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Kinetics of Solid-State Spinel Formation: Effect of Cation Coordination Preference

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Formation of the spinels $MgAl_2O_4$, $NiAl_2O_4$, and $ZnAl_2O_4$ from α-alumina and MgO, NiO, or ZnO was studied at several temperatures by measuring the fraction of reaction completed as a function of time. Apparent activation energies (in kJ mole^{-1}) were $MgAl_2O_4$, 185; $NiAl_2O_4$, 300; and $ZnAl_2O_4$, 230. At 1373 K, the rates of spinel formation followed the sequence $MgAl_2O_4 > ZnAl_2O_4 > NiAl_2O_4$. The results are discussed in terms of coordination preference of the involved divalent cations. © 1994 Academic Press, Inc.

INTRODUCTION

The process $XO_{(s)} + Y_2O_{3(s)} \rightarrow XY_2O_{4(s)}$, by which spinels ($XY_2O_4$) are formed from the parent (XO and Y_2O_3) metal oxides, is very often used as a prototype of heterogeneous solid-state reactions. The main reasons for this are the relative simplicity of the system and the close similarity between the anion sublattices of reactants and spinel products. This avoids topochemical complications which could otherwise make the analysis of kinetic data rather cumbersome. As a general rule, the mechanism of solid-state spinel formation is the counterdiffusion of cations through a nearly immobile (and approximately close packed) anion array (1–3). According to Tompkins (4) and to Stone and Tilley (5, 6) the corresponding kinetics depends mainly on two factors: (i) cation size and (ii) site-preference energy. The first of these factors is clearly related to strain energy in an elastic matrix model of cation diffusion. The second one refers to energy changes involved in the diffusion of metal ions through a series of tetrahedral and octahedral vacancies available in the anion sublattice of the spinel structure, where only one-half of the octahedral and one-eighth of the tetrahedral interstices are occupied by cations. This allows a voidal diffusion path, as pointed out by Azaroff (7). With decreasing cation size and with smaller energy changes between tetrahedral and octahedral coordination, the mobility of the ion should increase, leading to higher reactivity.

To verify the above hypothesis, Stone and Tilley (6) carried out pioneering work in which the rate of formation of a number of spinels was experimentally examined. Although their results were roughly in line with expectations, some apparent discrepancies were also observed. For aluminates, the reaction rates followed the sequence $CuAl_2O_4 > ZnAl_2O_4 \simeq MgAl_2O_4 > NiAl_2O_4$. The low rate found for $NiAl_2O_4$ formation was attributed to the high octahedral preference (8, 9) of the Ni^{2+} ion (~50 kJ mole^{-1}), while the rate of formation of $CuAl_2O_4$ could be influenced by tetragonal (Jahn–Teller) distortion, a point further pursued by Murthy *et al.* (10). However, given the above hypothesis, $MgAl_2O_4$ should form considerably faster than $ZnAl_2O_4$. The Zn^{2+} ion is about 12% larger than Mg^{2+} and, more significantly, Zn^{2+} has a strong tetrahedral preference (~35 kJ mole^{-1}) while Mg^{2+} shows very little site preference in spinel oxides (8, 9). We have reexamined this point and report here the results of a careful investigation on the kinetics of spinel formation in the systems XO/Al_2O_3 ($X = Mg^{2+}, Ni^{2+}, Zn^{2+}$). It is shown that reaction rates conform to expectations from arguments based on site-preference energy.

EXPERIMENTAL

To facilitate interpretation of kinetic data, some precautions were taken to standardize the reacting oxides and to define the geometry of the reaction interface. Al_2O_3 was used in spheres of 1.5–2 mm diameter, which were embedded into a mass of finely divided divalent metal oxide (particle size <2 μm). These reaction mixtures, contained in platinum crucibles, were subjected to isothermal heating at temperatures ranging from 1173 to 1723 K; temperature fluctuations were kept within ±10 K. Samples were removed from the furnace at various times and the progress of the reaction was determined. To this end, the unreacted divalent oxide was dissolved in dilute hydrochloric acid, in which α-Al_2O_3 and the spinels are insoluble, and the remaining solid material (alumina spheres covered with a spinel layer) were analyzed by complexometric titration with EDTA (after fusion with $KHSO_4$) and by quantitative X-ray diffraction. Further

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details of the analytical procedures were given elsewhere (11). The results of chemical and diffractometric analyses were found to be entirely consistent in all cases.

