EFFECT OF ADMIXTURES ON THE FORMATION OF $NiAl_2O_4$ BY SOLID PHASE REACTION

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The effect of silicon and of subgroups IVb—VIIIb elements on the rate of the reaction $NiO + Al_2O_3 = NiAl_2O_4$ proceeding in the solid phase in a powder system at 1100—1300°C was examined. A remarkable accelerating effect was found for V(V) and Ti(IV), whereas retardation of the $NiAl_2O_4$ formation was observed with Mo(VI) and Cr(III). The activation energies of the reaction in the presence of the various admixtures were determined.

In the present paper we follow up our previous work[1] dealing with the influence of admixtures on the rate of formation of $NiAl_2O_4$. The obtained results concerning the effect of elements of the groups I and II of the periodic system on the formation of the nickel spinel initiated the study of the effect of silicon and elements of the subgroups IVb – VIIIb; these elements can be contained in catalysts for catalytic oxidation conversion of hydrocarbons, and their effect is of interest from the point of view of the possible influencing of the course of the solid phase reaction.

EXPERIMENTAL

The α modification of aluminium oxide prepared as described previously[2] served for the measurements. The temperature of the final calcination of the starting material was 1300°C. The grain size of the aluminium oxide used for the powder reaction lay in the region 63—90 μm. The grain size of the nickel oxide powder employed was below 1 μm. The final maximum temperature of nickel oxide calcination was 1100°C.

The admixtures were introduced into the reaction mixture in the form of oxides, reagent grade purity, in 3% wt. amounts with respect to the aluminium oxide in the equimolar reaction mixture; the only exception was vanadium pentoxide, whose content amounted to 1·5% wt. only.

The procedure of powder mixing, preparation of the pellets of the reagents, conduction of the reaction, and method of analysis of the reaction products have been described in detail in the preceding papers[1,2].

RESULTS AND DISCUSSION

The measured rates of formation of the spinel in the presence of the admixtures are shown in Figs 1 – 3; the curves fitting the experimental points represent the isotherms calculated according to the Dunwald–Wagner rate equation

$$\alpha = 1 - (6/\pi^2)\,\left[\sum_{n=1}^{\infty}(n^{-2})\exp(-k_{DW}\tau)\right], \tag{1}$$

where α is the degree of conversion (mol/mol), k_{DW} is the rate constant (s^{-1}), and τ is the reaction time (s). The experimental values measured were evaluated by employing the numerical data calculated for the Dunwald–Wagner equation by Giess[3]. Straight lines passing the origin were obtained in all cases, which indicates that the Dunwald–Wagner equation is applicable to the description of the process of formation of $NiAl_2O_4$ in the presence of the admixtures. This follows also from a comparison of the experimental degrees of conversion and the course of the rate curves for the $NiAl_2O_4$ formation (Figs 1 – 3).

The activation energies of the reaction in the presence of the various admixtures were calculated from the Arrhenius equation using the rate constants given in Table I.

The effect of an admixture is characterized by the relative rate of the spinel formation, v^0, defined as the ratio of the spinel formation in the reaction mixture containing

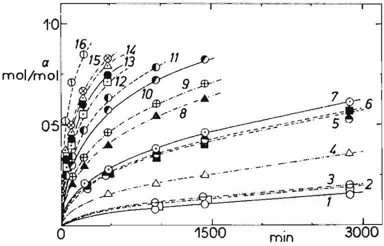

FIG. 1

Rate Isotherms for Reaction Mixtures Containing Si(IV) and Subgroup IVb Elements

1 – 1100°C, without subgroup, *1*; 2 – 1100°C, Th(IV), *2*; 3 – 1100°C, Si(IV), *3*; 4 – 1100°C, Zr(IV), *4*; 6 – 1100°C, Ti(IV), *5*; 5 – 1200°C, Th(IV), *6*; 7 – 1200°C, without subgroup, *7*; 8 – 1200°C, Zr(IV), *8*; 9 – 1200°C, Si(IV), *9*; 10 – 1250°C, without subgroup, *10*; 11 to 1200°C, Ti(IV), *11*; 12 – 1300°C, Th(IV) *12*; 13 – 1300°C, without subgroup, *13*; 14 – 1300°C, Zr(IV) *14*; 15 – 1250°C, Si(IV), *15*; 16 – 1300°C, Ti(IV), *16*.

the admixture, $d\alpha_{ad}/d\tau$, to that in the mixture from which the admixture is absent, $d\alpha/d\tau$, in the time $\tau = 0$. In fact, differentiating Eq. (*1*) and rearranging we obtain

$$v = (k_{ad}/k) \exp\left[\tau/(k - k_{ad})\right], \qquad (2)$$

which for $\tau = 0$ reduces to

$$v^0 = k_{ad}/k\,.$$

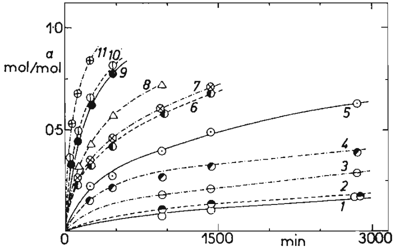

FIG. 2

Rate Isotherms for Reaction Mixtures Containing Subgroups *Vb* and *VIb* Elements

1—1100°C, without subgroup, *1*; 2—1100°C, U(VI), *2*; 3—1200°C, Mo(VI), *3*; 4—1200°C, without subgroup, *4*; 5—1200°C, U(VI), *5*; 6—1100°C, V(V) *6*; 7—1200°C, Cr(III) *7*; 8—1300°C, Mo(VI), *8*; 9—1300°C, without subgroup, *9*; 10—1200°C, V(V), *10*; 11—1300°C, U(VI), *11*.

