JOURNAL OF CATALYSIS **86**, 450–453 (1984)

Magnetic Crystallite Thermometry

Reaction temperature is not measured during heterogeneous catalytic experiments, and bulk fluid temperature is generally used in data analysis. Kinetic work is usually done under conditions where theoretical criteria indicate that temperature (and concentration) gradients affect observed rates by less than 5% (*1, 2*). A new method to determine the average crystallite temperature for magnetic metal catalysts is being developed to allow a direct check for temperature gradients. This note relates some early results of this magnetic crystallite thermometry performed during ethane hydrogenolysis over Ni/SiO_2 catalysts. This reaction system was selected to demonstrate the method, because (1) its parameter values are reasonable, (2) reaction occurs at reasonable rates at 500 K, where the magnetic moment density of nickel is a strong function of temperature (*3, 4*), (3) ethane does not affect the moment of Ni/SiO_2 samples in the presence of H_2 (*5–7*), and (4) the rate can be simply expressed as $r = kP_E(P_{H_2})^{-2}$ (*3*). The inverse order dependence of rate on H_2 pressure is used to advantage, as will be discussed.

Recent work in the analysis of supported magnetic metal catalysts (*8–10*) allows the determination of average magnetic phase temperature. These catalysts are often superparamagnetic (*5*); hence, the magnetic moment (M) at low, constant applied fields depends on temperature (T) as (*10*)

$$\frac{M(T_2)}{M(T_1)} = \frac{T_1}{T_2}\left[\frac{I_s(T_2)}{I_s(T_1)}\right]^2 \qquad (1)$$

where I_s is the sample average magnetic moment density. $I_s(T)/I_s$ (0 K) results for two Ni/SiO_2 catalysts are presented in Fig. 1. It is important that this ratio be determined for each sample in the temperature range of interest, as Fig. 1 also indicates an intrinsic crystallite size dependence (*10*). Equation (1) then relates average magnetic phase temperature to measured moment for a given sample at a given field.

It is more convenient for thermometry to use a curve relating sample moment, or a measure of it, to sample temperature. Such calibrations should be done in flowing H_2 between kinetic experiments, because sample moment depends upon surface coverage. Hydrocarbon fragments will build up on the surface of a fresh catalyst sample, reaching some steady-state level. Calibration after this steady state has been reached prevents interference with the thermometry. Surface coverage by H_2 will also change with temperature, and this is accounted for by flowing hydrogen over the sample during calibration.

An inexpensive, sensitive, and versatile device for low field magnetization work is the AC permeameter popularized by Selwood (*5, 11*). A dual secondary coil design, operable to 525 K and compatible with existing sample cells (*9*), was built and placed in an oven. The primary coil is excited by 15 V at 50 Hz, while the net output of the secondary coils is read on a DVM, converted to DC, and recorded on strip chart. A DC power supply is used to zero the output. With the current permeameter/sample configuration noise levels are 0.003 mV, response is linear, and sensitivity is about 5 mV/g of Ni. As only changes in output are important, a better estimate of sensitivity is not necessary.

The catalyst is 25% Ni/SiO_2 and has been studied extensively (*8–10*). About 0.5 g of catalyst, crushed to pass 100 mesh, is placed in the flow cell used for kinetics and magnetization studies. The catalyst is then

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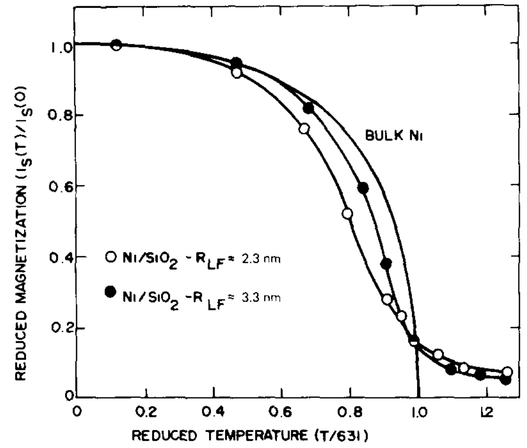

FIG. 1. Reduced moment density as a function of reduced temperature, R_{LF} is the radius calculated from the first volume moment determined from low field magnetization.

reduced in hydrogen at 673 K and cleaned in helium at 723 K (*8*). Hydrogen and helium flows are 50 ml/min. After reduction and cleaning, the cell is placed in the permeameter, and a flow of hydrogen (and sometimes helium) is established. The decrease in sample magnetization upon hydrogen chemisorption is about 15%, as expected for these samples. After thermal equilibration, ethane is introduced and kinetic experiments performed. Products are analyzed with a Varian 1200 GC-FID.

