KINETICS OF THE REACTION BETWEEN SOLID ACTIVE SODIUM CARBONATE OF THE SECOND GENERATION AND THE GASEOUS SULFUR DIOXIDE

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The results are presented of a detailed experimental kinetic study of the heterogeneous reaction between gaseous sulfur dioxide and the solid active sodium carbonate of the second generation which has been prepared by a controlled thermal dehydration of higher hydrates of the sodium carbonate. The measurements have been carried out in an all-glass kinetic apparatus with an integral fixed-bed reactor. The reaction course was studied in dependence on genesis and nature of the active sodium carbonate, on temperature and on composition of the gas phase. The reaction rate is significantly affected by presence of the water vapour which acts as a gaseous catalyst. Experimental data have been treated by using the model proposed by Erdös (Collect. Czech. Chem. Commun. *32*, 1653 (1967), and the values of the effective reaction rate constants have been computed. The kinetic study of active sodium carbonate of the second generation has been completed by the determination of microstructure (SEM) of solid samples before and after reaction, and by determining the solid surface composition before and after reaction by means of electronic spectra (ESCA).

Key words: Active sodium carbonate; Sulfur dioxide; Reaction kinetics.

The existence of two forms of the anhydrous sodium carbonate has been discovered previously[1]. The reactivity of these forms towards gaseous sulfur dioxide differs one from another by several orders of magnitude[2,3]. The highly reactive form of sodium carbonate prepared by a thermal decomposition of the sodium hydrogencarbonate was later named as the active sodium carbonate (active soda) of the first generation. Its high reactivity formed the basis of technical solutions leading to a series of patents[4–6] with a potential application in cleaning the waste gases. The exceptional properties of active soda of the first generation were studied even in a subsequent reaction of the sodium sulfite with a highly concentrated sulfur dioxide resulting in the sodium disulfite as a final product; here, the sodium sulfite has been formed from active soda of the first generation by reaction with the sulfur dioxide of a very low concentration. This study resulted in finding physico-chemical conditions of formation of a highly concentrated sodium disulfite in a dry way without the use of solvents[7,8]. An active soda of the second generation has been discovered in the eightieths[9,10] during a morphological

study of the sodium carbonate prepared by thermal decomposition of $NaHCO_3$ and of decahydrate of the sodium carbonate. The present paper summarises the results of an experimental study of kinetic and structural properties of active soda of the second generation and compares them with the properties of active soda of the first generation.

THEORETICAL

The heterogeneous reaction of solid sodium carbonate with gaseous sulfur dioxide, expressed by the equation of the general type

$$A \ (g) \ + \ BC \ (s) \ \longrightarrow \ AC \ (s) \ + \ B \ (g) \qquad\qquad (A)$$
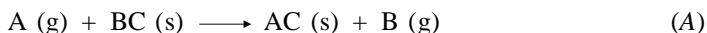
which takes place in an integral fixed-bed reactor without any change of the total substance amount, can be described in terms of dimensionless parameters M, Y, and W (ref.[11]). The parameter M is a characteristic quantity, defined by the expression

$$M = kPn_s/F \qquad\qquad (1)$$

indicating the working regime of the integral reactor. Parameter Y presents the relative outlet concentration of the reacting gas component and is expressed by the relation

$$Y = y_r/y_0 \ . \qquad\qquad (2)$$

Parameter W can be characterized as the degree of the stoichiometric loading of the bed and is defined as

$$W = y_0 F\tau/n_s = F_g\tau/n_s \qquad\qquad (3)$$

The mathematical solution of an integral fixed-bed reactor, in which the heterogeneous reaction

$$Na_2CO_3 \ (s) \ + \ SO_2 \ (g) \ \longrightarrow \ Na_2SO_3 \ (s) \ + \ CO_2 \ (g) \qquad\qquad (B)$$
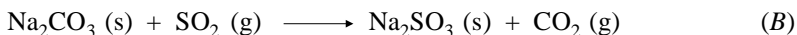
takes place and which is further described by the rate equation

$$r = kpx^{1/2}(1 - x)^{3/2} \ , \tag{4}$$

leads to a rather complicated relation between dimensionless parameters Y, W and M (ref.[11]), from which the rate constant can not be expressed explicitly. The condition for a solution in terms of the dimensionless quantities defined by relations (*1*), (*2*) and (*3*), consists in a linear dependence of partial pressure of the reacting gas component expressed by equation (*4*). An evaluation of the rate constant can be carried out graphically in the following way. From the experimentally obtained dependence of the quantity Y on W, the values of Y are read off for discrete values of the quantity W. The Y vs W dependences for different values of the parameter M have been computed by solving the equation given elsewhere[11], and plotted into diagrams. From these auxiliary diagrams, the values of the parameter M have been read off for a set of experimental Y–W pairs. Subsequently, the value of the effective rate constant k has been obtained from the relation

$$k = M/(M/k) \ , \tag{5}$$

where (M/k) represents an experimentally determinable quantity. The constancy of the value of the rate constant k for different corresponding Y–W pairs represents a test of the applicability of the mathematical solution of the integral reaction in the given case[11], and simultaneously verifies the validity of the kinetic equation (*4*).

EXPERIMENTAL

The starting materials for the preparation of active soda of the second generation were crystals of decahydrate or heptahydrate of the sodium carbonate. The decahydrate crystals were prepared from saturated solutions of the sodium carbonate (30 wt.%) and from industrial solution of the sodium carbonate by their cooling. The heptahydrate crystals of the sodium carbonate were obtained by evaporating the solvent under strongly reduced pressure, where the crystallization course has been kept in a narrow temperature interval from 32 to 35.3 °C (evaporative crystallization).