The alumina spheres (γ-polymorph) were obtained from Rhône-Poulenc and had a purity greater than 99.99%, as determined by spectroscopic analysis. MgO, NiO, and ZnO with a nominal purity 99.99% were supplied by Koch-Light Laboratories. To avoid complications from non-equilibrium lattice defects and solid-state phase transitions, the divalent metal oxides were calcined at 973 K prior to preparation of the reaction mixtures. Similarly, Al_2O_3 was calcined for 3 hr at 1673 K, thus ensuring total conversion into the stable α-form (checked by X-ray diffraction). This precaution avoided enhanced reactivity (Hedvall effect) at phase-transition temperatures.

RESULTS AND DISCUSSION

The fraction of reaction completed (x) as a function of time for each system and isothermal run is shown in Figs. 1a–c. This fraction is referred to the initial amount of α-alumina, since a large excess of the divalent metal oxide was used in the reaction mixtures. For the MgO/Al_2O_3 and ZnO/Al_2O_3 systems, isothermal runs were conducted at 1173, 1273, and 1373 K. However, for NiO/Al_2O_3, higher temperatures were used (1373, 1623, and 1723 K) owing to the very low reaction rates observed in a preliminary run at 1173 K. The ZnO/Al_2O_3 system was also studied at higher temperatures and the results have been already published (11); they are not shown here because a change in mechanism (due to volatilization of ZnO) renders them unsuitable for the present study. For the sake of comparison, the kinetic results obtained for the three systems at 1373 K are depicted at the same scale in Fig. 1d.

Inspection of Fig. 1 shows that the reaction is continuously decelerated in all cases, following approximately a parabolic rate law. This is the behavior expected for a diffusion-controlled process. The fact that the kinetic curves are not sigmoid can be taken as strong evidence against kinetic control by nucleation (12–14). The data corresponding to each isothermal run and system were analyzed following the Ginstling–Brounshtein (15) equation,

$$1 - 2x/3 - (1 - x)^{2/3} = Kt, \qquad [1]$$

which assumes that the diffusion coefficient of the mobile species is independent of time (t). Plots of the first member of Eq. [1] versus time were found to fit straight lines passing through the origin, as illustrated in Fig. 2 for the MgO/Al_2O_3 system. A modified Ginstling–Brounshtein equation (13),

