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RESEARCH NOTE

A Simple Method for Determining the Size of Nickel Oxide Crystallites in Catalysis

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A large number of commercial catalysts comprise NiO dispersed on many types of supports and are used directly in the oxide form or reduced to metallic nickel (1). An important characteristic of these catalysts, in fundamental research and in production quality control, is the crystallite size of the supported NiO. The purpose of this Research Note is to report a simple crystallite size determination technique to workers using supported NiO catalysts and to demonstrate where the method is applicable.

The most widely accepted and dependable method for measuring NiO crystallite size is X-ray diffraction line broadening (2). However, this technique requires sophisticated instrumentation and data analysis, especially when NiO loadings are low. In addition, extensive measurements over a wide range of angles are necessary to separate other contributions to line broadening such as crystal strain (3). This approach is expensive and time consuming, and simpler methods are needed.

We recently reported results showing that the magnetic susceptibility of bulk NiO at room temperature is a measure of crystallite size (4). Size-dependent superantiferromagnetism in normally antiferromagnetic NiO was first demonstrated by Richardson and Milligan in 1956 (5) and later confirmed by others (6–7). Although it was recognized that this superantiferromagnetism resulted from uncompensated magnetic spins in the crystallite lattice, the origin of the net crystallite moment was not clear. We demonstrated that nonstoichiometry plays no measurable role, with the effect due to uncompensated magnetic moments in the surface of the NiO crystallite. This becomes important as the NiO crystallite size decreases. More importantly, the magnetic susceptibility at 25°C, χ_{NiO}, obeys a relationship given by

$$\chi_{\mathrm{NiO}} = 9.0 \times 10^{-6} + 2.38 \times 10^{-4}/d_{\mathrm{XRD}}, \qquad [1]$$

with the crystallite size, d_{XRD}, measured by X-ray diffraction line broadening. With these constants, d_{XRD} is the cube root of the crystallite volume and has the units of nanometers. This expression has been upheld in work on promoted or doped bulk NiO (8), α-Al_2O_3-supported catalysts (9–11), and coprecipitated NiO/γ-Al_2O_3 (12), in which comparisons between magnetic susceptibility and X-ray diffraction line broadening measurements were made.

To apply Eq. [1] to a supported catalyst (e.g., NiO on α-Al_2O_3), the magnetic susceptibility per gram of NiO, χ_{NiO}, must be determined from the measured sample susceptibility, χ_{s}, using

$$\chi_{\mathrm{s}} = \mathrm{w}_{\mathrm{NiO}}\chi_{\mathrm{NiO}} + \sum w_i \chi_i, \qquad [2]$$

where w_{NiO} is the mass fraction of NiO in the sample, and $\sum w_i \chi_i$ is the sum of the products of the mass fraction, w_i, and the diamagnetic susceptibility contribution, χ_i, of each component present, including Ni ions and any adsorbed H_2O. Procedures for obtaining values of χ_i for constituent ions have been given by Selwood (13).

There are many methods for measuring χ_{s}. These have been summarized by Selwood (13) and Mulay (14) and fall into two types: induction and force determination. Induction techniques rely on the signal generated in a pick-up coil from a change in the permeability of the sample contained within it. Permeameters achieve this change with an alternating current through a primary coil. Generally, the secondary signal detected in pick-up coils is too small for supported NiO catalysts unless precision phase-sensitive amplifiers are used, which is the case in commercial "susceptometers" (e.g., Great Lakes Associates). Alternatively, the sample is magnetized by an external magnetic field and then moved in and out of the pick-up coil. This is the principle for the "vibrating sample magnetometer" (e.g., Princeton Applied Research) described in our previous publications. These methods are accurate and allow for measurements over a wide range of sample temperatures. The vibrating

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sample magnetometer has the added advantage that measurements in different magnetic fields are possible. Both of these methods are complicated and expensive.

Force detection methods are simpler. The Gouy method, long encountered in chemistry teaching laboratories, utilizes a cylindrical sample hanging from one arm of an analytical balance that measures the force exerted when a magnetic field is applied to the end of the sample. This is ideal for diamagnetic samples, especially liquids, and is appropriate for paramagnetic materials. Ferromagnetic impurities, such as Fe as low as 50 ppm, impart a magnetic field dependence to the susceptibility, and the Gouy method is not suitable since saturation corrections are complicated. However, the Faraday method, which uses a smaller spherical sample in a magnetic field gradient, is applicable if the magnetic field is varied so that ferromagnetic effects can be eliminated by extrapolation to infinite fields. The disadvantage is that forces are much smaller and more delicate microbalances are required.

Only measurements at 25°C are needed for routine measurements of NiO crystallite size via magnetic susceptibility, and perhaps the best approach for a limited budget is the Gouy method. Any existing analytical balance may be used, providing a source of magnetic field is available, either from a permanent magnet or an electromagnet. A commercial apparatus based on a modified Gouy principle is available at a moderate cost (Johnson Matthey Magnetic Susceptibility Balance Model Mark I and Mark II). A comparison of the economics of these various methods has been published (16).

