THE EFFECT OF PARTICLE SIZE ON THE REACTIVITY OF ACTIVE SODIUM CARBONATE TOWARDS SULFUR DIOXIDE

Karel MOCEK, Erich LIPPERT, Dušan HUSEK and Emerich ERDÖS

J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

The effect of particle size (0·33—1·0 mm) of the sodium carbonate on the reactivity of the active sodium carbonate prepared therefrom towards the sulfur dioxide was studied in a fixedbed integral reactor at a temperature of 150°C. The found dependence of the reaction rate on the particle size exhibits an unexpected course: at sizes of about 0·65 mm, a distinct minimum appears. The reaction rate decreases approximately ten times in the first branch of this dependence. The controlling factor of the reactivity of sodium carbonate, however, remains to be the method of preparing the active form.

The rate at which a chemical reaction proceeds is generally a function of temperature, pressure and concentrations of the reacting species or of the partial pressures of components in the gas mixture. In case of heterogeneous reactions in which solid phases take part, additional factors appear, such as the method of preparing the solid phase, the effect of genesis of the parent substance, and the effect of the particle size. The effect of the method of preparing the solid anhydrous sodium carbonate on its reaction with sulphur dioxide has been investigated previously, and it has been observed that the solid sodium carbonate exists in two forms which differ eminently one from another in their kinetic properties[1]. One form reacts with gaseous sulfur dioxide very slowly and incompletely, the conversion of which to solid anhydrous sodium sulfite amounts to some units of percents. The other form of sodium carbonate, denoted later as an active one, reacts under identical conditions very rapidly and almost completely. At space velocities of the order of magnitude of about 10^5 h^{-1} it is possible to attain a sulfur dioxide removal of the 99% and a conversion of the solid carbonate to sulfite exceeding 95%. The effective rate constant in the kinetic equation compared for the active and inactive forms of Na_2CO_3 differ from each other by a factor of almost 10^2 to 10^3. In addition the necessary conditions of formation of both forms of anhydrous sodium carbonate were determined[2]. The effect of genesis of the parent substance on the reactivity of the active sodium carbonate towards sulfur dioxide has been published previously[3]. In the present paper, the effect of the particle size of the sodium hydrogen carbonate (parent substance) on the reactivity of the active sodium carbonate prepared therefrom is investigated.

THEORETICAL

In a kinetic study of the heterogeneous reaction between gaseous sulfur dioxide and solid sodium carbonate in a differential reactor, it has been found[4] that in the range of low partial pressures (up to 0·3 kPa) of sulfur dioxide it is possible to express the reaction rate by the following equation

$$r = kpx^{1/2}(1 - x)^{3/2}\,. \qquad (1)$$

The value of the rate constant k is dependent on the partial pressure of water vapor which acts in the mentioned reaction as a gaseous catalyst. It appeared to be advantageous to describe the above reaction in an integral fixed-bed reactor in terms of dimensionless parameters M, Y, and W[5]. The meanings and definitions of these parameters have been given in the previous paper[3] as well.

The mathematical description of an integral fixed-bed reactor, where a chemical reaction described by rate equation (*1*) takes place, leads to a complicated relation between the dimensionless parameters of M, Y, and W from which the rate constant cannot be expressed explicitely[5]. A necessary condition for the above solution in terms of dimensionless quantities is the linear dependence of the reaction rate on the partial pressure of the reacting gaseous component. Nevertheless, the rate constant can be evaluated by using graphical methods. From an experimental course of the Y *vs* W dependence, the values of Y are read off for equidistant values of the quantity W. Solving the equation given in paper[5], the Y *vs* W dependence is computed for various values of the parameter M. From these auxiliary diagrams (or tabular values) the values of M are read off for the experimental pairs $Y - W$. The value of the effective rate constant k is then calculated from the relation

$$k = M/(M/k)_{\text{exp}}\,, \qquad (2)$$

where $(M/k)_{\text{exp}}$ is the experimentally determined value featuring the operating mode of the reactor. The mean degree of conversion of the solid, $\bar{x}$, can be determined by numerical integration of the relation

$$\bar{x} = \int_0^W (1 - Y)\,\mathrm{d}W \qquad (3)$$

or by graphical integration.

