AIP The Journal of Chemical Physics

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Citation: J. Chem. Phys. **75**, 3847 (1981); doi: 10.1063/1.442539
View online: http://dx.doi.org/10.1063/1.442539
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v75/i8
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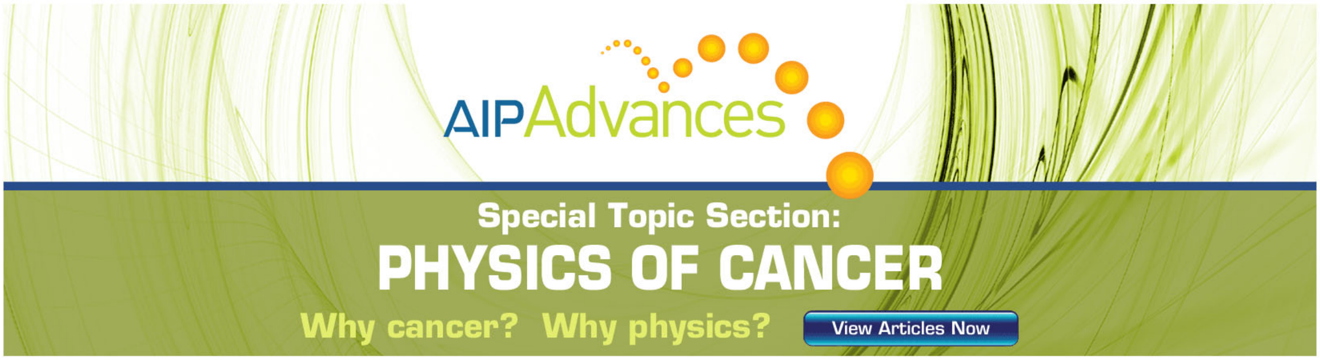

A study of the possible effects of an external magnetic field upon the reduction of NiO, Fe_2O_3, and Co_3O_4 by hydrogen

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(Received 22 May 1981; accepted 10 July 1981)

The reduction of NiO, Fe_2O_3, and Co_3O_4 by H_2 was followed using evolved gas analysis of the H_2O formed during the process. This technique is insensitive to the presence of an external magneteic field. Samples of these oxides were heated at several rates in flowing H_2 both with and without the application of an external field of 4–7 kOe. There were no differences observed in the reduction behavior due to the presence of this external field, contrary to some previous reports.

INTRODUCTION

There has been considerable interest, speculation, and controversy regarding the influence of an external magnetic field upon reaction rates of materials below their magnetic transition temperatures. Two classes of reactions and patterns of behavior have been observed. One class is the reaction of nickel metal and carbon monoxide to form nickel carbonyl. Initial reports[1–3] indicated a highly unique cyclic dependence of the reaction rate upon external magnetic field strength. A recent study,[4] however, suggests that this was an artifact.

The second class of reactions involves the reduction of metal oxides by hydrogen. In this case, no cyclic behavior has been observed but enhanced reactivity has been claimed for the reduction of some oxides of iron[5,6] and cobalt[7] but not in the case of nickel oxide.[8] These reduction rates have been followed by gravimetric techniques which are subject to several problems associated with the presence of a strong magnetic field. The attraction of the field for the magnetic reactant or product phase overwhelms the weight change associated with the loss of oxygen. Consequently, any variations in this attraction due to changes in the temperature, crystallinity, crystallite size, morphology, and rearrangement or movement are highly significant.

In order to alleviate these problems, an evolved gas analysis (EGA) technique has been developed whereby the moisture content in the gas stream is used to follow the course of the reaction.[9–11] This EGA method has been shown to give essentially identical results to thermogravimetric techniques but is not subject to influences by an external magnetic field. Samples of Fe_2O_3, Co_3O_4, and NiO where heated in hydrogen with and without the presence of an external magnetic field in order to determine if the magnetic field has a significant effect upon the rate or temperature at which the reaction occurs.