For the more “do-it-yourself” inclined researcher, an intriguing possibility has been described by Eaton and Eaton in which a permanent magnet Gouy apparatus was constructed very inexpensively (15). We fabricated a similar device, and a sketch of the apparatus is shown in Fig. 1. Two cobalt rare-earth permanent magnet discs (obtainable from any scientific hobby dealer) were epoxied to a U-shaped, mild steel magnetic yoke. The discs were 2 cm in diameter and 0.5 cm thick, and the complete assembly was approximately 38 × 28 cm and weighed about 50 g. During measurements, this magnet section is placed on the pan of a laboratory electronic balance (Mettler AC100) and a plexiglas sample holder is positioned as shown in Fig. 1 to hang from an opening at the top of the balance enclosure. A glass tube (6.5 mm o.d., 4 mm i.d., and sealed at the bottom) is attached to the vertical section of the sample holder and centered between the two disc magnets, where the magnetic field strength is approximately 4 kOe. A known amount of catalyst sample is then loaded into a 3-mm NMR tube, up to a standard length in the tube. When the sample tube is inserted into the holder tube, the induced force between the sample and the magnet causes the balance pan to move upward and downward for paramagnetic and diamagnetic samples, respectively. The apparent weight change recorded by the balance is proportional to the magnetic susceptibility of the sample, which is easily determined by comparing the weight loss with that from the sample tube containing the same length of a standard (such as ferrous ammonium sulfate) whose weight is known (13).

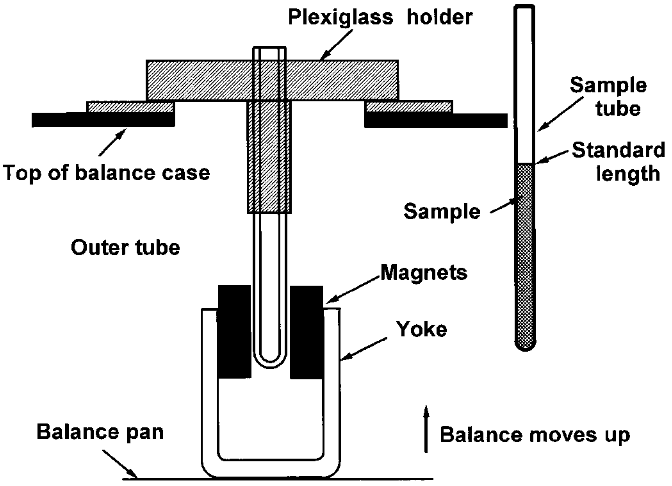

FIG. 1. Simple Gouy apparatus for measurement of magnetic susceptibility.

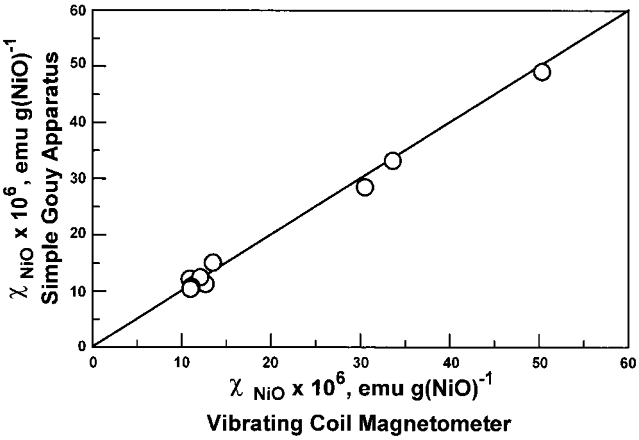

FIG. 2. Comparison of magnetic susceptibilities of NiO/α-Al_2O_3 samples (Series 3,Table 1) measured with the simple Gouy apparatus and a vibrating coil magnetometer.

The apparatus (excluding the electronic balance) can be made for less than \$100, and the measurement procedure is well suited to rapid, routine magnetic characterization of many samples. Figure 2 compares typical results for supported NiO/α-Al_2O_3 catalysts (Series 3 in Table 1) obtained with a high-precision vibrating coil magnetometer and the simpler Gouy apparatus. The agreement is very good ($\chi^2 = 0.7198$, indicating 99+% correspondence) and any differences are quite acceptable considering the cost and ease of using this simple device.

Figure 3 shows the relationship between magnetic susceptibility and the reciprocal of crystallite size for a large

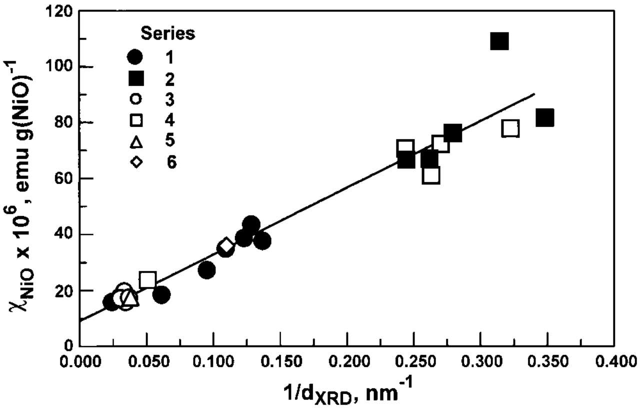

FIG. 3. Magnetic susceptibility of NiO measured with the simple Gouy apparatus versus crystallite sizes by X-ray diffraction line broadening; sample identification as given in Table 1.