EXPERIMENTAL

The rate measurements have been carried out in a kinetic apparatus described in previous papers[1,3]. The anhydrous sodium carbonate used in the measurements has been prepared by thermal decomposition of sodium hydrogen carbonate *in situ* in a stream of nitrogen. To detect the contingent border effect, two reactors of diameters 2·1 mm and 3 mm have been used. The kinetic experiments have been carried out with the following fractions: 0·33—0·42, 0·42—0·50, 0·50 to 0·60, 0·60—0·75, and 0·75—1·00 mm. The isobaric-isothermal conditions have been ensured by a small pressure drop across the bed (about 4 kPa) and by means of an efficient temperature control of the reactor which has been favourably influenced by a high degree of dilution of the reacting sulfur dioxide in the carrier gas (nitrogen). In the course of the study of the effect of particle size samples of the sodium carbonate prepared by seeding have been used.

The seeded $NaHCO_3$ particles have been obtained from a solution of sodium hydrogen carbonate by gradual cooling from the temperature of 50° down to 31°C, after adding seeds of particle size 0·25—0·33 mm obtained from precipitated $NaHCO_3$. The original substance used for preparing the solution of sodium hydrogen carbonate has been calcinated Na_2CO_3 (A.G.). Its concentration was chosen in such a way that after saturating it with gaseous carbon dioxide a saturated solution of the sodium hydrogen carbonate at 50°C resulted. The $NaHCO_3$ seeds were added under continuous maintenance of saturation with gaseous carbon dioxide. Thereafter the solution was gradually cooled down to 31°C during 40 hours.The separated sodium hydrogen carbonate was sucked off, washed with water, and dried in a stream of carbon dioxide. The dry substance has been screen separated into six fractions in the range of 0·25—1·0 mm, as mentioned above.

The kinetic measurements were carried out at a temperature of 150°C with nitrogen as the carrier gas, and on only one level of partial pressure of water vapor (2·06 kPa). The effects of temperature, carrier gas composition, partial pressure of water vapor[6], and the effect of genesis of the parent substance[3] have been investigated previously. From the experimental values of P, n_s, F, F_g, and τ, the parameter M/k and the degree of the bed stoichiometric loading W as a function of time, τ, have been computed. The relative outlet concentration of sulfur dioxide, Y, has been evaluated from the reading of the circulation conductance sensor[1] containing a H_2O_2 solution. The basic relations and the computation procedure have been given in the previous paper[3]. In this way, the dependences of Y *vs* W have been obtained at values of the M/k parameter in the range of $1{\cdot}7 \, . \, 10^2 - 7 \, . \, 10^2$.

RESULTS AND DISCUSSION

The effect of particle size on the course of the experimental dependence of Y on W at a value of the M/k parameter of about $1{\cdot}7 \, . \, 10^2$ is demonstrated in Fig. 1. The character of this dependence does not change on increasing the value of the M/k parameter four times. The partial pressure of sulfur dioxide in these experiments amounted to 0·28 – 0·33 kPa. From the experimental Y *vs* W dependence, the effective rate constant k has been evaluated in the following way. The relative outlet concentrations, Y, have been computed by means of the relation $Y = Y(M, W)$ derived in paper[5] for values of W from 0 to 1 with an interval of 0·05, and of M from 1 to 32 with an interval equal to unity. From these auxiliary tables, the corresponding values of M have been selected to suit experimental pairs of values Y and W. The effective rate constant k has been calculated from the relation (*2*), however, only in the range of Y from 0·1 to 0·45, where the circulation conductance sensor exhibits the relatively highest precision. The corresponding mean degree of conversion of the solid phase $\bar{x}$ has been determined by planimetering the experimental course of Y *vs* W above this curve, in agreement with relation (*3*). Thus the dependences of the mean degree of conversion of the solid phase, $\bar{x}$, on the degree of the bed loading, W, have been obtained for various particle sizes of the parent substance. These dependences are represented in Fig. 2 for a value of the M/k parameter of about $3{\cdot}5 \,.\, 10^2$. These dependences exhibit the same character even at other M values in the whole range investigated. From the figure, an increase of the reaction rate for particle sizes from 0·75 to 1·0 mm is apparent. This remarkable phenomenon can also be seen in Fig. 1.

For each pair of values of $\bar{x}$ and W the effective rate constant k has been computed in the way given above, and consequently, a relationship between the rate constant and the degree of conversion can be easily obtained. Such dependences were constructed for all investigated particle sizes. The dependence of the effective rate constant k on the mean particle size is visualized in Fig. 3 for conversion degrees of the solid phase $\bar{x} = 0{\cdot}8$, 0·85, and 0·90. From the figure, the existence of a minimum on the reaction rate dependence is apparent in the vicinity of particle sizes of 0·65 mm

