Thermochimica Acta, 233 (1994) 107–112
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)09810-Y

Kinetics and mechanism of the reduction of ammonia-synthesis catalysts[1]

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(Received 10 June 1992)

Abstract

The reduction of magnetite-derived ammonia synthesis catalysts was investigated. On the basis of data obtained by the analysis of DTG curves recorded at various heating rates, the activation energies of the reduction process (107 kJ mol^{-1} and 102 kJ mol^{-1}) were evaluated and the mechanism of the process discussed. The diffusion of gaseous reactants was estimated as the rate determining step.

INTRODUCTION

The heterogeneous reduction of iron oxide proceeds by a complex mechanism in which, besides the chemical reaction between the oxide and the reducing gas, diffusion processes between solid–solid and solid–gaseous phases are also of great importance. In view of such a complex reduction mechanism and the numerous parameters affecting the mechanism and kinetics of the reduction, the process of iron oxide reduction is still a subject of investigation. The latter refers particularly to the determination of the elementary reaction step controlling the overall reaction rate. As the slowest elementary reaction step, the processes considered were: the diffusion through the boundary layer of the stationary gas around the oxide grain; the reaction at the metal–oxide interfacial area; the diffusion of gaseous reactants inward and outward of the metal–oxide interfacial area.

Taking into consideration all the aforementioned reactions, Seth and Ross [1] derived a general rate equation for the reduction of Fe_2O_3. The experiments performed for verifying this equation showed that both the reaction at the interfacial area and the diffusion contribute in varying degrees to the rate-determining step in various stages of the reduction process, whereby particular solutions of the general equation are valid.

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[1] This paper was delayed for reasons beyond the control of the authors and the publisher.

Baranski et al. [2] showed that the results obtained by Seth and Ross can be quite well applied to ammonia-synthesis catalysts. For the mechanism of magnetite catalyst reduction by a stoichiometric H_2/N_2 mixture in the temperature range 723–823 K, a mixed model was proposed according to which neither the surface reaction nor the diffusion entirely control the overall reaction rate.

In our previous paper [3] comparative investigations of the reduction of magnetite (natural and synthetic) and of magnetite-derived catalysts were performed. The close agreement of values for the activation energies of the reduction obtained by the Coats–Redfern method (86–88 kJ mol^{-1}) for the same order of reaction ($n = 1$) indicated the same mechanism for the reduction of both magnetitie and catalyst, but within different temperature intervals in which the process is proceeding.

In the present paper the reduction mechanism is investigated with one of the synthesized samples by treating TG/DTG curves according to nonisothermal kinetic methods.

EXPERIMENTAL

The catalyst sample used was obtained by melting a mixture of magnetite, oxides of Al, Ca, Mg and Si, and K_2CO_3 at 1873 K. Magnetite was prepared by the precipitation of iron(III) oxide and subsequent reduction by glucose. Besides the basic phase Fe_3O_4, the sample contained SiO_2 (1.38 mass.%), Al_2O_3 (3.90 mass.%), CaO (1.8 mass.%), MgO (1.80 mass.%) and K_2O (2.73 mass.%). The preparation and analysis of the sample are described in detail in our previous papers [3, 4].

The reduction process was followed by means of TG/DTG analysis using a Du Pont 1090 thermal analyzer. The sample was heated at the rates of 3, 5, 10, 15, 20 and 25 K min^{-1}. The reduction was carried out in a stream of hydrogen; the flow rate of hydrogen was 4 l h^{-1}. Hydrogen was previously purified by passing it through columns of palladium catalyst for removal of O_2 and columns of $CaCl_2$ and molecular sieve 4A for removal of moisture.

RESULTS AND DISCUSSION

The process of catalyst reduction and conversion into its active form can be summarized as the process of the type: solid → solid + gas, in which the gaseous products diffuse through the solid phase. The kinetics of these reactions can be described by the general equation

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where $d\alpha/dt$ is the reaction rate, α is the degree of transformation, $k(T)$ is the rate constant depending on the temperature T, and $f(\alpha)$ is the function of the transformation degree. Introducing the expression for the rate constant $k = z\ \exp(-E/RT)$ the equation takes the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Z\,\mathrm{e}^{-E/RT} f(\alpha) \tag{2}$$

where E is the activation energy, and Z is the pre-exponential factor. Under nonisothermal conditions, at a linear heating rate $q = \mathrm{d}T/\mathrm{d}t$, the differential $\mathrm{d}\alpha/\mathrm{d}t$ is transformed into $\mathrm{d}\alpha/\mathrm{d}T$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{1}{q}\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{3}$$

Taking into account the linear heating rates and separating the variables, eqn. (2) becomes

$$\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{Z}{q}\,\mathrm{e}^{-E/RT}\,\mathrm{d}t \tag{4}$$

On the basis of this equation, numerous dependences of the thermal analysis parameters were derived, enabling an estimation of the activation energy of the process.