number of samples containing NiO. Descriptions of these samples are given in Table 1. The crystallite size was determined from X-ray diffraction line broadening, using the Debye–Scherrer method as modified by Williamson and Hall (3). X-ray data were obtained with a Seimens D 5000 High Temperature Diffraction System equipped with a position-sensitive detector. Pure (Series 1) and doped NiO (series 2) samples are included, together with supported catalysts prepared by impregnation (Series 3, 5, and 6) and coprecipitation (Series 4) techniques. The same linear relationship previously reported is observed, although with some scatter. A least-squares fit of the data in Fig. 3 differs from Eq. [1] by less than 1%. A comparison of the sizes from magnetic measurements and from X-ray diffraction is shown in Fig. 4. The agreement is good ($\chi^2 = 13.19$, <1% difference), considering the assumptions in both methods.

TABLE 1

Catalyst Samples Used in Figs. 2, 3, and 4

Series	Composition	Preparation	Reference
1	NiO	Precipitation from $Ni(NO_3)_2$ solution with NaOH, calcined in air at 300–700°C	(4)
2	NiO with 2–3 wt% CuO, Ag_2O, Al_2O_3, and ZrO_2	Coprecipitation from mixed nitrate solutions with Na_2CO_3, calcined in air at 300°C	(8)
3	5–21.3 wt% NiO on α-Al_2O_3	Multiple impregnation of $Ni(NO_3)_2$ on α-Al_2O_3 pellets, calcined at 650°C	(9)
4	2.5, 4.1, and 13.6 wt% NiO/ γ-Al_2O_3	Coprecipitated from mixed nitrate solutions with Na_2CO_3, calcined in air at 300°C	(12)
5	5 wt% NiO on $MgAl_2O_4$	Impregnation of $Ni(NO_3)_2$ on $MgAl_2O_4$ pellets, calcined in air at 650°C	None
6	5 wt% NiO on $CaAl_2O_4$	Impregnation of $Ni(NO_3)_2$ on $CaAl_2O_4$ pellets, calcined in air at 650°C	None

We recommend both the simple magnetic susceptibility measuring device and the crystallite size determination method to those in the catalysis community working with NiO catalysts. Rapid determination of NiO crystallite size in suitable samples is possible. The mass fractions of NiO and adsorbed water must be known to apply Eq. [2]. Traces of Fe, derived from impurities and operations such as pelleting and grinding, are sometimes found in catalyst supports and these impart a field dependence that obscures the magnetism of the NiO. This is easily detected by measuring the susceptibility at different magnetic field strengths, which means that a second magnet device with a different magnetic field must be used.

The most serious drawback is the presence of other paramagnetic compounds, such as NiO–Al_2O_3 spinels that often occur when high concentrations of NiO on Al_2O_3 are heated at high temperatures. The magnetic susceptibility of the spinels merely adds to that of the NiO, and there is no way to detect their presence from single-temperature measurements. Usually anomalous results are obtained and Eq. [1] cannot be used. To use the method successfully, the presence of other paramagnetic compounds must be ruled out, either from the history of the sample or by means of structure determination techniques. We have found, for example, that if $NiAl_2O_4$ cannot be detected by X-ray diffraction (i.e., <5 wt%), then the error introduced into the size determination is insignificant.

It is intriguing to speculate on whether this simple crystallite size measurement can be applied to other transition oxides of interest in catalysis. In principle, any oxide that displays superantiferromagnetism is a candidate. Since Neel demonstrated superantiferromagnetism in CoO, FeO, and Fe_2O_3 (17), these are definite possibilities. However,

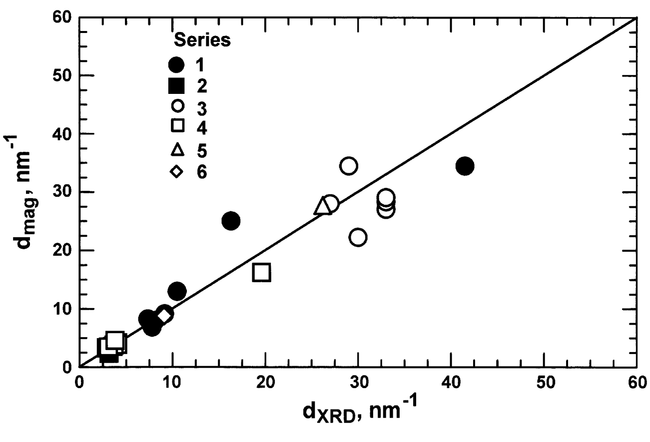

FIG. 4. Comparison of crystallite sizes of NiO measured with the simple Gouy apparatus and X-ray diffraction line broadening; sample identification as given in Table 1.

experimental data similar to those that established Eq. [1] are not yet available. The question of ferrimagnetic oxides, such as Fe_3O_4, is problematic, since the underlying saturation moments displayed by these materials would probably overwhelm any nonbalance due to size effects.

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