The prepared crystals of decahydrate or of heptahydrate were dehydrated in a glass column with a fluid grate[10,12,13]. The product of fluid drying of both hydrates has been the monohydrate of sodium carbonate, which represents a stable solid phase at a laboratory temperature of about 25 °C.

The starting material for the preparation of active soda of the first generation was a dry sodium hydrogencarbonate at least of commercial quality (mostly of analytical grade quality). Some samples of hydrogencarbonate were prepared by saturation of aqueous solutions of the sodium carbonate (17–18 wt.%) or industrial solutions of the sodium carbonate with a carbon dioxide gas. The sodium hydrogencarbonate prepared in this way has been dried in air at a temperature of about 25 °C or in an atmosphere of the carbon dioxide at an elevated temperature.

The dehydration of the monohydrate of sodium carbonate (the actual precursor of active soda of the second generation) and the decomposition of the sodium hydrogen carbonate (the precursor of

active soda of the first generation) into the anhydrous sodium carbonate were carried out in situ in a stream of dry nitrogen at elevated temperature always before the start of a kinetic experiment.

The kinetic measurements were carried out in a flow apparatus[2,14] constructed previously, which has been slightly modified for measurements in an integral regime[15]. The gas mixtures containing sulfur dioxide of low concentration have been prepared by means of the saturation methods[16]. The experimental procedure employed in kinetic measurements was almost identical with those described in previous papers[2,14]. The determination of sulfur dioxide concentration in the gas has been carried out after its absorption in a hydrogen peroxide solution by means of the conductometry[17]. The remaining alkalinity of the solid after the end of experiment (nonreacted sodium carbonate) has been determined by titration with 0.01 M sulfuric acid using phenol red as an indicator. The formed carbon dioxide was removed from the solution by boiling.

RESULTS

The result of kinetic experiments consists in the determination of dependence of the relative outlet concentration Y on the degree of stoichiometric loading of the bed W for a given value of the parameter M/k, i.e. in the determination of break-through curve of the sulfur dioxide through the bed of solid sodium carbonate. From the dependences determined in this way, the effective rate constants of the reaction (B) have been evaluated as described above.

The Nature of the Y vs W Dependence for Different Forms of the Solid Sodium Carbonate

In Fig. 1, the break-through curves of sulfur dioxide are shown for three different samples of active soda of the second generation prepared from Na_2CO_3 hydrates, and for a sample of active soda of the first generation. In Fig. 2, the break-through curves of sulfur dioxide are presented for two different samples of active soda of the second generation prepared from the Na_2CO_3 hydrates and for a sample of active soda of the first generation. The break-through curves for different forms of the solid sodium carbonate are compared in Fig. 3. From Figs 1–3 it is evident, that the break-through curves of both forms of active soda are similar or even identical, and simultaneously, that they differ significantly from other less active or inactive forms. The proof for analogous kinetic behaviour of both active forms (first and second generation) is based on the average values of effective rate constant of the reaction (B) in absence of oxygen given in Table I.

Temperature Dependence of the Reaction (B)

Temperature dependence of the reaction (B) in the range from 130 °C up to 350 °C in coordinates of Y vs W is shown for active soda of the first generation in Fig. 4, and for active soda of the second generation in Fig. 5. These plots are given for the reaction (B)

in the presence of oxygen (6 vol.%) and of carbon dioxide (11 vol.%). The temperature dependences for both active forms are compared at unit stoichiometry ($W = 1$) in Fig. 6.

Effect of Gas-Phase Composition

The effect of gas phase composition on the reaction course of both forms of active soda was investigated for the reaction in an inert gas (nitrogen) and for the reaction in the presence of oxygen (6 vol.%) and carbon dioxide (11 vol.%). The content of sulfur dioxide and of water vapour was the same in both cases. The corresponding plots for active soda of the first and of the second generation are shown in Fig. 7. Rate constants and the degrees of conversion x (at $W = 1$) are contained in Table II. Here B2 denotes sodium hydrogencarbonate and D5 denotes active soda of the second generation, $Na_2CO_3 \cdot H_2O$.

Effect of Ageing of the Sample of Active Soda of the Second Generation

The effect of ageing of active soda of the second generation (prepared from deca-hydrate) is manifested by changes in its reactivity which is expressed by the degree of conversion of the solid phase at unit stoichiometry. The results of these kinetic measurements at three different temperatures are given in Table III.
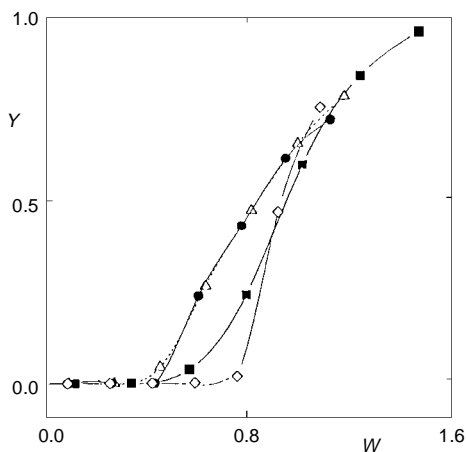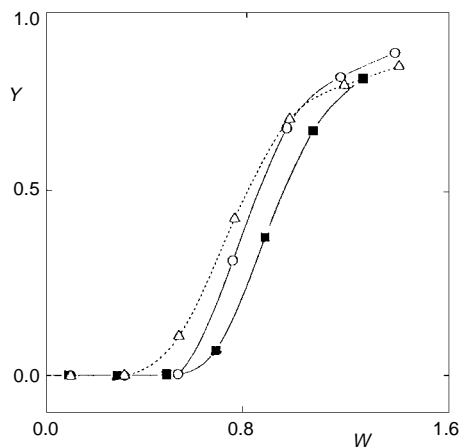

