O_3-supported MoO_3 preparation employed in this work contained sufficient SiO_2 to yield a Si atoms/100 Mo atoms ratio of the order of 50 and although a temperature level of 596° was investigated, reduction below the +4 oxidation state was not observed.

The effect of a single reduction–oxidation cycle on the ease of subsequent reduction was also investigated in the case of the regenerated, alumina-supported MoO_3. Contrary to the results experienced with regenerated bulk MoO_3, the reduction–oxidation cycle was ineffective in increasing the susceptibility of the reoxidized, supported material to reduction. During a period of 23 hours at 374°, the diffraction patterns showed no indication of reduction; however, at 430° (approximately the same temperature required for reduction of the original material) reduction was evident after 3 hours of operation and was essentially complete 14 hours later. Based on these observations, "surface clean-up" apparently is not too important a factor where highly specific portions of a surface, rather than the total surface, are involved.

Although the foregoing data and discussion have been restricted to the chemical reactions observed between the gas and the solid, it is obvious that the microreactor apparatus possesses great utility for the study of heterogeneous catalysis *per se;* however, such application is beyond the scope of the present paper.

Acknowledgment.—The author wishes to express his appreciation to Humble Oil and Refining Company for permission to publish this research. He is indebted to Professor W. O. Milligan for helpful discussions and suggestions during the course of these investigations. The contributions of R. W. Terry and H. W. Oliver of the Company's Instrument Department, who fabricated the special apparatus required, and of Mrs. C. E. W. Souby and Miss V. Harleston, who carried out the experimental work, are gratefully acknowledged.

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[12] R. H. Griffith, P. R. Chapman and P. R. Lindars, *Discussions Faraday Soc.*, No. 8, 258 (1950).

[CONTRIBUTION FROM THE UNIVERSITY OF PITTSBURGH AND MELLON INSTITUTE]

The Adsorption of Normal Paraffins on Cracking Catalysts[1]

BY ROBERT C. ZABOR AND PAUL H. EMMETT

Adsorption measurements have been made for *n*-butane, *n*-heptane and *n*-octane on a Houdry S-46 cracking catalyst in the temperature range from room temperature up to and above the lowest temperature at which decomposition occurs. The adsorption appears to be physical in nature up to about 150°. Above this temperature, and even at cracking temperatures, the adsorption is very small, being equal to or less than 0.005 millimole (~0.1 cc.) per gram of catalyst.

Numerous papers[2–6] have been presented in recent years which postulate that the decomposition of hydrocarbons over cracking catalysts results from the combination of the hydrocarbon molecule with the hydrogen ion on the surface of the catalyst to form carbonium ions[7] or polarized complexes. However, since no adsorption data for paraffins on cracking catalysts have been published, it has been impossible to judge the extent to which carbonium ions or chemisorbed hydrocarbons are actually present on a catalyst during cracking. The present paper reports the results of an experimental study of the adsorption of *n*-butane, *n*-heptane and *n*-octane on a Houdry S-46, silica–

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[1] Contribution from the Multiple Fellowship of Gulf Research & Development Company, Mellon Institute, and the University of Pittsburgh, Pittsburgh, Penna.

[2] C. L. Thomas, J. Hickey and G. Stecker, *Ind. Eng. Chem.*, **42**, 866 (1950).

[3] C. L. Thomas, *ibid.*, **41**, 2564 (1949).

[4] B. S. Greensfelder, H. H. Voge and G. M. Good, *ibid.*, **41**, 2573 (1949).

[5] R. C. Hansford, *ibid.*, **39**, 849 (1947).

[6] B. S. Greensfelder and H. H. Voge, *ibid.*, **37**, 514, 983, 1038 (1945).

[7] F. C. Whitmore, THIS JOURNAL, **54**, 3274 (1932).