In his study on the kinetic analysis of thermal derivative curves, Ozawa [5] derived an expression relating the variation of the heating rate and the peak temperature T_{m}, i.e.

$$\mathrm{d}\ln q = -\frac{E}{R}\,\mathrm{d}\ln(1/T_{\mathrm{m}}) \tag{5}$$

Thus, eqn. (5) predicted the linear plot of $\ln q$ vs. $1/T_{\mathrm{m}}$. Because this method uses the variation of the heating rate and peak temperature T_{m} not only from DTA and DSC curves, but also from derivative curves, it is more general than any other; therefore, it is applicable to a wide variety of reactions.

Antić and Colović [6] also derived a simple dependence between the reaction rate and the temperature of the characteristic point, from which the activation energy of the process can be calculated

$$\mathrm{d}\ln V_{\mathrm{m}} = -\frac{E}{R}\,\mathrm{d}\ln(1/T_{\mathrm{m}}) \tag{6}$$

The method is applicable regardless of the experimental technique applied (DTA, DTG or DSC).

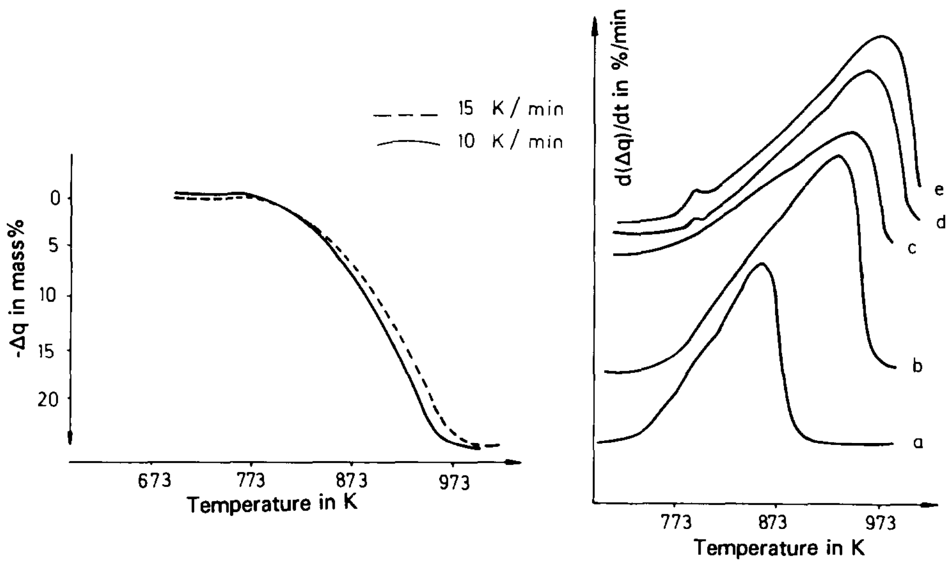

Fig. 1. TG and DTG curves for the reduction of catalyst sample at various heating rates: (a) 3 K min^{-1}; (b) 10 K min^{-1}; (c) 15 K min^{-1}; (d) 20 K min^{-1}; (e) 25 K mib^{-1}.

TG and DTG curves of our sample recorded at various heating rates used in analyzing the reduction process are shown in Fig. 1.

The analysis of DTG curves, aimed at estimating the activation energies of the reduction process of the catalyst from the shift of the maximum of DTG curves recorded at various heating rates, were carried out according to eqns. (5) and (6). The corresponding straight lines and values obtained for the activation of the reduction energy are shown in Fig. 2.

The values for the activation energy obtained by using various calculation methods are very close. The differences with respect to previously reported values for E_a [3] probably originate from the different conditions applied (different apparatus, different measurement, geometry, different amounts of sample used, etc.).