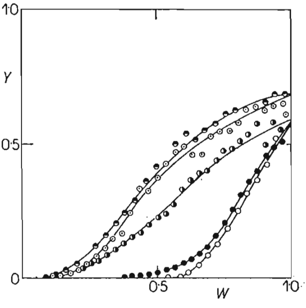

FIG. 1

Effect of Particle Size on Experimental Course of the Y *vs* W Dependence in Reaction of Active Sodium Carbonate with Sulfur Dioxide with Parameter $M/k \approx 1{\cdot}7 \,.\, 10^2$; $p = 0{\cdot}3$ kPa, $p_{H_2O} = 2{\cdot}06$ kPa

Particle sizes: ○ 0·33—0·42, ● 0·42—0·50, ⊙ 0·50—0·60, ◒ 0·60—0·75, ◑ 0·75—1·00mm

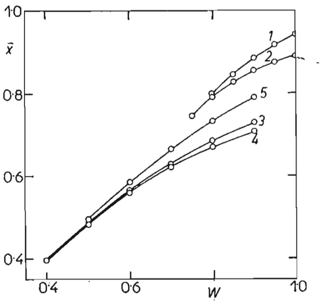

FIG. 2

Effect of Particle Size on Dependence of Mean Degree of Conversion of Solid Phase $\bar{x}$ on Degree of Stoichiometric Loading of Bed W at Parameter $M/k \approx 3{\cdot}5 \,.\, 10^2$

1 0·33—0·42, *2* 0·42—0·50, *3* 0·50—0·60, *4* 0·60—0·75, *5* 0·75—1·00 mm.

for all given degrees of conversion. This mentioned extreme is followed by an increase of the reaction rate up to the particle size of 1 mm. The value of the effective rate constant k for particles of 0·33 to 0·42 mm, which can be read off in Fig. 3 for $\bar{x} = 0{\cdot}85$ or $0{\cdot}90$ ($k = 6{\cdot}47 \,.\, 10^{-2}$ or $3{\cdot}52 \,.\, 10^{-2}$ resp.) is in agreement with the value given for the same kind of sample in the previous paper[3]. The course of the reaction rate in dependence on the particle size, illustrated in Fig. 3 is very notable and hitherto not yet described. From the existing theories, Mample's theory[7] explains the effect of particle size by a superposition of random surface nucleation and of the growth of the formed nuclei at a constant radial rate. This theory, however, is capable to render solely the occurrence of a maximum, not of a minimum which has been observed in our case.

The first branch of the observed dependence could be explained by the influence of transport phenomena, although it does not seem probable that either diffusion through the solid layer or even external diffusion[8] would be the rate controlling step. The increasing branch could be interpreted by a spontaneous disintegration due to the changes of molar volumes in the course of the reaction (an increase by 14·4%).

In conclusion, it may be stated that the rate of the reaction between active sodium carbonate and the gaseous sulfur dioxide exhibits a remarkable behaviour as to the particle size effect. In the range of particle sizes from 0·25 to 0·65 mm the reaction rate decreases more than ten times, and on increasing the particle size up to 1 mm, it moderately increases. The experimental results found here represent a pendant to the previous communication on the effect of genesis of the parent substance[3], and in analogy, even here it can be stated that the effect of particle size is not decisive for the reactivity of the active sodium carbonate towards sulfur dioxide. The most important factor keeps to be the method of preparing the active form of sodium carbonate.

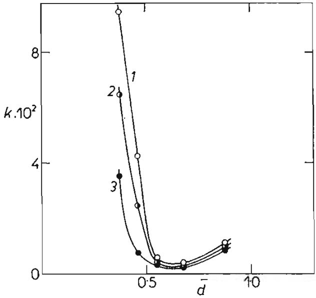

FIG. 3

Dependence of Effective Rate Constant k on Mean Particle Size $\bar{d}$, mm at Various Values of Mean Degree of Conversion of Solid Phase $\bar{x}$

1 $\bar{x} = 0{\cdot}8$, *2* $\bar{x} = 0{\cdot}85$, *3* $\bar{x} = 0{\cdot}90$.

LIST OF SYMBOLS

$\bar{d}$	mean particle diameter (mm)
F	total gas feed rate (mol s^{-1})
F_g	feed rate of the reacting gas component (mol s^{-1})
k	effective rate constant (s^{-1} kPa^{-1})
M	dimensionless parameter defined in paper[3]
n_s	amount of reacting solid substance in reactor (mol)
p	partial pressure of reacting gas component (kPa)
P	total pressure (kPa)
r	reaction rate given by equation (*1*)
x	degree of conversion of the reacting solid
$\bar{x}$	mean degree of conversion of the solid phase defined by equation (*3*)
Y	relative outlet concentration of reacting gaseous component defined in paper[3]
W	dimensionless parameter defined in paper[3]
τ	time (s)

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