

## EFFECT OF ADMIXTURES ON THE FORMATION OF $\text{NiAl}_2\text{O}_4$ IN A SOLID-STATE REACTION

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Effect of some 1st and 2nd group elements of periodic system on the rate of the  $\text{NiO} + \text{Al}_2\text{O}_3 \rightleftharpoons \text{NiAl}_2\text{O}_4$  solid-state reaction within a temperature range of 1100–1300°C has been examined. A strong accelerating effect of  $\text{Zn}^{2+}$  ions as well as retarding action of  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  ions have been found. The activation energy values of the reaction in presence of individual admixtures have been established.

The catalytic inactive  $\text{NiAl}_2\text{O}_4$  spinel is produced in catalysts designed for the oxidation conversion of hydrocarbons in a solid-state reaction<sup>1</sup>. The rate of this reaction is, in addition to the value of the reaction temperature, affected by many other factors which may be roughly divided into two groups<sup>2</sup>, very significant for the formation of  $\text{NiAl}_2\text{O}_4$  being the effect of admixtures in the reaction system, *i.e.* in the catalyst.

Most of the authors<sup>3–5</sup> suppose the formation of  $\text{NiAl}_2\text{O}_4$  to take place by a counter-current diffusion of  $\text{Ni}^{2+}$  and  $\text{Al}^{3+}$  cations, while it is not quite clear, which of the cations determines rate of the reaction. An increase of the number of cation vacancies in  $\text{NiAl}_2\text{O}_4$  after incorporation of the admixtures should in principle increase the rate of diffusion and *vice versa*. The size of the ionic radius as well as possibility to form the solid solutions may also play an important role. Finally, for the  $\text{NiAl}_2\text{O}_4$  spinel, also the fact can be in presence of admixtures applied that a mixed spinel (degree of conversion 0.75–0.8 (ref.<sup>1,2</sup>)) is concerned in which a change of  $\text{Ni}^{2+}$  and  $\text{Al}^{3+}$  cations between one another in their lattice positions takes place. The admixtures can by their nature influence degree of conversion, this fact being reflected also in the possibility of diffusion through the spinel already produced.

The data on the effect of admixtures on the reaction between  $\text{NiO}$  and  $\alpha\text{-Al}_2\text{O}_3$  have not been found in the literature. Donnert<sup>5</sup> examined  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ca}^{2+}$  ions, built in the  $\gamma\text{-Al}_2\text{O}_3$  lattice, on the rate of formation of  $\text{ZnAl}_2\text{O}_4$ ,  $\text{MgAl}_2\text{O}_4$ , and  $\text{NiAl}_2\text{O}_4$ . The quoted cations decreased the rate of  $\text{ZnAl}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$  formation in the sequence  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ca}^{2+}$ , whereas they increased the rate of the  $\text{NiAl}_2\text{O}_4$  formation in the sequence  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Ba}^{2+}$ .

During the formation of other spinels, containing the  $\text{Al}^{3+}$  ion, interesting studies have been made<sup>6,8</sup> on the effect of admixtures in  $\text{MgAl}_2\text{O}_4$ . Of the spinels containing the  $\text{Ni}^{2+}$  ion,  $\text{NiCr}_2\text{O}_4$  was studied.

The aim of the present paper is to examine the effect of some admixtures which can occur in catalysts for the oxidation conversion of hydrocarbons used in the gas industry, whose model is given by a two-component system  $\text{NiO}-\alpha\text{-Al}_2\text{O}_3$ .

## EXPERIMENTAL

The  $\alpha$ -modification of aluminium oxide used for the measurements was prepared from crystalline R.G. aluminium nitrate by precipitation with ammonia solution<sup>2</sup>. Final calcination of the product was carried out at 1300°C for a period of 9 hours. Fraction of 63–90  $\mu\text{m}$  was used for the powder reaction itself.

Nickel oxide was prepared from crystalline R.G. nickel nitrate by thermal decomposition at 600°C and subsequent stabilization at 1100°C for a period of 2 hours. The grain size of the powder thus achieved did not exceed 1  $\mu\text{m}$ .

The admixture (Table I) were introduced separately as R.G. oxides, except for potassium and lithium, into the reaction mixture. Potassium was added as carbonate, lithium in terms of hydroxide. The amount of the oxide added was always equal to 3 weight per cent, when calculated for the amount of aluminium oxide present in the reaction mixture.