FIG. 1

Experimental dependence of Y on W for the reaction of SO_2 with active soda of the first generation (■ B1) and of the second generation prepared from decahydrate (Δ D1, ● D2, ◇ D3). Temperature 150 °C, concentration of SO_2 0.14 vol.%, concentration of H_2O 2 vol.%, $M/k \approx$ 355 kPa s

FIG. 2

Experimental dependence of Y on W for the reaction of SO_2 with active soda of the first generation (■ B2) and of the second generation prepared from heptahydrate (○ H5, Δ H6). Temperature 150 °C, concentration of SO_2 0.14 vol.%, concentration of H_2O 2 vol.%, $M/k \approx$ 390 kPa s

TABLE I
Values of effective rate constants of the reaction (*B*); temperature 150 °C, $c_{SO_2} = 0.14$ vol.%, $c_{H_2O} = 2$ vol.%

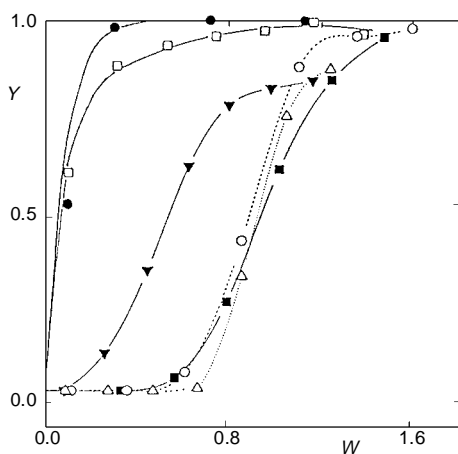| Active soda	$k . 10^2$, kPa^{-1} s^{-1}		
	commercial sample	from pure Na_2CO_3 solutions	from industrial Na_2CO_3 solutions
1st generation	3.57	–	9.75
2nd generation (deca)	–	2.64	4.73
2nd generation (hepta)	–	2.41	2.24
			5.97
			13.65

FIG. 3
Experimental dependence of *Y* on *W* for the reaction of SO_2 with different forms of the solid sodium carbonate: ■ B active soda of the first generation, ○ H active soda of the second generation (from heptahydrate), △ D active soda of the second generation (from decahydrate), ● U inactive anhydrous sodium carbonate (commercial sample), ▼ S sodium sesquicarbonate (commercial sample), ▢ *M* monohydrate of the sodium carbonate (commercial sample). Temperature 150 °C, concentration of SO_2 0.14 vol.%, concentration of H_2O 2 vol.%, $M/k \approx 340$ kPa s
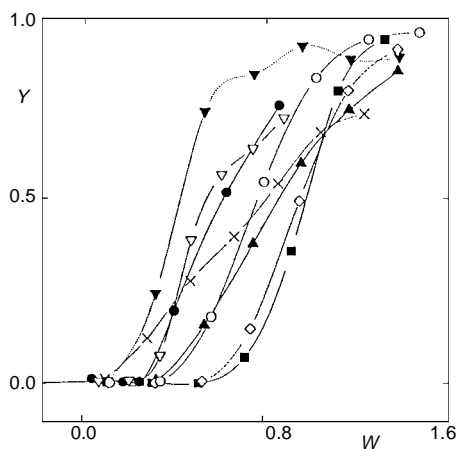

FIG. 4
Effect of temperature on the course of reaction of SO_2 with active soda of the first generation in coordinates *Y* vs *W*. Temperature (°C): ■ 130, ▲ 150, ● 180, ▽ 210, ▼ 255, × 285, ◇ 310, ○ 350. Composition of the reaction mixture: 0.14 vol.% SO_2, 2 vol.% H_2O, 11 vol.% CO_2, 6 vol.% O_2

Effect of Water Vapour on the Course of Reaction (B)

Dependence of the course of the reaction (B) on the water vapour content was studied with three samples of active soda of the second generation (deca variant) and of one sample of active soda of the first generation at two levels of water vapour concentration in the gas phase (2 or 5 vol.%). The reaction courses are shown in Fig. 8 and quantitatively demonstrated in Table IV.

TABLE II
Effect of gas phase composition on the value of k and on the degree of conversion x (at $W = 1$) for active soda of the first and the second generation. Temperature 150 °C, $M/k \approx 365$ kPa s. Composition of reaction mixture: Subscript 1: 0.14 vol.% SO_2, 2 vol.% H_2O, inert N_2. Subscript 2: 0.14 vol.% SO_2, 2 vol.% H_2O, 11 vol.% CO_2, 6 vol.% O_2, inert N_2