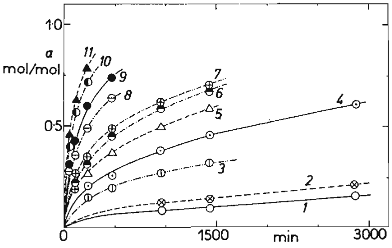

FIG. 3

Rate Isotherms for Reaction Mixtures Containing Subgroups *VIIb* and *VIIIb* Elements

1—1100°C, without subgroup, *1*; 2—1100°C, Fe(III), *2*; 3—1100°C, Co(II), *3*; 4—1100°C, Mn(II), *4*; 5—1200°C, without subgroup, *5*; 6—1200°C, Fe(III), *6*; 7—1200°C, Co(II), *7*; 8—1200°C, Mn(II), *8*; 9—1300°C, without subgroup, *9*; 10—1300°C, Fe(III) *10*; 11—1300°C, Co(II), *11*.

TABLE I

Rate Constants and Activation Energies of Nickel Spinel Formation in the Presence of Admixtures

Admixture	$k_{DW} . 10^7$, s^{-1} for t_r, °C				E kJ mol^{-1}	A
	1 100	1 200	1 300	1 400		
—	1·2	27·2	138·5	300	527·5	$9·7 . 10^{14}$
Si	2·1	83·5	443·3	—	620·4	$5·2 . 10^{18}$
Ti	23·2	181·0	—	983	348·3	$2·4 . 10^9$
Zr	7·8	63·2	—	396	365·1	$3·5 . 10^9$
Th	2·0	22·5	—	257	516·6	$5·0 . 10^{14}$
V	77·2	543·0	—	—	—	—
Cr	0·0	92·7	—	1 234	—	—
Mo	0·7	13·2	—	200	525·0	$3·5 . 10^{14}$
U	2·3	52·2	—	728	526·7	$1·1 . 10^{15}$
Mn	12·7	128·3	—	—	—	—
Fe	1·5	71·0	—	374	450·5	$1·5 . 10^{12}$
Co	4·7	78·3	—	834	484·0	$5·7 . 10^{13}$

TABLE II

The Relative Rate Constants for the Formation of $NiAl_2O_4$ in the Presence of the Various Admixtures

Admixture	v^0 for t_r, °C		
	1 100	1 200	1 300
—	1	1	1
Si	1·7	3·0	—[a]
Ti	18·8	6·5	3·3
Zr	6·3	2·3	1·3
Th	1·6	0·8	0·8
V	62·6	19·6	—
Cr	0·0	3·3	4·1
Mo	0·5	0·5	0·7
U	1·9	1·9	2·4
Mn	10·3	4·6	—
Fe	1·2	2·6	1·2
Co	3·8	2·8	2·8

[a] For $t_r = 1250$°C, $v^0 = 3·2$.

Of the group IV elements, silicon, titanium, zirconium, and thorium were applied. At the reaction temperature 1100°C, the rate of the $NiAl_2O_4$ formation was enhanced by the presence of these elements ($v^0 > 1$). The fastest was the nickel spinel formation in the presence of titanium ($v^0 = 18{\cdot}8$), the slowest in the presence of thorium ($v^0 = 1{\cdot}6$). As the reaction temperature increased, the relative rate of the spinel formation decreased for Ti^{4+}, Zr^{4+}, and Th^{4+}; in the case of Th^{4+} the drop of the rate was such that at temperatures above 1200°C, v^0 was less than unity. The effect of silicon is different from that of the other elements: the relative rate rises with increasing reaction temperature (Table II). This shows up also in the value of the reaction activation energy, which only in the case of silicon is higher than that for the reaction mixture containing no admixture (Table I).

Of the subgroups Vb and VIb elements, V(V), Cr(III), and U(VI) were tested. At the reaction temperature 1100°C, the highest reaction rate was observed with vanadium ($v^0 = 62{\cdot}6$); this remained true also at higher reaction temperatures, although the relative rate of the spinel formation decreased. Uranium raised somewhat the rate of formation and this effect did not change appreciably on increasing the reaction temperature. The influence of chromium was of interest: at 1100°C it inhibited completely the formation of $NiAl_2O_4$; the spinel formation could be observed only at temperatures above 1200°C.