Mixing of equimolar powder mixture of aluminium and nickel oxides was accomplished for two hours in an alcoholic suspension. Afterwards, alcohol was evaporated off so that a segregation should not occur. The powdered mixture obtained was after additional drying pressed by a pressure of 80 MPa to pellets 1.3 g in weight, of diameter 15 mm, and 3 mm thick.

The proper reaction of the  $\text{NiAl}_2\text{O}_4$  formation took place after introducing the pellet made of the reaction mixture into the isothermal zone of a tubular resistance furnace. The isothermal zone was 35 mm high and temperature varied within  $\pm 3^\circ\text{C}$ . The degree of conversion was determined by X-ray diffraction using internal standard method<sup>9</sup>. For the given experimental arrangement and degree of conversion within 10 to 80%, the standard deviation varied from  $\pm 1$  to  $\pm 2\%$ .

## RESULTS AND DISCUSSION

The results of the measurements of the rate of spinel formation in presence of admixtures are given in Figs 1 and 2. The measured values of the conversion degree  $\alpha$

TABLE I

Survey of the Properties of the Elements Used

Element	Ionic radius $\text{\AA}$	Preferential octahedral energy <sup>15</sup> , kcal/mol
$\text{Ni}^{2+}$	0.69	9.0
$\text{Al}^{3+}$	0.51	— 2.5
$\text{Li}^+$	0.68	— 3.6
$\text{K}^+$	1.3	—
$\text{Cu}^{2+}$	0.72	— 0.1
$\text{Mg}^{2+}$	0.66	— 5.0
$\text{Ca}^{2+}$	0.99	— 30.7
$\text{Zn}^{2+}$	0.74	— 31.6
$\text{Ba}^{2+}$	1.34	—

are denoted by points; the curves passing through them correspond to theoretical isotherms calculated according to the Dunwald-Wagner equation

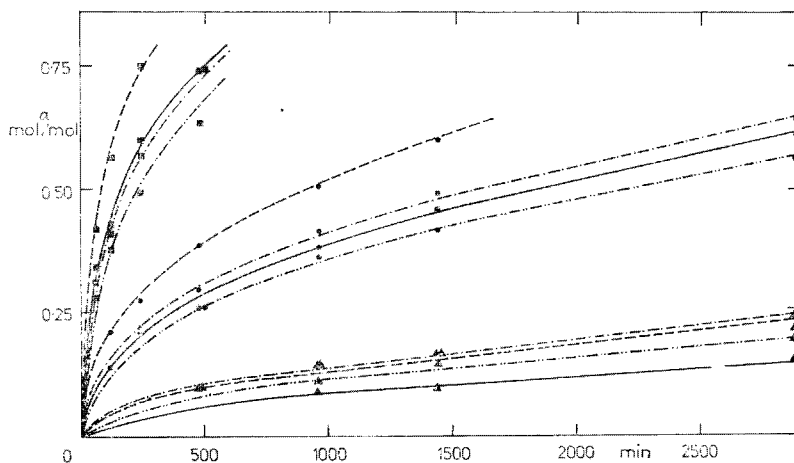


FIG. 1

Isothermal Rate Curves of Reaction Mixtures Containing Admixtures of the 1st Group of Periodic System

▲ 1100°C, ● 1200°C, ■ 1300°C; —  $\text{Al}_2\text{O}_3$ , - - - Cu, - · - · K, - · - · Li

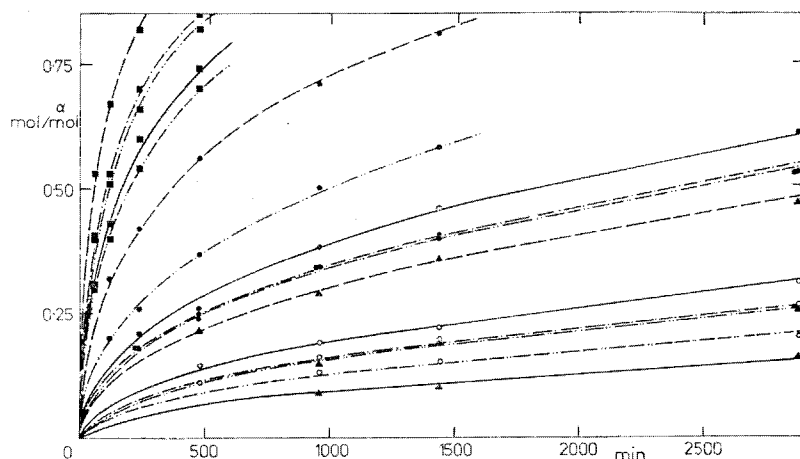


FIG. 2

Isothermal Rate Curves of Reaction Mixtures Containing Admixtures of the 2nd Group of Periodic System