Coupled magnetization–kinetic experiments are performed at around 500 K, using two procedures. One method is to introduce ethane (at constant total pressure) into an H_2 stream which is in equilibrium with the Ni/SiO$_2$ catalyst sample. The other method of performing crystallite thermometry is changing from a very low reaction rate to a higher one. Due to the negative-order dependence of rate on H_2 pressure, this is easily accomplished by reducing the H_2 partial pressure in a flow of H_2 and ethane. With either experimental procedure, there is often a small increase in sample moment due to H_2 desorption followed by a decrease due to a rise in average crystallite temperature. If it is assumed that desorption and reaction rate increase occur in series, then the difference in AC permeameter output voltage between the maximum and the final steady value is the measure of temperature rise. Comparisons with voltage changes upon equivalent changes in H_2 pressure in flowing H_2 and He indicate that the maximum error resulting from this series assumption is 1 K and estimated temperature rises will be low. A better method of accounting for adsorption–desorption affects is being sought. After magnetization has stabilized, conversion data is taken, and the reaction rate is lowered.

It is interesting to compare measured bulk fluid to catalyst pellet temperature differences with those calculated using observed rates (*1*, *2*). Both direct calculation and the criterion developed by Anderson (*2*) indicate isothermal catalyst particles for all experiments performed. This means any temperature difference is lumped in the external film. Then the average crystallite temperature is that of the catalyst particle, neglecting any crystallite to support gradients. Though not critical in this work, criteria for the absence of concentration gradients (*1*, *2*) are well satisfied, even in the worst cases.

Three sets of data are presented in Table 1. These experiments were performed by going from a low reaction rate to a higher one, as has been described. In each set, the first experiment, with low conversion, serves as the base case for establishing temperature changes. Changes in crystallite temperature, as determined from magnetization data, are reported as $(\Delta T)_m$ after subtracting any change in bulk fluid temperature and rounding to the nearest degree. $(\Delta T)_m$ is then the measured change in interphase temperature gradient from the base case, and is the particle to fluid temperature difference if that of the base case is zero. $(\Delta T)_c$ is the calculated interphase gradient reported to the nearest degree, and is zero for each base case.

The measured temperature rises are higher than those calculated, except in set C (probably because of round-off). This is

TABLE 1

Summary of Thermometry Experiments[a]

Run	$F_1 \times 10^5$ $\left(\frac{\text{mol}}{\text{s}}\right)$	y_1 (%)	y_2 (%)	y_3 (%)	T^b (K)	P (atm)	x (%)	$(\Delta T)_c{}^c$ (K)	$(\Delta T)_m{}^c$ (K)	Mears' criterion[d]
A 1	1.6	32	68	0	504	1	0.54	0	—	Pass
2	1.5	88	12	0	505	1	6.8	4	8	Fail
3	1.6	31	69	0	504	1	0.30	0	0	P
4	1.6	85	15	0	505	1	5.0	3	5	F
B 1	1.6	21	34	45	499	1	2.1	0	—	P
2	1.6	24	22	54	500	1	7.8	2	5	F
3	1.6	21	34	45	499	1	2.1	0	0	P
4	2.7	35	20	45	507	1	28.0	11	17	F
C 1	13	83	17	0	505	1.2	0.65	0	—	P
2	13	88	12	0	505	1.2	1.3	1	1	F
3	13	83	17	0	505	1.2	0.75	0	0	P
4	13	90	10	0	505	1.2	1.4	1	1	F
5	13	83	17	0	505	1.2	0.75	0	0	P
6	13	88	12	0	505	1.2	1.4	1	1	F

[a] Subscripts: 1 = Ethane, 2 = Hydrogen, 3 = Helium; y_i's are mole fractions, x is fractional conversion of ethane.

[b] Thermocouple at bed exit.

[c] Rounded to nearest degree, also see text.

[d] Refers to Mears' criterion for interphase temperature gradients.

not unexpected considering that interphase transport calculations at low Reynolds numbers are unreliable and that average reaction rates are used in calculating temperature differences. The constant reaction rate approximation is poor in some of the high conversion cases in sets A and B, as the conversion of hydrogen is as much as 50%. Though only experiment B4 showed a large increase in bulk fluid temperature, the interphase temperature differences may reasonably vary with bed length, as rates will. If the differential reactor approximation is sound, as in set C, problems still exist. The assumption that each crystallite has the same temperature, made for tractability, may not be reasonable if catalytic activity depends on crystallite size or orientation.

Experiment set C demonstrates one use of magnetic crystallite thermometry in kinetics. For ethane hydrogenolysis, an interphase temperature difference of 0.6 K will effect the observed rate by 5%. The last column in Table 1 indicates whether Mears' criterion (*1*, *2*) for the absence of interphase temperature gradients is passed. The measured temperature differences between the crystallites and bulk fluid are in agreement with Mears' criterion, for the experiments performed. Further testing of this common approach to checking for the influence of interphase energy transport at low flow rates is underway.

Experiment sets A and B indicate another use for the thermometry. External temperature gradients will usually be the first to disguise kinetics as the observed rate increases. The average catalytic crystallite temperature would then serve as the best available estimate of reaction temperature. This adds flexibility to kinetic experiments, as higher observed rates are allowed.

ACKNOWLEDGMENTS

Financial support from the National Science Foundation and the Petroleum Research Fund is gratefully acknowledged.

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Received June 1, 1983; revised November 3, 1983