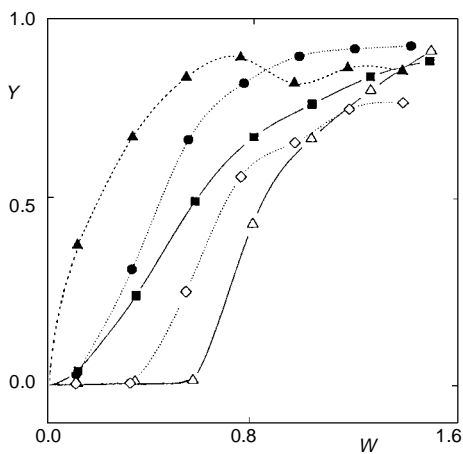| Sample	x_1 at $W = 1$	$k_1 . 10^2$, kPa^{-1} s^{-1}	x_2 at $W = 1$	$k_2 . 10^2$, kPa^{-1} s^{-1}
B2	0.89	3.28	0.79	1.17
D5	0.85	2.82	0.50	0.65

FIG. 5
Effect of temperature on the course of reaction of SO_2 with active soda of the second generation in coordinates Y vs W. Temperature (°C): ■ 130, ● 150, ▲ 180, △ 310, ◇ 350. Composition of the reaction mixture: 0.14 vol.% SO_2, 2 vol% H_2O, 11 vol.% CO_2, 6 vol.% O_2
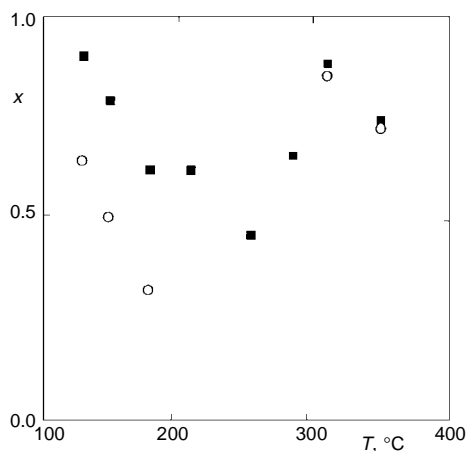
FIG. 6
Temperature dependence of the conversion x (at $W = 1$) of active soda of the first and the second generation (prepared from decahydrate) in the reaction with SO_2 (■ active soda of the first generation, ○ active soda of the second generation). Composition of the reaction mixture: 0.14 vol.% SO_2, 2 vol.% H_2O, 11 vol.% CO_2, 6 vol.% O_2

TABLE III

Effect of ageing on reactivity of active soda of the second generation prepared from decahydrate (D4, D5, D6). Composition of reaction mixture: 0.14 vol.% SO_2, 2 vol.% H_2O, 11 vol.% CO_2, 6 vol.% O_2, inert N_2

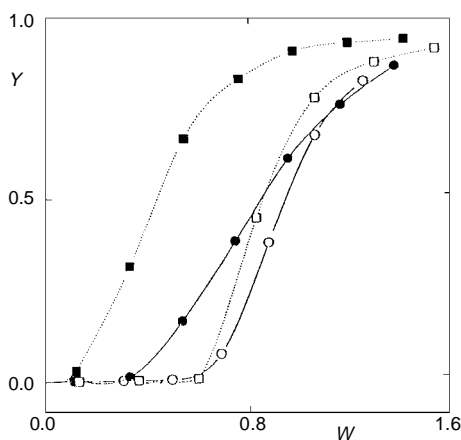| Sample	Age of sample	x ($W = 1$)		
		130 °C	150 °C	300 °C
D6	55 months	0.355	0.350	0.735
D5	after preparation	0.640	0.500	0.860
rel. change, %		−45	−30	−15
D4	12 months	0.410	0.345	0.560
D5	after preparation	0.640	0.500	0.860
rel. change, %		−36	−31	−35

FIG. 7

Effect of the gas phase composition on the course of dependence of Y vs W for the reaction of SO_2 with active soda of the first and the second generation prepared from decahydrate. Temperature: 150 °C, $M/k \approx 365$ kPa s. ◯ Active soda of the first generation 0.14 vol.% SO_2, 2 vol.% H_2O; ● active soda of the first generation 0.14 vol.% SO_2, 2 vol.% H_2O, 11 vol.% CO_2, 6 vol.% O_2; ◻ active soda of the second generation 0.14 vol.% SO_2, 2 vol.% H_2O; ◼ active soda of the second generation 0.14 vol.% SO_2, 2 vol.% H_2O, 11 vol.% CO_2, 6 vol.% O_2
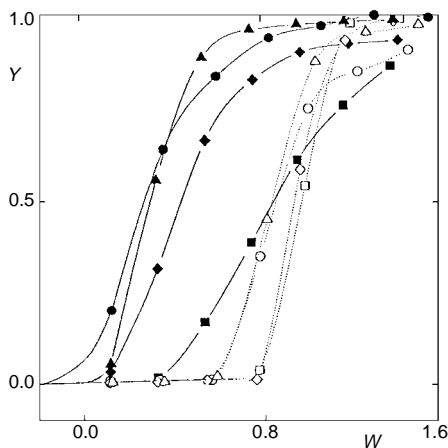

FIG. 8

Effect of the water vapour on the course of dependence of Y vs W for the reaction of SO_2 with active soda of the first (B2) and of the second generation (prepared from decahydrate, samples D4, D5 and D6). Temperature: 150 °C, $M/k \approx 355$ kPa s. Composition of the reaction mixture: 0.14 vol.% SO_2, 11 vol.% CO_2, 6 vol.% O_2. ◼ Sample B2, 2 vol.% H_2O, ◻ sample B2, 5 vol.% H_2O; ● sample D4 2 vol.% H_2O, ◯ sample D4, 5 vol.% H_2O; ◆ sample D5, 2 vol.% H_2O, ◇ sample D5, 5 vol.% H_2O; ▲ sample D6, 2 vol.% H_2O, △ sample D6, 5 vol.% H_2O

Morphological Study of Sodium Carbonate

The microstructure of sodium carbonate samples was studied by means of the scanning electron microscope (SEM). Every sample for the SEM analysis has been covered with a layer of gold 20 nm thick before measurements. The microstructure of the samples has been determined in their original state, further on after their activation at 130 °C, and after a partial conversion ($x = 0.25$) with the sulfur dioxide at 130 °C.