■ 1300°C, ● 1200°C, ○ 1150°C, ▲ 1100°C; —  $\text{Al}_2\text{O}_3$ , - - - Zn, - · - · Ba, - · - · Mg, - · - · Ca

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

where  $\alpha$  is the degree of conversion,  $k_{\text{DW}}$  denotes the rate constant, and  $\tau$  is time of the reaction. Evaluation of experimental data was made by means of numerical data expressing dependence  $k\tau = F(\alpha)$  and calculated<sup>10</sup> for the Dunwald-Wagner equation. The evaluation is based on assignment of theoretical  $k\tau$  values to each experimental value of the conversion degree and on subsequent plotting the  $k\tau$  dependence on  $\tau$  in the graph. In all the cases, straight lines passing through origin of the coordinate system were obtained; it follows from this fact that kinetics of the  $\text{NiAl}_2\text{O}_4$  formation in presence of the admixtures employed is well-described by isothermal Dunwald-Wagner equation, consequently by the same equation as in the reaction mixtures without admixtures<sup>2</sup>.

The activation energy of the reaction in presence of individual admixtures (Table II) was calculated from the Arrhenius relation using rate constants  $k_{\text{DW}}$  presented in Table II.

From the first group of the periodic system we employed lithium, potassium, and copper as admixtures. At the reaction temperature of 1100°C the nickel spinel was formed considerably more rapidly in presence of the given admixtures than in a reaction mixture without them (Fig. 1, Table I). With the increasing temperature of the reaction, value of the relative rate of spinel formation,  $v_0$ , (Table III) decreased for a reaction mixture with potassium to such extent that there is no difference at temperatures above 1250°C between the rate of spinel formation in the reaction mixtures with potassium and without it.

TABLE II

Rate Constants ( $k_{\text{DW}}$ ), Activation Energies ( $E$ ), and Frequency Factors ( $A$ ) for the Reaction Systems Applied

Admixture	$k_{\text{DW}} \cdot 10^5/\text{min}^{-1}$					$E$ kcal/mol	$A$
	1 100°C	1 150°C	1 200°C	1 250°C	1 300°C		
—	0.74	3.53	16.6	83.1	180	126.0	$9.7 \cdot 10^{14}$
Li	1.56	—	14.4	—	125	98.6	$7.2 \cdot 10^{10}$
K	1.92	—	19.6	—	172	99.5	$1.3 \cdot 10^{11}$
Cu	1.83	—	34.4	—	352	123.4	$7.3 \cdot 10^{13}$
Mg	2.31	—	30.5	—	268	105.6	$1.8 \cdot 10^{12}$
Ca	—	1.46	12.4	—	152	125.5	$4.2 \cdot 10^{14}$
Zn	9.35	—	83.2	—	543	103.4	$1.9 \cdot 10^{12}$
Ba	—	2.38	12.6	—	297	134.4	$1.3 \cdot 10^{16}$

The relative rate of spinel formation,  $v$ , is defined as ratio of the rate of spinel formation in the reaction mixture with an admixture ( $d\alpha_p/d\tau$ ) to the rate of spinel formation without an admixture ( $d\alpha/d\tau$ ) at time  $\tau$ . By differentiating the Dunwald-Wagner equation and arranging the definition ratio, we get relationship  $v = k_p/k \exp[\tau(k - k_p)]$ . By comparing the rates at time  $\tau = 0$ , this relationship is simplified to expression  $v^0 = k_p/k$ , which is denoted in the text as "relative rate of spinel formation".

The same situation set in with lithium at the temperature of 1200°C. Likewise, if copper is present in the reaction mixture, value of the relative rate of spinel formation decreases with the increasing temperature of the reaction. Nevertheless, even at 1300°C the  $k_{DW}$  rate constant for the reaction mixture containing copper was nearly twice as high as the rate constant for the reaction mixture without the admixtures.