The subgroups VIIb and VIIIb were represented by Mn(II), Fe(III), and Co(II); these elements raised the rate of formation of $NiAl_2O_4$ in the whole temperature region examined (Fig. 3, Tables I and II). The relative rate of the nickel spinel formation at 1100°C is lowest in the presence of iron ($v^0 = 1{\cdot}2$) and highest in the presence of manganese ($v^0 = 10{\cdot}3$). The relative rates decrease with increasing reaction temperature, still $v^0 > 1$ in the whole temperature region.

For a discussion of the effect of the admixtures on the rate of diffusion through the $NiAl_2O_4$ spinel layer we divided the admixtures into groups according to the values of the preferential energy of the cations and according to the oxidation degree. The first group contains elements forming bivalent cations with negative values of the octahedral preferential energy, *i.e.* Mn(II) and Co(II). Incorporated in the spinel $NiAl_2O_4$, which is a mixed spinel with the degree of conversion $0{\cdot}75-0{\cdot}8$, these cations should occupy tetrahedral sites and thus bring about an increase of concentration of the Al^{3+} ions in the octahedral positions. If the Al^{3+} ions diffuse *via* the octahedral positions[4], the rate of diffusion of the Al^{3+} ions increases in the presence of Co^{2+} or Mn^{2+} ions, and provided that in turn this rate controls the overall rate of the spinel formation, the latter rises, too. Our experimental results corroborate this concept, particularly if compared with those reported previously[1]. The presence of bivalent elements with negative values of the octahedral preferential energy resulted in an increase of the spinel formation rate at the reaction temperature 1100°C, following the order of the decreasing values of the preferential octahedral energy of the ions:

Ion	Cu^{2+}	Mg^{2+}	Co^{2+}	Mn^{2+}	Zn^{2+}
$k_{DW} \cdot 10^7$	3·0	3·8	4·7	12·7	15·5
$P(\nu)$	−0·1	−5·0	−9·9	−14·7	−31·6

At higher reaction temperatures, inversion in this order occurred between magnesium and copper.

The effect of chromium, forming trivalent cations with preference for the octahedral lattice positions in the spinel, cannot be explained in terms of its influence on the diffusion through the spinel; in fact, at the temperature 1100°C, $NiAl_2O_4$ did not form at all when chromium was present in the reaction mixture. The retarding effect of chromium lies probably in a slowing-down of the reaction on the phase boundary. A thin layer of the spinel $NiCr_2O_4$ can be assumed to form, hindering the diffusion of the ions to the reaction boundary.

Fe^{3+} are analogous to Al^{3+} in that they also possess a negative value of the octahedral preferential energy. They should not thus affect the nickel spinel formation rate appreciably, as was also observed ($v^0 = 1{\cdot}2$).

Vanadium, featuring preference for tetrahedral positions and formation of pentavalent cations, should enhance the rate of formation of $NiAl_2O_4$. The experimental rates found in the presence of vanadium are, however, so high that obviously other factors participate here in addition. Probably decisive is the role of the melt formed from the compound $AlVO_4$, which melts incongruently at 695°C (ref.[5]). This assumption is supported also by the results obtained by Rasch[6], who found that vanadium favours essentially the formation of $MgAl_2O_4$.

Cations more than trivalent with preference for the octahedral positions were represented by Ti^{4+}. Taking into account the condition of conservation of electroneutrality we can assume that on its incorporation in the crystal lattice of the nickel spinel, the corresponding number of cation vacancies will arise; this will then result in an increase of the nickel spinel formation rate. This concept is in agreement with the experimental results.

The last group comprises those elements about which it has not been stated in the basic literature[7,8] what positions in the spinel crystal lattice they should occupy. The presence of the ions Si^{4+}, Zr^{4+}, Th^{4+}, Mo^{6+}, and U^{6+} should bring about formation of cation vacancies, for the condition of electroneutrality to be met. The experimental results confirmed this assumption for most of the admixtures (Table II). Only in the presence of molybdenum, the spinel formation rate was lower than if no admixture was present. As this may be due to a reduction of the reaction surface, we tested experimentally the effect of molybdenum on the aluminium oxide surface area. The aluminium oxide with molybdenum was prepared in the same manner as pure aluminium oxide[2] except that 3% wt. molybdenum trioxide was added to the starting aluminium oxide gel. Specific surface measurements showed intense sintering:

while the specific surface of pure aluminium oxide after 9 hours' calcination at 1 300°C was 4·5 m^2/g, that of the sample containing molybdenum was as low as 0·6 m^2/g. As the phase diagram of the system MoO_3–Al_2O_3 is not known, the only fact to be utilized for the explanation of the influence of molybdenum, lowering the rate of formation of $NiAl_2O_4$ and intensifying the sintering of aluminium oxide, is that MoO_3 melts[9] at 780°C; the one-component melt can bring about intense sintering of Al_2O_3 before $NiAl_2O_4$ is formed, and at the same time act against the formation of $NiAl_2O_4$.

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