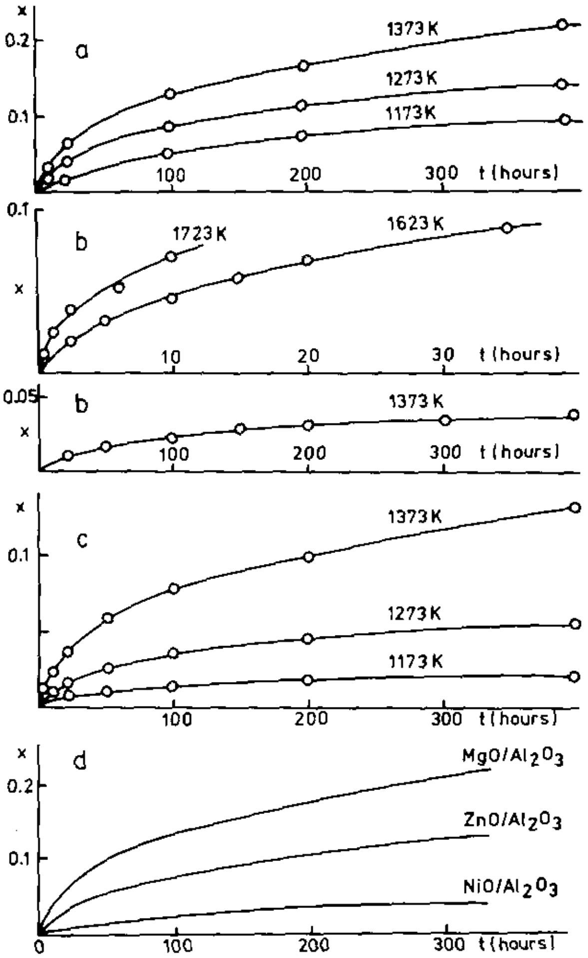

FIG. 1. Fraction of reaction completed, x, as a function of time at various temperatures: (a) MgO/Al_2O_3; (b) NiO/Al_2O_3; (c) ZnO/Al_2O_3; (d) comparison of the three systems at 1373 K.

$$1 - 2x/3 - (1 - x)^{2/3} = K \ln t, \qquad [2]$$

which assumes a diffusion coefficient changing inversely with time, was also used and found to be inadequate to describe the experimental results. Plots of the first member of Eq. [2] versus ln t did not give straight lines.

Equation [1] was also used to calculate the corresponding values of the rate constant (K) for the different systems and isothermal runs. These values are shown in the Arrhenius plot of Fig. 3. Apparent activation energies, derived from the slope of the corresponding straight lines in Fig. 3, are given in Table 1. For comparison, some reported literature values are also shown in this table. In general terms, the agreement can be considered satisfactory, especially when due consideration is given to the fact that the rate and (apparent) activation energy of a solid-state reaction can be critically dependent on experimental conditions. On the other hand, activation energies

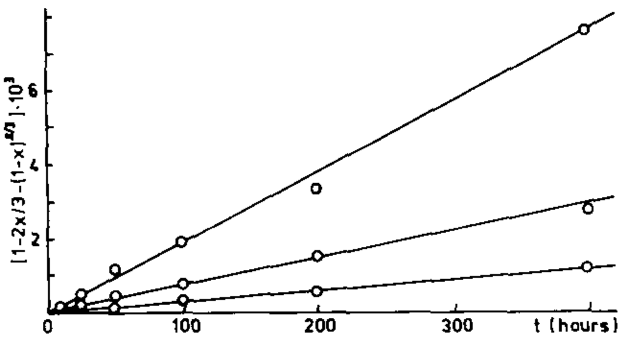

FIG. 2. Illustration of the validity of the Ginstling–Brounshtein reaction rate model. System MgO/Al_2O_3.

TABLE 1

Apparent Activation Energy (E_a, kJ $mole^{-1}$) for the Different Reaction Systems

System	E_a	Reference
MgO/Al_2O_3	185	Present work
	171	(16)
	205	(17)
NiO/Al_2O_3	300	Present work
	326	(18)
	430	(6)
ZnO/Al_2O_3	230	Present work
	230	(19)

calculated from solid-state kinetic data are often subject to considerable experimental error. Our own values (Table 1) are not likely to have a precision better than ±25 kJ $mole^{-1}$.

Figure 1d clearly shows that reaction rates for spinel formation follow the sequence $MgAl_2O_4 > ZnAl_2O_4 > NiAl_2O_4$, which is also consistent with the corresponding values of activation energy shown in Table 1. For $MgAl_2O_4$ and $ZnAl_2O_4$, these results are at variance with those of Stone and Tilley quoted in the Introduction. Close inspection of the work done by these authors showed that they compared reaction rates at 1473 K. We have recently shown (11) that formation of $ZnAl_2O_4$ from ZnO and Al_2O_3 follows a cation counterdiffusion mechanism at temperatures lower than 1400 K. However, at a higher temperature volatilization of ZnO brings about a solid–gas route which considerably increases the reaction rate. This phenomenon is very likely to have been the cause of the high reaction rate observed by Stone and Tilley in the formation of $ZnAl_2O_4$.

Our present results provide strong evidence to support the hypothesis that cation coordination preference affects reaction rates, in the sense outlined in the Introduction.