Samples of the starting $NaHCO_3$ (precursor of the active soda of the first generation) and of the anhydrous Na_2CO_3 (commercial sample) exhibited a compact non-porous
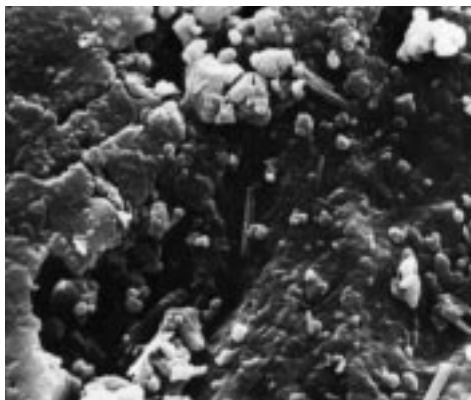
FIG. 9

Microstructure of the anhydrous sodium carbonate (inactive soda), magnification 5 000

FIG. 10

Microstructure of active soda of the first generation ($NaHCO_3$ after thermal decomposition), magnification 7 000
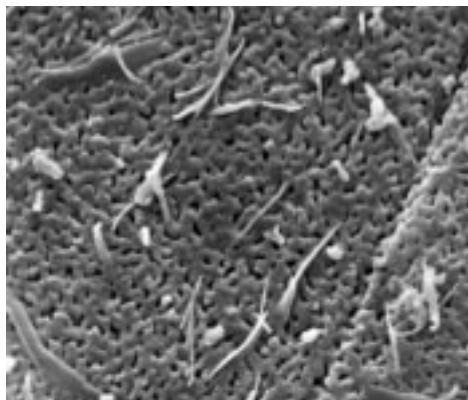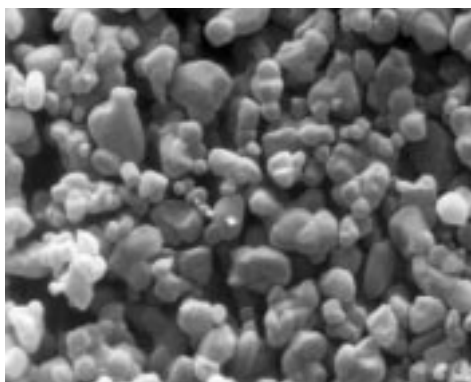

FIG. 11

Microstructure of active soda of the second generation (prepared from decahydrate of Na_2CO_3) after thermal decomposition, magnification 7 000
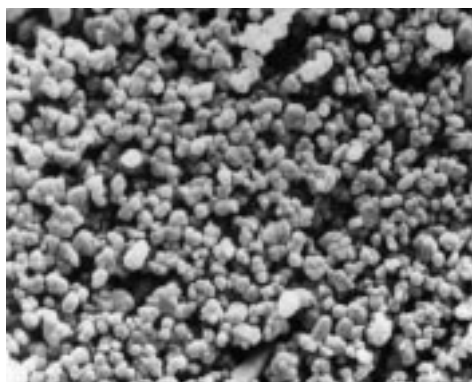

FIG. 12

Microstructure of active soda of the second generation (prepared from decahydrate of Na_2CO_3), augmentation 5 000

structure (Fig. 9), whereas the samples of active soda of the first generation (after thermal decomposition of $NaHCO_3$) and of the second generation (deca variant) show a distinct porous structure (Figs 10–12). The porous structure remains practically preserved even after the conversion with sulfur dioxide.

The determination of specific surface of active soda of the first and of the second generation, and of the inactive form of sodium carbonate (commercial anhydrous sodium carbonate) has been performed previously[9] by means of the dynamic method using nitrogen as absorbate in the helium as a carried gas at a temperature of 78 K. For active soda of the first and of the second generation, the values were obtained in the range of 10–11 m^2 g^{-1}. The anhydrous sodium carbonate exhibited the specific surface one order lower (0.5–1.0 m^2 g^{-1}).

Chemical Composition of the Solid-Phase Surface

This study will be the subject of a separate paper, however, it seems to be suitable to mention shortly some findings, which can be in a causal context with the differences in reactivity of the solid phase.