EXPERIMENTAL PROCEDURES AND RESULTS

The EGA cell[10] and data processing[9,11] have been described in detail elsewhere. Briefly, however, it is based upon a Parametrics Model 3000 moisture sensor. The output of this device is a voltage proportional to the dew point of the gas stream. It is independent of flow rate and has rapid response.

The samples were Co_3O_4, Fisher reagent; Fe_2O_3, C. K. Williams high purity, and NiO derived from Fisher reagent $NiCO_3$ calcined in air for 1 h at 460 or 1000 °C. Surface areas were obtained by BET methods using N_2 adsorption (for the values, see figure captions).

Samples of the oxides were dried at 130 °C in vacuum overnight, transferred to the EGA cell, and heated at 10 °C min^{-1} in a flow of H_2 at 300 ml min^{-1}. Earlier work[11] in the absence of a magnetic field had shown pronounced effects due to outgassing of NiO. Hence, samples of NiO were also run at 2.0 °C min^{-1} in the same flow of H_2 but without the prior vacuum heating step. Samples were run both at 0 and at 4 or 7 kOe external magnetic fields.

The shape of the pole faces and the sample position were chosen so that the resulting field gradient forced the magnetic samples towards the bottom of the fused silica crucible.

RESULTS AND DISCUSSION

The results using the predried samples are summarized in Figs. 1–3 for Fe_2O_3, Co_3O_4, and NiO, respectively. The presence of an intermediate species during the reduction of Fe_2O_3 is suggested by the shoulder near 300 °C for the curves in Fig. 1. Reduction to Fe_3O_4 theoretically represents about 11% of the total weight loss and appears to be a reasonable explanation for the low temperature peak. Further reduction does not show any evidence of an FeO intermediate. This is expected because below 540 °C FeO is unstable with respect to disproportionation into Fe_3O_4 and Fe. No intermediate species, e.g., CoO are evident during the reduction of Co_3O_4 (see Fig. 2).

The major point, however, is that there are no significant differences in the reduction rates induced by the external magnetic field for any of the oxides Fe_2O_3, Co_3O_4, or NiO, as indicated by the close correspondence of each pair of curves in Figs. 1–3. For the coarser sample of NiO which was not preheated (Fig. 4) and heated at a slower rate in a lower magnetic field, the agreement between the two curves is again excellent. The two-step nature of the reduction without preheating in vacuum, which was observed earlier,[11] is evident again. It is not the purpose of this paper to elucidate the mechanism of reduction of these materials but rather to determine whether there are effects of an external

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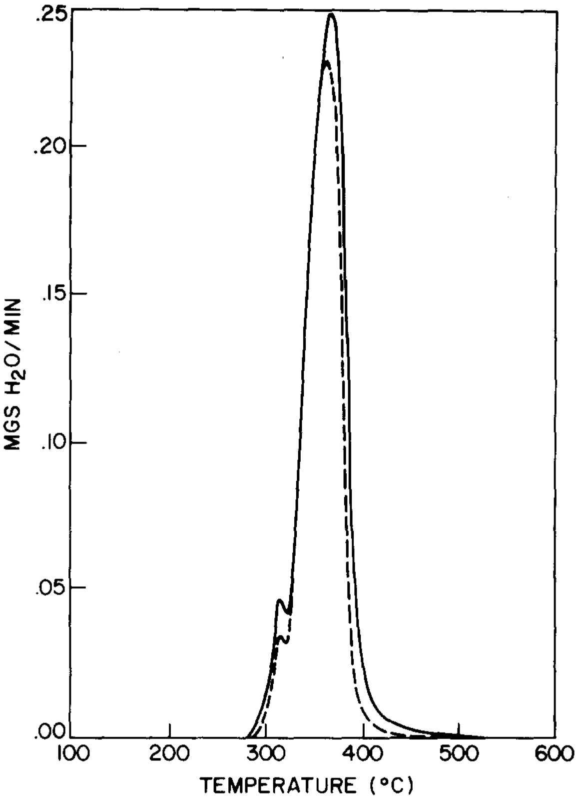

FIG. 1. EGA curves for the reduction of Fe_2O_3 (0.6 $m^2 g^{-1}$) by H_2 at 10 °C min^1: – 5.26 mg, 34.8% total wt. loss, 0 kOe; --- 4.80 mg, 34.8% total wt. loss, 7 kOe.