The analysis of thermal curves obtained under nonisothermal conditions consists of a series of kinetic methods for the examination of the reaction

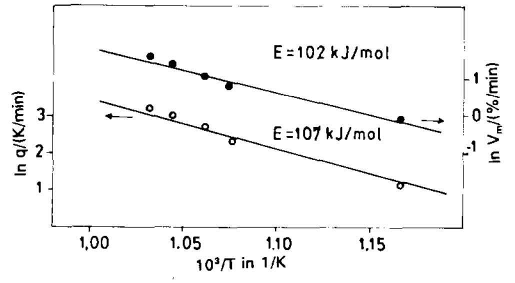

Fig. 2. Plots of ln V_m vs. $1/T_m$ and ln q vs. $1/T_m$.

mechanism and evaluation of the kinetic parameters. Starting from the basic equation for the reaction rate (eqn. (1)) and the assumption that a nonisothermal reaction occurs in a short time interval isothermally, Šatava [7] and Šesták and Berggren [8] derived a linear dependence of the function $\log g(\alpha)$ on $1/T_\alpha$

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{ZE}{Rq} p(x) \tag{7}$$

where Z is the pre-exponential factor and $p(x)$ is a function defined by the equation

$$p(x) = \mathrm{e}^{-x}/x - \int_{+x}^{\infty} (\mathrm{e}^{-u}/u)\,\mathrm{d}u = \mathrm{e}^{-x}/x + E_i(-x) \tag{8}$$

where $u = E/RT$, $x = E/RT_\alpha$ and T_α is the temperature at which a fraction α of the starting material has reacted. Both functions $g(\alpha)$ and $p(x)$ in the logarithmic form are approximately linear functions of $1/T_\alpha$. The estimation of the reaction mechanism includes a simple plot of $\log g(\alpha)$ vs. $1/T_\alpha$ for various possible values of $g(\alpha)$. The values of $\log g(\alpha)$ vs. $1/T_\alpha$ give a straight line for the most probable reaction mechanism, being represented by the function of $g(\alpha)$ for an experimentally determined fraction α. From the slope of this straight line the corresponding value for the activation energy can be calculated according to

$$E = -tg\,\alpha + \sqrt{tg^2\,\alpha + 8tg\,\alpha\bar{T}} \tag{9}$$

where $\bar{T}$ denotes the mean value of the temperature for the range within which the reaction proceeds and $tg\,\alpha$ is the slope of the selected linear plot of $\log g(\alpha)$ vs. $1/T_\alpha$.

In the present paper we have checked the results obtained by equations D_1–D_4 and R_2–R_3 reported in refs. 7 and 8, in which the slowest elementary processes are assumed to be the diffusion and the phase boundary reaction.

Table 1 shows the results obtained from TG curves for the heating rates

TABLE 1

Kinetic parameters obtained from TG curves using various kinetic equations

Mechanism	10 K min^{-1}		15 K min^{-1}	
	E_a/ (kJ mol^{-1})	Corr. coeff.	E_a/ (kJ mol^{-1})	Corr. coeff.
D_1	76	0.9934691	86	0.9930397
D_2	86	0.9960971	93	0.9951968
D_3	98	0.9979759	101	0.9970167
D_4	91	0.9968879	96	0.9958882
R_2	44	0.9972469	47	0.9962220
R_3	47	0.9979758	49	0.9970167

of 10 and 15 K min^{-1}. Table 1 also contains the correlation coefficients of the straight line $\log g(\alpha) = f(1/T)$ for different kinetic equations and the corresponding values of the activation energy.

On the basis of the values presented in Table 1, two mechanisms for the process reduction could be accepted as being formally valid: one in which the three-dimensional diffusion is the rate-determining step (Jander's equation D_3); the other in which the rate-determining step is the phase boundary reaction (equation R_3). Taking into consideration the values for the activation energy and comparing them with those previously obtained, it may be assumed that diffusion is probably the step which controls the reduction process.

CONCLUSION

The kinetics and mechanism of the reduction of ammonia-synthesis catalyst were investigated by the methods of TG/DTG analysis. The investigations were carried out with laboratory-synthesized magnetite-derived catalyst sample otained by the precipitation of iron(III) oxide and subsequent reduction with glucose.

From various functional dependences of the maximum on DTG curves and the heating rate, values of 102 kJ mol^{-1} and 109 kJ mol^{-1} for the activation energy of the reduction were estimated. The diffusion of gaseous reactants was assumed to be the rate determining step of the complex heterogeneous reduction of the magnetite phase (Fe_3O_4).

ACKNOWLEDGMENT

This work was supported by the Republic Research Fund of Serbia.

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