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REACTIVITY AS A FUNCTION OF DISPERSION

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ABSTRACT

Reactivity as a function of dispersion was studied in reduction by H_2 of hematite, hematite-in-alumina solid solutions and spinel formation in $MgO.Al_2O_3$, $MgO.Fe_2O_3$, $ZnO.Al_2O_3$ and $ZnO.Fe_2O_3$ systems. The degree of dispersion was controlled utilizing the advantages offered by a special preparation method: the spray-decomposition technique.

INTRODUCTION

Reactivity as a function of dispersion has been studied in a wide range of material systems and solid-state reactions. The purpose of this work is to add new data to this old field of investigation utilizing the possibilities offered by a new solid-sample preparation technique: /thermal/ spray decomposition of liquid systems. The details of this technique have been published elsewhere /ref.1/. We have prepared and studied three material systems:

i. hematite samples of different particle size and preparation temperature
ii. Fe_2O_3 in Al_2O_3 type real and supersaturated solid solutions
iii. MgO or ZnO and Fe_2O_3 or Al_2O_3 containing pre-spinel oxide systems

In cases i. and ii. the reducibility, while in the case iii. the ease of spinel-formation was studied as a function of dispersion.

METHODS AND RESULTS

i. Reducibility of hematite by H_2

When the kinetics of the reduction of hematite is controlled by diffusion of H_2 and H_2O through the product layer, a strong dependence upon particle-size is expectable /ref.2/. Temperature of ignition influences at the same time the defect-structure of the sample thus influencing also the reactivity /ref.3/. When these effects are not separated, e.g. by preparing samples of

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different particle size at different ignition temperatures /ref.4/ the conclusions can be misleading.

To study the significance of particle size and temperature of ignition, separately, spray-decomposition /ref.1/ and "drop-decomposition" preparation techniques were applied /see Table 1/. Drop decomposition means that the solution was decomposed dropwise in a Pt crucible heated at the same temperature as that of the furnace at spray-decomposition. Thus the conditions of preparation can be taken as identical, except the size of the decomposed droplets and the quality of the product can also be considered as identical, except the particle size /as controlled by the droplet--size/. X-ray diffractograms showed pure and well crystallized hematite phase in all cases.

The reducibility was studied by TPR and isotherm reduction. Results obtained by the latter method are also listed in Table 1. It is confirmed that both the particle diameter /diffusion/ and the ignition temperature /defect-structure/ have an effect upon the reducibility of hematite.

TABLE 1

Preparation and properties of hematite samples

Sample denotation	Preparation and Heat-treatment	F m^2g^{-1}	$\bar{d}$ /um	k450 min^{-1}
S-500	spd, 500°C, air 24 hr, 500°C, air	12.3	0.8	8.6
S-800	spd, 800°C, air 24 hr, 800°C, air	2.7	1.4	5.7
D-500	dd, 500°C, air 24 hr, 500°C, air	6.5	8.6	4.6
D-800	dd, 800°C, air 24 hr, 800°C, air	3.2	11.6	3.75

$\left.\begin{array}{l}\text{spd: spray-decomposition}\\ \text{dd: drop-decomposition}\end{array}\right\}$ of 1M $Fe/NO_3/_3$

$\bar{d}$: mean particle diameter

k_{450}: rate constant of reduction a 450°C /zero order/

ii. Reducibility of Fe_2O_3 in Al_2O_3 solid solutions

It is a well-known experimental fact that a transition metal ion dissolved in the matrix of a non-reducible oxide is much less reducible than in itself. In addition to earlier studies referring to hematite-in-corundum solid solutions, we prepared and studied hematite-in-amorphous alumina solid solutions and oversaturated solid solutions. These samples were prepared by thermal decomposition of the aerosol of the aqueous solution of the component nitrates /spray-decomposition/. The details of preparation and phase analysis have been published elsewhere /ref.5/.

The reducibility was studied by GC pulse technique /using N_2 as carrier gas/. It turned out that at a given temperature the reduction resulted in a given degree of conversion and increase of temperature increased this "equilibrium" conversion. It is understandable if we consider that the time of the reaction is controlled by the time of residence of H_2 pulses. This residence time limits the depth of the product layer which can be passed through by H_2, thus the reduction stops at a given conversion. Reoxidation of the reduced samples was also studied by the same technique. Results are summarized in Table 2.

TABLE 2
Reduction and reoxidation of Fe_2O_3 in Al_2O_3 solid solutions

Sample	Phase	Temperature °C	Degree of reduction by H_2 %	Degree of reoxidation by O_2 %
AlFe1*	real solid solution with isolated iron ions	500	0.0	---
AlFe10	real solid solution with strong interactions of iron ions	428	0.0	---
		454	3.6	3.5
		498	7.0	6.8
AlFe24	supersaturated solid solution	388	2.1	1.2
		422	6.2	5.1
		471	12.3	12.2
AlFe31	supersaturated solid solution	430	17.0	16.7
		478	17.1	16.8

* figures denote Fe-content in atomic /cationic/ per cent

At a given sample the increase of temperature /the rate of diffusion/ increases the degree of reduction. Comparing the different samples it turnes out that greater Fe_2O_3 content facilitates the reduction, i.e. there is a pronounced difference if the Fe^{3+} ions are isolated or interacting with each other. Reoxidation is reversibile. All the solid solutions are more resistant against reduction as compared with pure hematite /where the reduction starts at 350°C/.

iii. Effect of the degree of dispersion upon reactivity in spinel formation as studied by "pre-spinel" oxide systems prepared by different methods

The ease of spinel-formation in $MgO.Al_2O_3$, $MgO.Fe_2O_3$, $ZnO.Al_2O_3$ and $ZnO.Fe_2O_3$ systems has been investigated as a function of the mutual dispersion of the component oxides. Four preparation methods were applied to obtain samples of different degree of component-distribution: spray-decomposition, drop-decomposition, slow evaporation and reversed coprecipitation. Samples were heat--treated first at 500 °C then at 1000 °C. Phase analysis showed pure and well-crystallized spinel already at 1000 °C in the case of spray-decomposition, while the other methods /following the above sequence/ provided either less crystallized spinel or spinel phase mixed with the component oxide phases. Results can be interpreted concerning the different effectivity of the methods to produce oxide systems in which the components are uniformly distributed at the atomic level /ref.6/.

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