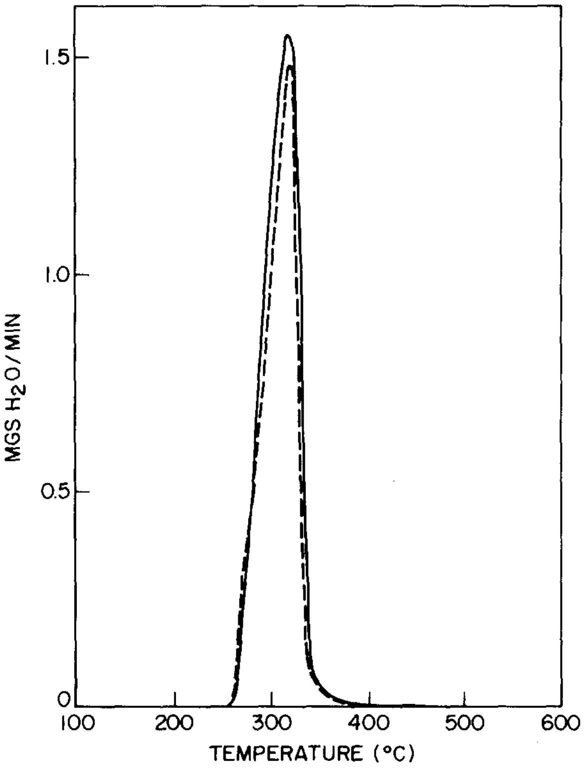

FIG. 2. EGA curves for the reduction of Co_3O_4 (1.6 $m^2 g^{-1}$) by H_2 at 10 °C min^1: – 25.34 mg, 28.5% total wt. loss, 0 kOe; --- 24.57 mg, 28.5% total wt. loss, 7 kOe.

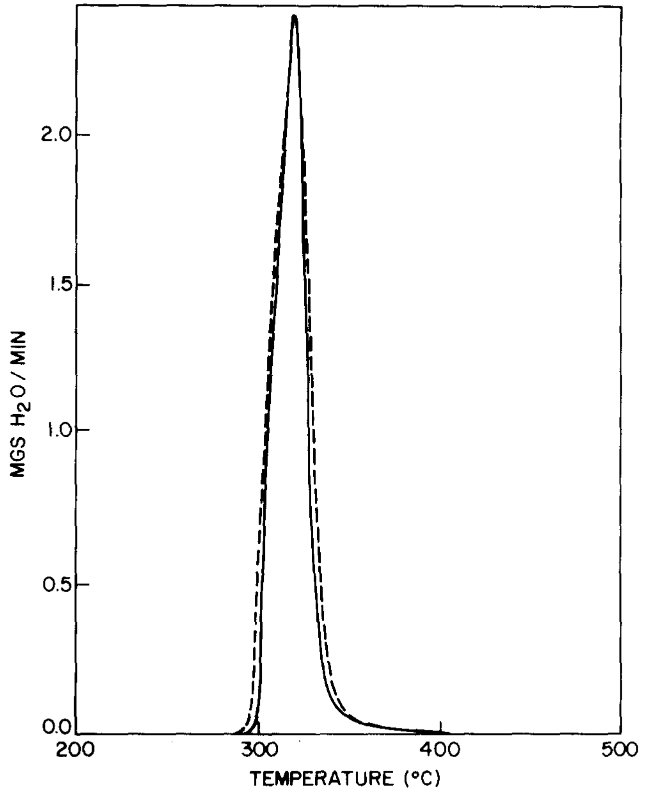

FIG. 3. EGA curves for the reduction of NiO (57 $m^2 g^{-1}$) by H_2 at 10 °C min^{-1}: – 24.38 mg, 23.3% total wt. loss, 0 kOe; --- 25.76 mg, 23.1% total wt. loss, 7 kOe.