From the second group of elements of the periodic system magnesium, zinc, calcium, and barium were employed. Zinc and magnesium highly increase the rate of spinel formation over the temperature range used, zinc increasing the rate considerably more than magnesium. With the increasing temperature of the reaction, value of the relative rate of spinel formation decreases (Table III) in presence of both elements in the reaction mixture, but even at 1300°C it holds that  $v^0 > 1$ .

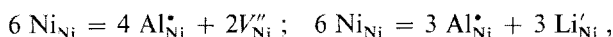
Of the alkali earths elements calcium decreases the conversion degree over the whole temperature range of the studied reaction in comparison with the reaction mixture without the admixtures, whereas barium at the temperatures below 1250°C only.

To discuss the effect of admixtures on the rate of diffusion through the nickel spinel, we divided the elements admixed into groups according to values of the

TABLE III  
Values of Relative Rates of the NiAl<sub>2</sub>O<sub>4</sub> Spinel Formation

Admixture	$v^0$			
	1 100°C	1 150°C	1 200°C	1 300°C
—	1.0	1.0	1.0	1.0
Li	1.97	—	0.87	0.69
K	2.59	—	1.18	0.95
Cu	2.47	—	2.07	1.95
Mg	3.12	—	1.83	1.49
Ca	—	0.41	0.75	0.84
Zn	12.6	—	5.01	3.12
Ba	—	0.67	0.76	1.65

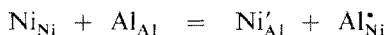
preferential energy of cations and according to valency. According to the criteria given, lithium stands in the first place, having  $\text{Li}^+$  cation and negative value of preferential octahedral energy. Lithium can be effective in two ways. By entering into tetrahedral positions it raises increase of the number of  $\text{Al}^{3+}$  ions in octahedral positions of the spinel (when compared with the spinel produced from the reaction mixture without admixture), which becomes evident in a higher rate of nickel spinel formation. The second possible explanation of the effect of lithium gets out of the fact that at temperatures above  $1000^\circ\text{C}$  a nonstoichiometric nickel spinel<sup>11</sup> is being formed which contains cation vacancies  $V''_{\text{Ni}}$ . On incorporation of the  $\text{Li}^+$  ion into the lattice of nonstoichiometric spinel, two vacancies for every three incorporated  $\text{Li}^+$  ions are destroyed, as follows from the comparison of the following relations:



where  $\text{Ni}_{\text{Ni}}$  is the  $\text{Ni}^{2+}$  cation in tetrahedral position,  $\text{Al}_{\text{Al}}$  is the  $\text{Al}^{3+}$  cation in octahedral position,  $\text{Ni}'_{\text{Al}}$  denotes the  $\text{Ni}^{2+}$  cation in octahedral position in spinel,  $\text{Al}_{\text{Ni}}^*$  is the  $\text{Al}^{3+}$  cation in tetrahedral position, and  $\text{Li}'_{\text{Ni}}$  is the  $\text{Li}^+$  cation in tetrahedral position.

Such a decrease of the number of vacancies should become evident by a slow-down of the rate of spinel formation. Experimental results show that the mechanism of the lithium effect mentioned at first, is predominantly applied.

The second group comprises bivalent cations with a negative value of the preferential energy:  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ . The cations quoted should not substantially affect the rate of diffusion, since on incorporating them into the crystal lattice, additional equilibrium defects should not arise. The  $\text{NiAl}_2\text{O}_4$  spinel, however, is a mixed spinel having a conversion degree of 0.75–0.80 [ref.<sup>12</sup>], in which equilibrium defects characterized by relation



take place.