Surfaces of the sodium carbonate samples of different origin were analyzed by means of photoelectronic spectra using the ESCA method. Thickness of the surface layer analyzed by means of this method depends on the material and the kinetic energy of electrons; a typical value amounts to 5 nm. The electronic spectra have been measured by means of the electronic spectrometer ESCA 3 Mk II. (VG Scientific) at a pressure of rest gases in the range of 10^{-6} Pa. An aluminium anode Al Kα (1 486.6 eV)

TABLE IV
Effect of water vapour on degree of conversion x ($W = 1$) of active soda of the first and the second generation. Temperature: 150 °C, $M/k \approx 355$ kPa s. Composition: 0.14 vol.% SO_2, 2 or 5 vol.% H_2O, 11 vol.% CO_2, 6 vol.% O_2, inert N_2

Sample	x	W	$x, W = 1$	H_2O vol.%
D4	0.350	1.673	0.345	2
	0.928	1.577	0.840	5
D5	0.545	1.529	0.500	2
	0.969	1.501	0.910	5
D6	0.366	1.505	0.350	2
	0.878	1.630	0.840	5
B2	0.896	1.489	0.790	2
	0.978	1.538	0.915	5

of input 220 W served as radiation source. In the measurement of spectra, the transmission energy of analyzer $E_p = 20$ eV with the distinguishing of 1.1 eV on the line of Au ($4f_{7/2}$) was the same. The Fermi level of spectrometer was used as a reference level. To calibrate the spectra, the electronic line C ($1s$) of bond energy of 284.8 eV was used.

The surface layers of active soda of the first and second generation and a commercial sodium carbonate monohydrate exhibited an overstoichiometric amount of sodium after a thermal activation. An elevated concentration of sodium on the surface has been ascertained as well after a bombardment of sodium carbonate samples with the Ar$^+$ ions. The return to original state occurred after an exposition of the sample in the air or after a longer time of preserving the sample in a closed vessel. The results are given in Table V.

Two chemical states of sulfur, S^{4+} and S^{6+}, have been found by means of dry sulfur dioxide adsorption with all samples studied (except of $NaHCO_3$ in the original state). The total surface concentration of sulfur atoms increases with increasing sodium concentration.

TABLE V
Surface composition of activated samples (atomic concentrations of C and of O are referred to atomic concentrations of Na)

Sample	C	O	Note
Active soda of 1st generation prepared from $NaHCO_3$	0.36	1.18	
	0.47	1.57	after 47 days[a]
	0.42	1.21	activation in another reactor
	0.43	1.14	heating of sample under vacuum[b]
$Na_2CO_3 \cdot H_2O$ prepared from $Na_2CO_3 \cdot 10\,H_2O$	0.35	1.24	
	0.44	1.55	after 109 days[a]
$Na_2CO_3 \cdot H_2O$ commercial sample	0.40	1.12	
	0.40	1.07	after 18 h in vacuum[c]
	0.41	1.21	activation in another reactor
	0.42	1.25	activation 45 min in air[d]
	0.26	0.95	activation and bombarded[e]
	0.41	1.44	activation and bombarded, then 15 min left in air

[a] Activated sample was kept in a closed glass vessel. [b] Sample was activated 5 min in vacuum of spectrometer at 150 °C. [c] Sample was kept under vacuum in spectrometer. [d] After a thermal activation in a stream of dry nitrogen, the sample was exposed to ambient atmosphere. [e] After a thermal activation in dry nitrogen, the sample was bombarded for 10 min by Ar$^+$ ions of energy of 5 keV.

The surface concentration of reaction products with the sulfur dioxide depends on the precursor, from which the active form of Na_2CO_3 is prepared, on the method of preparing the active form, on the course of the activation process, and on the composition of the reaction mixture. The main reaction product in the reaction of active soda of the first and of the second generation with the sulfur dioxide in the presence of oxygen is the sulfate, in the absence of oxygen the main product is the sodium sulfite. In the case

TABLE VI
Surface composition of samples after the reaction with a gas mixture containing 0.14 vol.% SO_2, 11 vol.% CO_2, 6 vol.% O_2, 2 vol.% H_2O (atomic concentration of C and of O are referred to the concentration of Na). The reaction temperature 130 °C

Sample	x	C	O	S^{4+}	S^{6+}
Active soda of 1st generation prepared from $NaHCO_3$	0.23	0.21	1.10	0.020	0.140
	0.61	0.08	1.61	~0	0.440
	0.78	0.04	1.44	~0	0.450
	0.78[a]	0.02	1.39	~0	0.360
Active soda of 2nd generation $Na_2CO_3 . H_2O$[b]	0.04	0.19	1.42	0.023	0.180
$Na_2CO_3 . H_2O$ commercial sample	0.06	0.20	1.72	0.180	0.220
	0.08	0.16	1.49	0.210	0.240
	0.08[c]	0.28	1.256	0.086	0.067

[a] Sample was kept for 14 hours under vacuum in spectrometer. [b] The reaction temperature was 180 °C. [c] Sample was pulverized before measurement.
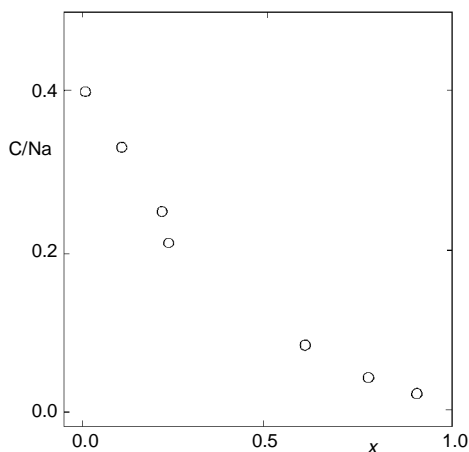

FIG. 13
Dependence of the relative carbon concentration (from CO_3^{2-}) on the degree of conversion x of active soda of the first generation after reaction with SO_2 at a temperature of 130 °C

of the inactive form of sodium carbonate, the relative amounts of tetravalent and of hexavalent sulfur reaction product is comparable regardless of the presence of oxygen in the reaction mixture. The surface composition of products of the reaction with sulfur dioxide is given in Table VI.