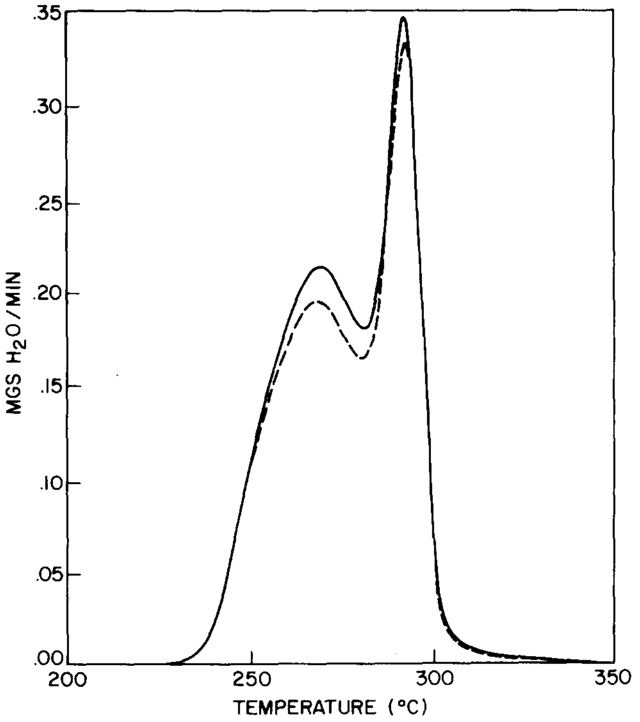

FIG. 4. EGA curves for the reduction of NiO (1.0 $m^2 g^{-1}$) by H_2 at 2 °C min^{-1}: – 25.61 mg, 21.2% total wt. loss, 0 kOe; --- 24.69 mg, 21.2% total wt. loss, 4 kOe.

magnetic field on whatever mechanism is involved.

Clearly, there are no significant advantages in performing the reductions in a magnetic field such as more rapid rates or reduction in the temperature of the reaction. Earlier gravimetric results[5-7] which imply such changes are probably due to distortions of the gravimetric measurements brought on by magnetic effects arising from, e.g., amorphous to superparamagnetic to bulk crystalline transitions as the reaction zones grow and/or rearrangement or alignment of the particles during the reaction.

[1] G. S. Krinchik, R. A. Shvartsman, and A. Y. Kipnis, JETP Lett. 19, 231 (1974).

[2] G. S. Krinchik and R. A. Shvartsman, Sov. Phys. JETP 40, 1153 (1975).

[3] E. L. Kremer and A. Y. Kipnis, Russ. J. Phys. Chem. 52, 18 (1978).

[4] P. DeGroot and K. Dransfeld, Z. Anorg. Allg. Chem. 446, 39 (1978).

[5] M. W. Rowe, S. M. Lake, and R. Fanick, Nature (London) 266, 612 (1977).

[6] R. Skorski, Nature (London) 240, 15 (1972).

[7] M. W. Rowe, D. A. Edgerley, M. Hyman, and S. M. Lake, J. Mater. Sci. 14, 999 (1979).

[8] M. W. Rowe, R. Fanick, D. Jewett, and J. D. Rowe, Nature (London) 263, 756 (1976).

[9] P. K. Gallagher and E. M. Gyorgy, in *Thermal Analysis*, edited by H. G. Wiedeman (Birkhauser, Boston, 1980), Vol. I, pp. 113–118.

[10] W. R. Jones, Thermochim. Acta (in press).

[11] P. K. Gallagher, E. M. Gyorgy, and W. R. Jones J. Therm. Anal. (in press).