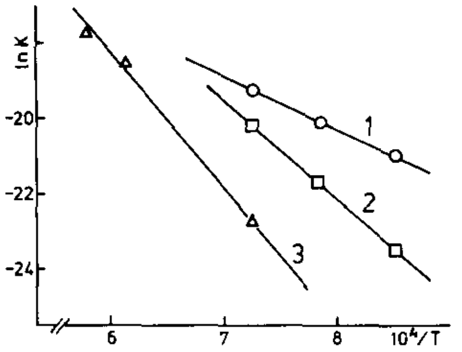

FIG. 3. Arrhenius plot for calculation of activation energies: (1) MgO/Al_2O_3; (2) ZnO/Al_2O_3; (3) NiO/Al_2O_3.

Tetrahedral preference of Zn^{2+} and octahedral preference of Ni^{2+} make migration of these cations (through the spinel layer) more difficult, because of the site-preference energy lost in going from a tetrahedral to an octahedral site (or vice versa). We must bear in mind that voidal diffusion in the spinel structure always implies alternating changes in coordination symmetry of the migrating cation. The Mg^{2+} ion, which has no site preference, moves more readily, thus leading to the observed higher rate of $MgAl_2O_4$ formation.

The foregoing discussion makes the implicit assumption that diffusion of the divalent cation (through the spinel layer) plays a role in controlling the reaction kinetics. This is equivalent to accepting that the diffusion coefficients of the divalent cations involved (Mg^{2+}, Ni^{2+}, Zn^{2+}) are not much greater than the corresponding value for Al^{3+}. Nagata *et al.* (20) gave strong evidence to support this assumption, at least in the case of $ZnAl_2O_4$, but the fact remains that no precise data on diffusion coefficients for all the cations involved (particularly for Al^{3+}) seem to be available. However, very reliable data for the gallate spinels $CoGa_2O_4$ and $NiGa_2O_4$ were reported by Schmalzried (21) and by Laqua *et al.* (22), respectively. A summary of these data is given in Table 2. They cover a composition range which spans both sides of the stoichiometric value. This is a relevant feature, since the growing spinel layer is likely to have (transient) deviations from stoichiometry. The data shown in Table 2 conclusively prove that diffusion coefficients for the divalent cations are of the same order as the corresponding values for the trivalent cation (Ga^{3+}). There are no a priori reasons suggesting that Al^{3+} diffusion in aluminate spinels could be significantly slower than Ga^{3+} diffusion in gallate spinels. In fact, Al^{3+} (because of its smaller size) should diffuse faster than Ga^{3+}. Thus, the assumption that diffusion of the divalent cation plays a role in determining the overall kinetics of aluminate spinel formation seems to be well justified.

TABLE 2

Tracer Diffusion Coefficients ($cm^2\ sec^{-1}$) for $^{60}Co^{2+}$ and $^{67}Ga^{3+}$ in $Co_{1-a}Ga_{2+2a/3}O_4$ at 1783 K in Air (21) and for $^{63}Ni^{2+}$ and $^{67}Ga^{3+}$ in $Ni_{1-a}Ga_{2+2a/3}O_4$ at 1858 K (22)

a ($Co_{1-a}Ga_{2+2a/3}O_4$)	D_{Co}	D_{Ga}
-0.073	$3.14 \cdot 10^{-10}$	$7.17 \cdot 10^{-11}$
-0.037	$6.29 \cdot 10^{-10}$	$2.31 \cdot 10^{-10}$
0.036	$3.83 \cdot 10^{-9}$	$3.93 \cdot 10^{-9}$
0.101	$6.63 \cdot 10^{-8}$	$1.10 \cdot 10^{-8}$

a ($Ni_{1-a}Ga_{2+2a/3}O_4$)	D_{Ni}	D_{Ga}
-0.085	$5.02 \cdot 10^{-11}$	$5.45 \cdot 10^{-11}$
-0.050	$8.96 \cdot 10^{-11}$	$2.04 \cdot 10^{-10}$
0	$2.25 \cdot 10^{-10}$	$4.59 \cdot 10^{-10}$
0.110	$2.67 \cdot 10^{-9}$	$1.62 \cdot 10^{-8}$

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