In Fig. 13, the dependence of the atomic ratio of C/Na on the conversion x is represented for the active soda of the first generation, which shows the presence of carbonate anion in the surface layers at a high degree of conversion.

DISCUSSION

The reactivity of active soda of the second generation with respect to sulfur dioxide, expressed by the value of effective rate constant, is in the order of magnitude the same as in the case of active soda of the first generation, and has an analogous reaction course. The rate constant of the reaction of active soda of the second generation at a temperature of 150 °C is approximately by 30% lower than with the active soda of the first generation. Differences in the rate constant within a range less than one order of magnitude for studied samples of active soda of the first and of the second generation can be explained by the presence of traces of metals (e.g. Co) and organic substances of unknown composition in some samples prepared from industrial solutions. The value of effective rate constant can be affected by different conditions of the fluid drying of higher hydrates of sodium carbonate into active soda of the second generation (monohydrate form) as well, and in some cases by non-keeping exact conditions of evaporative crystallization of the Na_2CO_3 heptahydrate (temperature interval of 3.3 °C only).

Water vapour affects significantly the reactivity of active soda of both the first and the second generation. An increase of the water vapour content from 2 to 5 vol.% leads to an expressive increase of the reactivity of active soda of the first and the second generation at a temperature of 150 °C. The effect of water vapour on the reactivity at a lower temperature can be explained by a catalytic action of water vapour[18], and by different rates of formation of sodium sulfite and of the subsequent oxidation to sulfate.

The presence of oxygen in the gas mixture containing sulfur dioxide (in addition to carbon dioxide) decreases the reactivity of active soda of the first and the second generation. The rate constant of reaction (B) decreases by 77% for active soda of the second generation at a temperature of 150 °C as compared with the value found in the absence of oxygen ($2.82 . 10^{-2}$ and $0.65 . 10^{-2}$ kPa^{-1} s$^-$). The rate constant of reaction (B) for active soda of the first generation at a temperature of 150 °C decreased almost by 65% as compared with the value found in the absence of oxygen and of carbon dioxide ($3.28 . 10^{-2}$ and $1.17 . 10^{-2}$ kPa^{-1} s^{-1}). The decrease of reaction rate of reaction of active soda with sulfur dioxide in the presence of oxygen has been already explained previously[3] by an oxidation of the formed sulfite to sulfate.

Temperature dependence of the reaction rate of active soda of the second generation with sulfur dioxide at a water content of 2 vol.% (6 vol% O_2, 11 vol% CO_2) in the temperature range of 130–350 °C passes through a minimum at temperatures between 200 and 250 °C. In the case of active soda of the first generation the minimum is found at a temperature of 250 °C under otherwise identical conditions. With the temperature rising above 250 °C, the reaction rate increases for both forms of active soda and a maximum is found at a temperature of about 300 °C. Decrease of the reaction rate of active soda in the interval of 130–250 °C found for active soda of both the first and the second generation can be explained by the presence of oxygen. In this case an oxidation of the primary reaction product – sodium sulfite – to sulfate takes place and a part of reaction centers is blocked by the oxidation. It was shown previously[19], that the most important increase of the rate of sulfite oxidation takes place in the range from 140 to 180 °C. An additional increase of temperature from 200 to 300 °C results in an increase of the rate of the reaction (*B*), and the consecutive oxidation of sulfite to sulfate takes then place with a lower velocity. During the experiments at higher temperatures, changes of colour of the upper layer of bed of the reacting substance were taking place from the yellowish brown at temperatures above 250 °C over brown up to black at about 300 °C. The black colour did not appear at temperatures from 350 to 450 °C, and after the end of the experiments at these temperatures the bed was white like in the case of experiments performed at temperatures up to 250 °C.

The effect of ageing of samples of active soda of the second generation (precursor is monohydrate of the sodium carbonate) measured at a temperature of 150 °C in absence of both oxygen and carbon dioxide resulted in a decrease of its reactivity towards sulfur dioxide approximately by 10%. A more significant decrease of reactivity was observed in the presence of both oxygen and carbon dioxide. Here, at temperatures ranging from 130 to 150 °C, a decay of 31–45% was found. At a temperature of 300 °C, the decrease of reactivity of active soda of the second generation is lower under otherwise identical conditions (15–35%). It is evident from Table III, that the main changes of reactivity due to ageing take place during the first year from the preparation of the sample. The effect of ageing has been observed earlier but it was interpreted as a reduction of total inner pore surface in consequence of their redistribution caused by the air humidity[20].

Morphologic study carried out by means of the scanning electron microscope (SEM) confirmed a porous structure of active soda of the first and the second generation. The porous structure remains practically preserved even after the reaction with sulfur dioxide. Microstructure of the precursor of active soda of the first generation, the sodium hydrogencarbonate, the commercial anhydrous sodium carbonate, and the commercial monohydrate of sodium carbonate is entirely non-porous.

An analysis of the surface layers of active soda of the first and of the second generation, and of the commercial monohydrate of sodium carbonate by means of photoelectron spectra (ESCA) led to the finding of overstoichiometric amounts of sodium. It indicates

a possible occurrence or an easy formation of anion vacancies in the active sodium carbonate. Additional experimental findings (e.g. evaluation of carbon dioxide during activation) support the hypothesis of partial decomposition of carbonate groups on the surface of the sample.

