[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Hydrogenation of Ethylene at Surfaces of Certain Oxides. II. Molybdenum Oxide Compounds

BY JOHN F. WOODMAN, HUGH S. TAYLOR AND JOHN TURKEVICH

Following the study of the activity of zinc oxide and zinc chromite surfaces described in the preceding paper,[1] a series of experiments was carried out to test the activity of some molybdenum compounds, in view of the well-known industrial applications of the oxides and sulfides of this element in hydrogenation and cracking of oils and tars. Catalytic masses were prepared by decomposition and reduction of ammonium phosphomolybdate, ammonium paramolybdate, and ammonium nickel molybdate. Suspicion of the presence of metallic nickel in extremely active catalysts produced by reduction of the nickel compounds suggested tests of the efficiency of hydrogen sulfide as a poison for these surfaces and measurements of the magnetic susceptibilities of the materials.

Experimental Details

Apparatus and Procedure.—The catalytic system was the same as that used in the static experiments on zinc oxide.[1]

The magnetic susceptibilities were determined by the method of Gouy.[2] Measurements were carried out with magnetic fields up to about 4800 gausses, the magnet current being increased from zero to 12 amp. in steps of about 2 amp., then reduced again to zero in the same manner, with the change in weight of the sample determined at each step. For purposes of calculation, the results were plotted against current and values taken from the smooth curve at intervals of 2 amp. The relationship between current and field strength was established by calibration with Mohr salt, for which χ, the specific susceptibility, was taken as 32.1×10^{-6} cgsm. unit at $22°$.[3]

The finely divided samples were contained in uniform 5 mm. Pyrex tubes, each filled to a depth of 12.2 cm. Reduced samples were filled into the tubes under vacuum and sealed off without access to air. Measurements were corrected for the small diamagnetic effect of the tubes.

During measurements the sample tube hung freely in a Pyrex jacket through which dry nitrogen gas had been passed for one-half to one hour.

Only the measurements at room temperature are reported; others at 0, -80 and $-190°$ gave similar results.

Materials.—Ammonium phosphomolybdate, $3(NH_4)_2O\cdot P_2O_5\cdot24MoO_3\cdot6H_2O$, was prepared following the analytical procedure.[4] The yellow product was dried at $120°$.

Molybdenum oxide was prepared by heating ammonium paramolybdate to $300°$ in a current of air until the off-gas gave no test for ammonia.

Ammonium nickel molybdate was prepared by dissolving 145 g. of ammonium paramolybdate in one liter of water, and adding the filtered solution to a solution of 27 g. of nickel nitrate hexahydrate in 100 cc. of water. The whole was heated to boiling, with mechanical stirring, while precipitation took place. Next, the solution was diluted with water to three liters, cooled, and allowed to settle. The slightly greenish supernatant liquid was decanted, and the precipitate stirred once with three liters of water containing 25 g. of ammonium nitrate. It was then filtered with suction, and washed with 100 cc. of water. The bluish, finely crystalline product was dried overnight at $125°$. From this product all the catalysts containing nickel were prepared as subsequently noted. The most probable formula for the preparation, according to Barbieri,[5] is $(NH_4)_4H_6[Ni(MoO_4)_6]\cdot5H_2O$.

Hydrogen sulfide was synthesized from hydrogen and molten sulfur at $350°$.

Results and Discussion

Phosphomolybdate and Molybdenum Oxide Catalysts.—A catalyst from 1.5 g. of ammonium phosphomolybdate (B), heated for eight hours in a current of dry air, evacuated for thirty-six hours (BI) and then treated with hydrogen for nineteen hours, followed by a further evacuation, all at $300°$, changed progressively from mustard yellow, through light green to black, after reduction. The preparation (BII) failed to show significant activity in catalyzing the reaction of a 3:1 mixture of hydrogen and ethylene below $256°$.

A preparation ignited in an air stream at $475°$ for six hours, then reduced with hydrogen at 450–$475°$ for eight hours, was similarly inactive at $256°$, the half-life value, t_{50}, being about two and a half hours. A preparation of this nature has been shown by Kingman[6] to be an excellent catalyst for the reduction of phenol at 280–$350°$.

