

NOTES

On the Nature of Catalytic Activity of Nickel and Platinum Graphimets

The well-known phenomenon of shape selectivity, which is a key factor in some industrial processes, arises from the fitting of the reactants into a small pore or cage, where the catalytic site is located. Typical examples are zeolites with appropriate pore sizes or with modified structures.

The constitution of transition metal intercalated graphite, the characteristic interlayer distance of which varies between 0.6 and 0.9 nm, gives rise to high expectations of shape selectivity in heterogeneous catalytic reactions, if they occur within the layers. The assumed structure of the substances consists of a regular sandwich-like arrangement of graphite sheets and intercalated metal layers (1), which are potential hosts of catalytic sites. The commercial producer of these materials, Ventron (2), claims that the "graphimets" prepared from metal chloride intercalated graphite by reduction with lithium biphenyl contain "atomically dispersed metals" (3) within the graphite layers.

The location of the catalytic activity in the nickel and platinum graphimets, which are catalysts of high potential for hydrogenation, is the subject of our study. An unambiguous verification of the quasi-two-dimensional monatomic layered structure of nickel in graphite has never been fully achieved (1), and in fact there is evidence of the presence of metal particles (4, 5). However, the unusual structure of these materials seems to be well established by magnetic measurements, which support the existence of very small particles with dimensions in the range of a few tenths of a nanometer (5). Thus, the following questions should be answered: (i) What are the real compositions and structures of the nickel and platinum graphimets? (ii) Do

they retain their structure, whatever it is, under conditions of catalysis? (iii) Are the catalytically active sites within the bodies of the graphimets or on their accessible surfaces?

To decide whether the catalytic sites are associated with the original metal intercalated layers or rather with supported metal particles, the catalyst samples were subjected to XPS, TEM, XRD, DSC, chemical analysis, surface area measurements, and activity tests prior to pretreatments intended to convert the intercalated material, if any, into supported particles, and also after these transformations. A summary of the experimental data is presented in Table 1.

The first fact to consider about the original, nontreated nickel graphimets is its composition. The amount of chloride found in the sample by chemical analysis was equivalent to a nickel chloride content of 16 wt%. The XRD reflections, however vague they were, proved the presence of metallic nickel and nickel oxide phases. The lack of XRD reflections of a nickel chloride phase suggests the presence of a nickel chloride intercalate, but no direct evidence was found to support this fact.

On the other hand, no detectable amount of nickel was found on the surface of the graphimets sample by XPS. The dispersions determined by TEM and hydrogen chemisorption differed significantly, and the surface areas calculated via hydrogen chemisorption and hydrogen-carbon monoxide titration differed even more. These facts suggest the presence of nickel in a form that is not readily, if at all, accessible for gas molecules larger than hydrogen. We conclude that Ventron nickel graphimets is not a uniform material. It consists, at least in

TABLE I
Summary of Experimental Results

Sample	Pretreatment (hours at 400°C)	XPS		TEM		Specific surface area			XRD phases found other than graphite	Composition, total metal, metal, chloride	DSC, beginning of exothermic transformation (°C)	Conversion of cyclo- hexene ^a (%)
		B.E. (eV)	Metal/C atomic ratio × 10 ³	Range of particle size (nm)	Dispersion	Dispersion by H chemi- sorption	By H chemi- sorption (m ² /g)	By H-CO titration				
Nickel graphimet	—	—	0	2-60	0.1	0.04	3.94	0.35	(Ni, NiO)	16, 9, 16	295	60
	2, He	—	—	—	—	—	—	—	Ni, NiO NiCl ₂	— — —	—	—
	2, O ₂	854.9	11	—	—	—	—	0.40	NiO	— — —	No peak up to 500	74
	6, O ₂	853.7	29	Up to 500	—	—	—	0.84	—	— — —	—	to 92
Platinum graphinet	—	71.7	7	1.2-8	0.36	0.36	0.98	—	Not sensitive enough	1.3, 1.3, 0	No peak up to 500	100

^a Pulse microreactor, 10-mg catalyst (activation, 400°C, 2 hr, H), 2 μl reactant, 200°C.

part, of mixtures of graphite, nickel oxide, metallic nickel, and perhaps finely divided nickel chloride. It comprises structures that encapsulate a considerable proportion of these materials into the interior of the graphite crystals. This presumably includes some more or less regular intercalated layers, filled with nickel chloride, that are consequently not easy to detect, and also rafts of nickel and/or nickel oxide between the graphite layers.

This complex material decomposed exothermally about 295°C (DSC), i.e., a usual temperature for the activation of nickel catalysts. In helium, the products of this transformation were separate phases of nickel, nickel oxide, and nickel chloride, the characteristic reflections of which were detected by XRD. Oxygen treatment at 400°C converted all the above materials into nickel oxide, the huge particles of which were seen on TEM micrographs. In contrast to the untreated samples, XPS detected a significant signal of nickel on the surfaces of the pretreated samples. The specific surface area also increased. We assumed that the nickel graphimmet was completely converted into graphite-supported nickel oxide. As evidence, no peak was observed in the DSC curve for the decomposed material.

The catalytic activities of the treated and untreated graphimmet samples were tested in a pulse microreactor connected to a gas chromatograph. All the nickel graphimmet catalysts were active in the hydrogenation of cyclohexene. As the free metallic surface was increased by the destruction of the original graphimmet structure, increasingly higher conversions of cyclohexene were achieved under otherwise identical reaction conditions. The catalytic activity was approximately proportional to the specific surface area.

It is concluded that the catalytic sites are located on the surfaces of supported nickel particles, which are also present in the original graphimmet sample. In fact, the structure of the nickel graphimmet is not stable enough

to endure catalytic conditions at higher temperatures. For this reason, shape selectivity cannot be achieved. However, it is still worth considering the possible catalytic action of rafts of metallic nickel residing between graphite sheets as in narrow pores, since at present this possibility cannot be excluded entirely.

In contrast, the platinum graphimmet contains only metallic platinum in the form of metal particles (TEM) detectable on the surface by XPS and hydrogen chemisorption. TEM and chemisorption gave the same dispersion. All the experimental evidence indicates that this graphimmet consists of platinum particles supported on graphite. As was to be expected, this material was stable (DSC) and highly active in the hydrogenation of simple alkenes (6).

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