The reaction of an inactive sodium carbonate with sulfur dioxide yielded a compact surface layer of reaction products, whereas, in the case of active soda, the dependence of C/Na ratio on conversion indicates the presence of carbonate ions in surface layers even at a high degree of conversion. This dependence can be explained by a different way of growth of reaction products on the surface of carbonate. With the active carbonate, the growth of reaction products takes place only on specific spots of the surface, whereas, with the inactive sodium carbonate, a compact layer of products is formed on the whole surface, and the reaction cannot proceed further.

CONCLUSION

Experimental study of the reactivity of active soda of the second generation, prepared by a controlled dehydration of higher hydrates of the sodium carbonate, proved a high reactivity with respect to sulfur dioxide, comparable with active soda of the first generation. The effective rate constant for active soda of the second generation is only 30% lower than for active soda of the first generation.

The reactivity of active soda of the second generation with respect to sulfur dioxide depends on composition of the gas phase, namely on the content of oxygen and water vapour, which acts as a gaseous catalyst of the reaction.

The rate constant of active soda of the second generation in the reaction with sulfur dioxide can be affected at maximum to the extent of one half of order of magnitude by the presence of trace admixtures in crystallization solutions and by the conditions of fluid drying of the decahydrate or heptahydrate of Na_2CO_3 to monohydrate.

Temperature dependence of the reactivity of active soda of the second generation in the presence of oxygen passes through a minimum in the temperature range of 200–250 °C. The effect of ageing on the reactivity of active soda of the second generation is manifested mostly during the first year from the preparation of sample, due to the presence of oxygen in reaction with sulfur dioxide.

The morfology of active soda of the second generation is practically identical with of that active soda of the first generation and remains unchanged even after the reaction with sulfur dioxide.

The main reaction product yielded by the reaction of active soda of the second generation with sulfur dioxide in presence of oxygen is sodium sulfate and in the absence of oxygen sodium sulfite. One of the main reasons of low reactivity of commercial monohydrate or anhydrous sodium carbonate is the formation of surface compact layer of reaction products which hinders the further progress of reaction.

SYMBOLS

F	total gas feed rate, mol s^{-1}
F_g	feed rate of reacting gas component, mol s^{-1}
k	effective rate constant, kPa^{-1} s^{-1}
M	dimensionless parameter defined by Eq. (*2*)
n_s	amount of reacting solid substance in reactor, mol
p	partial pressure, kPa
r	reaction rate defined by Eq. (*5*)
y_r	mole fraction of reacting gas component in outlet
y_o	mole fraction of reacting gas component in feed
x	degree of conversion of reacting solid
Y	variable defined by Eq. (*3*)
W	variable defined by Eq. (*4*)
τ	time, s
c_{SO_2}	SO$_2$ concentration, vol.%
c_{H_2O}	water vapour concentration, vol.%

REFERENCES

1. Erdos E., Mocek K., Marecek J., Bares J.: Czech. Discovery No. 26 (1982).
2. Bares J., Marecek J., Mocek K., Erdos E.: Collect. Czech. Chem. Commun. *35*, 1628 (1970).
3. Marecek J., Mocek K., Erdos E.: Collect. Czech. Chem. Commun. *35*, 154 (1970).
4. Erdos E., Bares J., Marecek J., Mocek K.: Czech. 129 889 (1968); Chem. Abstr. *71*, 84330 (1969).
5. Erdos E., Bares J., Marecek J., Mocek K.: Czech. 147 063 (1972); Chem. Abstr. *78*, 163596 (1973).
6. Erdos E., Marecek J., Mocek K., Camr R., Holovacky J., Prokupek J.: Czech. 171 524 (1976); Chem. Abstr. *84*, 111089 (1976).
7. Vobis J., Mocek K., Erdos E.: Collect. Czech. Chem. Commun. *56*, 1575 (1991).
8. Mocek K., Vobis J., Erdos E.: Czech. 260 926 (1988); Chem. Abstr. *112*, 9483 (1990).
9. Mocek K., Beruto D.: Mater. Chem. Phys. *14*, 219 (1986).
10. Mocek K., Erdos E., Lippert E., Beruto D.: Czech. 265 828 (1988); Chem. Abstr. *110*, 41434 (1988).
11. Erdos E.: Collect. Czech. Chem. Commun. *32*, 1653 (1967).
12. Cermak J., Mocek K., Erdos E., Vesely V., Hartman M., Lippert E., Wald J.: Czech. 266 617 (1990); Chem. Abstr. *110*, 41434 (1988).
13. Vlcek A., Neuzil L., Bejcek V., Mocek K., Wald J.: Czech. 270 337 (1990); Chem. Abstr. *112*, 39249 (1990).
14. Mocek K., Lippert E., Husek D., Erdos E.: Collect. Czech. Chem. Commun. *44*, 1201 (1979).
15. Lippert E., Mocek K., Erdos E.: Collect. Czech. Chem. Commun. *47*, 3348 (1982).
16. Erdos E., Bares J.: Collect. Czech. Chem. Commun. *29*, 2718 (1964).
17. Erdos E., Bares J.: Collect. Czech. Chem. Commun. *31*, 427 (1966).

18. Erdos E., Bares J.: *Proceedings of the 5th International Symposium on Reactivity of Solids*, p. 676. Elsevier, Amsterdam 1965.
19. Marecek J., Subrt J., Erdos E.: Collect. Czech. Chem. Commun. *40*, 1657 (1975).
20. Cyran M. J., Copenhafer W. C.: U.S. 4 588 569 (1986); Chem. Abstr. *105*, 48280 (1986).