Ammonium paramolybdate decomposed at $300°$, evacuated at $450°$ and reduced for eight hours at $300°$ gave on evacuation a black catalyst mass. It showed no activity for ethylene hydrogenation at $256°$ nor was its activity increased by further reduction at $450°$.

Nickel Molybdate Catalysts.—A 1.5-g. sample of ammonium nickel molybdate (A) was heated

(1) Woodman and Taylor, THIS JOURNAL, **62**, 1393 (1940).
(2) Gouy. *Compt. rend.*, **109**, 935 (1889); see also Klemm, "Magnetochemie," Leipzig, 1936, pp. 50–52.
(3) Jackson, *Phil. Trans. Roy. Soc.* (London), **A224**, 1 (1923).
(4) Treadwell and Hall, "Analytical Chemistry," 7th ed., Vol. II, p. 382.

(5) Barbieri, *Atti accad. Lincei*, [5] **23**, II, 357 (1914).
(6) Kingman, *Trans. Faraday Soc.*, **33**, 784 (1937).

slowly in a dry air stream to 300° and kept there for nine hours while ammonia was evolved. The tube was then cooled, evacuated, and the air stream replaced by pure hydrogen for four hours. During the succeeding twenty hours a stationary hydrogen atmosphere caused further reduction. The catalyst was then evacuated for six and a half hours at 350°, further reduced at 305° for fifteen hours, and then thoroughly evacuated at 350°. The product (AII) was black. Its activity was very high, a half-life of three minutes being recorded at −80° for a $3H_2:1C_2H_4$ mixture. The rate was not increased by raising the temperature; the observed rate of change of pressure was determined by diffusion processes.

Catalyst masses (AI) prepared as above but without the hydrogen reduction were olive-green to gray in color. Evacuation at 350° for thirteen hours caused a color change to blue, evidently with formation of a lower oxide of molybdenum. This material showed no hydrogenation activity at 0, 100, 156 and 218°, even though before each run the surface was left in contact with hydrogen for eight hours at a temperature five to ten degrees higher than the operating temperature. Treatment with hydrogen at 270° for six hours caused water formation and the catalyst became black. Its activity was then similar to that of the reduced catalyst already discussed. The reduction of a component of the catalyst, occurring at 270–300°, is thus essential to its activity in ethylene hydrogenation.

That the high activity of the reduced nickel-molybdenum oxide catalysts was due to the presence of metallic nickel highly dispersed through the molybdenum oxide was indicated by three different lines of approach. Measurements of the magnetic susceptibility, discussed in the next section, gave an estimate of the amount of nickel present. This estimate was in agreement with measurements of the hydrogen sulfide required to poison the catalysts completely for hydrogenation. The inactivity of the other molybdenum oxide preparations not containing reducible metals discussed above, afforded indirectly a third corroboration.

Magnetic Measurements.—Values of χ, the specific susceptibility, calculated for samples of the nickel–molybdenum oxide compounds (A) which had undergone the various treatments described, are contained in Table I. For comparison, values for some preparations from ammonium phosphomolybdate (B) are included.

The striking feature of this table is the decrease in susceptibility with increasing field strength which occurs in the case of the reduced samples prepared from ammonium nickel molybdate. This behavior is characteristic of ferromagnetic substances. Its occurrence in the present instance can only indicate that under the conditions of preparation of these samples, some of the nickel present became reduced to the metal.

If we make the plausible assumption that the susceptibilities of the various phases present are additive, it is possible to calculate approximately the percentage of the total nickel present as metal after the various treatments. The additive relationship is

$$(m_1 + m_2) \chi = m_1\chi_1 + m_2\chi_2 \qquad (1)$$

where m_1 is the mass of the ferromagnetic material, χ_1 its specific susceptibility, m_2 and χ_2 are the corresponding quantities for the remaining, non-ferromagnetic material, and χ is the observed susceptibility of the sample. For χ_1, we may take the values for pure metallic nickel at room temperature,[7] and we know $(m_1 + m_2)$ and χ from the measurement at the same temperature. It is then possible to set up an equation of the form of (1) for each field strength. Solution of these equations simultaneously gives the approximate weight of nickel present in each sample.