Occupation of tetrahedral positions by the admixtures quoted leads to bringing down the degree of conversion and thus to an increase of concentration of  $\text{Al}^{3+}$  (ions in octahedral positions). In case of the diffusion of  $\text{Al}^{3+}$  ions through octahedral positions, the rate of diffusion will increase as a result of the incorporation of cations having negative values of preferential octahedral energy, and under the condition that this rate of diffusion defines total rate of the spinel formation, this fact will manifest itself in the increase of the latter rate. Experimental results confirmed validity of this assumption for the  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Zn}^{2+}$  ions. The rate of the  $\text{NiAl}_2\text{O}_4$  formation at  $1100^\circ\text{C}$  increased in presence of the given cations with the decreasing value of their preferential energy, *i.e.* in the following sequence:

Admixture	Rate constant $k_{\text{DW}} \cdot 10^5; 1100^\circ\text{C}$ $\text{min}^{-1}$	Preferential octahedral energy kcal/mol
$\text{Cu}^{2+}$	1.8	- 0.1
$\text{Mg}^{2+}$	2.3	- 5.0
$\text{Zn}^{2+}$	9.3	-31.6

The  $\text{Ca}^{2+}$  ion, which belongs to the same group, behaves in a somewhat different manner, for its presence brings down, in comparison with the reaction mixture without admixtures, the rate of the studied reaction. To explain this fact additional experiments will be needed. As one possible reason stands here formation of the  $\text{CaO} \cdot 6 \text{Al}_2\text{O}_3$  compound whose thin layer limits the rate of diffusion of the  $\text{Al}^{3+}$  ion towards the reaction interface.

Barium whose  $\text{Ba}^{2+}$  ion enters, according to Donnert<sup>5</sup>, the octahedral position in the  $\text{NiAl}_2\text{O}_4$  spinel, thus being analogous to the  $\text{Ni}^{2+}$  ion, was placed into the third group of admixtures. It should not therefore substantially influence the rate of the of the  $\text{NiAl}_2\text{O}_4$  formation. In fact, the rate of the nickel spinel formation was in presence of  $\text{Ba}^{2+}$  ions in the reaction mixture (up to a temperature of  $1250^\circ\text{C}$ ) lower than in the mixture without admixtures. The reason for it is obviously the same as in case of  $\text{Ca}^{2+}$  ions, since both elements produce a  $\text{Me}0.6 \text{Al}_2\text{O}_3$  compound having hexagonal lattice. All what has been said of the effect of  $\text{Ca}^{2+}$  ions is therefore valid for the explanation of the effect of the  $\text{Ba}^{2+}$  ions.

Potassium, an element of the cations of which no reference is given in the fundamental literature<sup>13,14</sup>, into which position of the spinel crystal lattice they could preferentially enter, has been placed in the fourth group of admixtures. In presence of potassium in the reaction mixture, the rate of the reaction studied was at the reaction temperature of  $1100^\circ\text{C}$  greater than in the reaction mixture without admixtures, but at temperatures of  $1250^\circ\text{C}$  already, the rates of reactions were for both types of the reaction mixtures equalized. The effect of  $\text{K}^+$  ions is obviously due to steric distortion of the structure after incorporation of this relatively large ion into the spinel lattice (Table I).

#### REFERENCES

- Vignes M., Jeannot M.: *Compt. Rendus du 72<sup>e</sup> Congrès de l'Industrie du Gaz*, p. 314. Paris 1965.
- Macák J., Koutský B.: *This Journal* 38, 2561 (1973).
- Petit F. S., Randklev E. H.: *J. Amer. Ceram. Soc.* 49, 199 (1966).
- Stone F. S., Tilley R. J. D. in the book: *Reactivity of Solids* (G. M. Schwab, Ed.), p. 583. Elsevier, Amsterdam 1965.
- Donnert D.: *Thesis*. Technische Hochschule, Graz 1968.
- Armijo J. S.: *Thesis*. Stanford University, Stanford 1969.
- Rieke R., Blicke K.: *Deut. Keram. Ges.* 12, 1963 (1931).

8. Rasch H.: *Tonind. Ztg.* 91, 405 (1967).
9. Koutský B.: *Thesis*. Institute of Chemical Technology, Prague 1971.
10. Giess E. A.: *J. Amer. Ceram. Soc.* 46, 377 (1963).
11. Lejus A. M.: *Haut. Tempér. Réfract. I*, 53 (1964).
12. Romeijn F. C.: *Philips Research Reports* 8, 304, 321 (1953).
13. Kröger F. A.: *The Chemistry of Imperfect Crystals*. 1st Ed. p. 1039. North-Holland, Amsterdam 1964.
14. Krupička S.: *Fyzika ferritů a příbuzných magnetických kyslíčků*, 1st Ed. p. 594. Academia, Prague 1969.
15. Miller A.: *J. Appl. Phys.* 30, Suppl. 248 (1959).

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