Assuming the composition of the decomposed and reduced samples to be closely represented by the formula $2NiO \cdot 6Mo_2O_3$, the calculated percentage of the total nickel present which has been reduced to the metal is shown in the last column of Table I. These values are of course to be considered as indicative only of order of magnitude, and as such are not significantly changed by selection of other formulas.

Poisoning with Hydrogen Sulfide.—Two catalysts corresponding to AII of Table I were tested for resistance to hydrogen sulfide by adding increasing amounts of this gas to the reaction mixtures in successive runs. In each case a reproducible minimum of hydrogen sulfide was found to be required in any single run to cause complete cessation of reaction at −80°. The poison was apparently completely removed by evacuation at 350° between runs, and the series of runs with increasing amounts of the sulfur compound could be repeated, with no observable retardation until the critical amount was present. We attribute this unusual behavior on poisoning to the fact that

(7) "International Critical Tables," Vol. VI. p. 403.

TABLE I

MAGNETIC SUSCEPTIBILITIES OF MOLYBDENUM OXIDE COMPOUNDS

Material[a]	T, °C.	Magnet current, amp.	$\chi \times 10^6$ obsd.	% Ni reduced[b]
A	27	2–12	$(4.3)^c$	0
AI	23	2	367	
		4	209	
		6	147	~10
		8	119	
		10	102	
		12	93	
AII	21	2–12	$(5.9)^c$	0
AIII	24	2	1523	
		4	750	>30
		6	549	
		8	424	
B	26	2–12	$(0 \pm 1)^d$	
BI	24	2–12	$(\sim0.1)^d$	
BII	26	2–12	$(\sim0.2)^d$	

[a] Catalyst A, ammonium nickel molybdate; B, ammonium phosphomolybdate. I, decomposed at 300°; II, decomposed at 300°, reduced at 300°; III, decomposed at 475°, reduced at 475° for twelve hours. [b] % total Ni present as metal. [c] These figures represent the mean of measurements at each field strength, the values differing by <5%, and showing no trend. [d] These susceptibilities were too low for accurate measurement with our apparatus.

reaction was immeasurably rapid at −80° when *any* metallic nickel was present.

Table II compares the results of the hydrogen sulfide poisoning with those of the magnetic measurements, on corresponding samples.

TABLE II

METALLIC Ni IN NICKEL–MOLYBDENUM OXIDE CATALYST REDUCED AT 300°, BY MAGNETIC MEASUREMENTS AND H₂S POISONING

Catalyst	a	b
Wt., g.	1.25	0.64
Total moles Ni, calcd.	11×10^{-4}	5×10^{-4}
Moles Ni metal, from χ	11×10^{-5}	5×10^{-5}
Moles H₂S to poison	12×10^{-5}	4×10^{-5}

Ogden[8] has measured the adsorption of hydrogen by material prepared in essentially the same way as that described in this section and found it to differ entirely from the adsorption characteristic of metallic nickel. The preparation showed no observable hydrogen adsorption from −78 to +110°, whereas nickel shows its maximum adsorptive capacity at 0°. His failure to detect adsorption characteristic of nickel is doubtless due to the very small amount of the metal present.

It is apparent from the results noted above that the activity of these nickel–molybdenum oxide structures is a function of their content of metallic nickel; and that, lacking reduction sufficient to produce the metal, such materials resemble other molybdenum oxide structures not containing nickel or any reducible metal, in being ineffective as catalysts for ethylene hydrogenation below 250°. It is striking that these molybdenum compounds fail to show activity comparable to that of zinc oxide, which hitherto had not been classed among the surfaces on which hydrocarbon reactions might be secured.

Summary

1. A catalyst prepared by decomposition and reduction of ammonium nickel molybdate at 300° is active at −80° in the hydrogenation of ethylene. Magnetic susceptibility measurements, together with poisoning experiments using hydrogen sulfide, have suggested that this activity is due to metallic nickel, very highly dispersed.

2. Catalysts prepared from ammonium phosphomolybdate and ammonium paramolybdate have shown negligible activity for ethylene hydrogenation below 256°.

(8) G. Ogden, Master's Thesis, Manchester, 1932.