EFFECTS OF THE GAS PHASE COMPOSITION AND GENESIS OF THE ACTIVE SODIUM CARBONATE ON ITS REACTIVITY TOWARDS GASEOUS MIXTURE $SO_2 + NO_x$

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The reactivity of the solid active sodium carbonate towards gaseous mixture $SO_2 + NO_x$ has been measured in the dependence on oxygen and carbon dioxide contents and on genesis of the solid substance. The fixed bed flow reactor working under integral conditions has been used. It was found that the reactivity of the active sodium carbonate of the 1st generation towards gaseous mixture $SO_2 + NO_x$ is higher than the reactivity of the active sodium carbonate of the 2nd generation. In the temperature range of 130–180 °C the partial pressures of oxygen and carbon dioxide have no decisive influence on the reactivity of the active sodium carbonate of the 1st generation.

Key words: Sulfur dioxide; Nitrogen oxides; Active sodium carbonate; Reactivity; Influence of oxygen and carbon dioxide.

A sufficient reactivity of the solid material and its adequate useful capacity are decisive factors for a successful application of any dry method of the abatement of gaseous pollutants.

In the frame of fundamental research the existence of two forms of anhydrous sodium carbonate has been discovered[1] the reactivity of which towards gaseous sulfur dioxide differs one from another by several orders of magnitude[2]. The highly reactive form of sodium carbonate prepared by a thermal decomposition of the sodium hydrogencarbonate was later named the active sodium carbonate (active soda) of the first generation. During a morphological study of the sodium carbonate prepared by thermal decomposition of the sodium carbonate decahydrate[3] an active soda of the second generation has been discovered. Kinetic properties of the active sodium carbonate of the first generation in the isolated reaction with SO_2 have been described previously[2,4]. The results of an experimental study of kinetic and structural properties of active soda of the second generation and the comparison with the properties of active soda of the first generation have been published recently[5]. A detailed experimental study of the simultaneous reactions of the active sodium carbonate of the first generation with gaseous mixture $SO_2 + NO_x$ revealed that a simultaneous removal of 90% SO_2 on average and 50% NO_x at least is feasible[6].

This article represents a comparison of the reactivity of both active sodium carbonates towards gaseous mixture $SO_2 + NO_x$ and the effects of oxygen and carbon dioxide on the reactivity of the active soda of the first generation are described. The knowledge of the last mentioned effects is of importance for analysis of the results from fluidized bed reactor.

EXPERIMENTAL

Chemicals

Active sodium carbonate of the first generation was prepared *in situ* by thermal decomposition of dry sodium hydrogencarbonate precursor in a stream of dry nitrogen at temperatures above 130 °C before each kinetic experiment in the fixed bed reactor[2,4]; $NaHCO_3$ was analytical grade product of the Solvay Company (Belgium).

Active sodium carbonate of the second generation was prepared by dehydration of the sodium carbonate decahydrate crystals in a stream of air at a laboratory temperature of about 25 °C in a glass column with a fluid grate[5]. The product of fluid drying has been the monohydrate of sodium carbonate (the actual precursor of active soda of the second generation). The dehydration of the sodium carbonate monohydrate into the anhydrous sodium carbonate was carried out *in situ* in a stream of dry nitrogen at elevated temperatures (mostly above 130 °C) always before the start of the kinetic experiment[5].

Reactivity Measurements

Reactivity measurements were carried out in a flow apparatus with the experimental procedure described in the previous paper[6]. The preparation of the gaseous mixture $SO_2 + NO_x$ has been performed by a continual mixing of two gaseous streams[7].

Analytical Methods

The same analytical methods were used both for the gas phase and for the solid phase as described in the previous article[6].

RESULTS AND DISCUSSION

For presentation of reactivity experiments the same dimensionless quantities and symbols have been used as described in the paper[6]. As a measure of the reactivity the degree of solid conversion x_1 at the normalized stoichiometric ratio (NSR) equal to 1 has been chosen.

Influence of Genesis of the Active Sodium Carbonate

A systematic reactivity study was performed at SO_2/NO_x ratios of about 2.0 or 0.5, within the temperature range of 130–180 °C at two different NO/NO_2 ratios ($NO/NO_2 < 5$ and $NO/NO_2 = 8–10$) and at hydrodynamic regime of the reactor[2] M/k proportional to the contact time of the gas with the solid $\tau_g = 0.03$ s. All ratios SO_2/NO_x and NO/NO_2 are molar. All experiments were performed with 5 vol.% water vapour.

Typical breakthrough curves of SO_2 and NO_x for active soda of the first and the second generation, respectively, are shown on Fig. 1. The results of the simultaneous SO_2/NO_x reactivity experiments with both active soda samples over the temperature range of 130–180 °C are summarized in the Table I.

TABLE I
Degree of the solid phase conversion x_1 for both active soda samples in dependence on temperature and SO_2/NO_x and NO/NO_2 ratios, respectively

Sample	130 °C	150 °C	180 °C
	$SO_2/NO_x \approx 2$, $NO/NO_2 \approx 10$		
1st generation	0.41	0.60	0.63
2nd generation	0.17	0.16	0.25
	$SO_2/NO_x \approx 2$, $NO/NO_2 \approx 5$		
1st generation	0.48	0.45	0.60
2nd generation	0.19	0.20	0.31
	$SO_2/NO_x \approx 0.5$, $NO/NO_2 \approx 10$		
1st generation	0.37	0.34	0.28
2nd generation	0.17	0.18	0.30
	$SO_2/NO_x \approx 0.5$, $NO/NO_2 \approx 5$		
1st generation	0.37	0.34	0.38
2nd generation	0.17	0.22	0.26

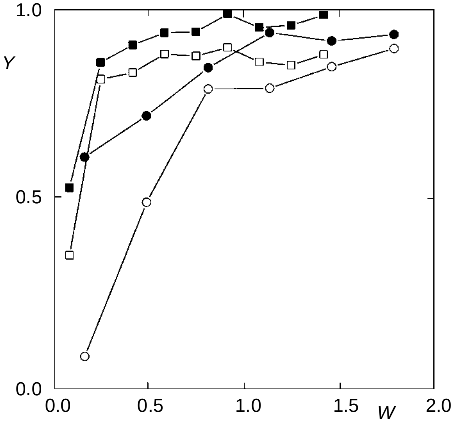

FIG. 1
SO_2 and NO_x breakthrough curves for the active soda of the first (the second, respectively) generation samples at 150 °C; $SO_2/NO_x = 2.1$, $NO/NO_2 = 5$, $v = 5.1\%$, $\tau_g = 0.03$ s, W is calculated with respect to the loading by the sum of the components; the active soda of the 1st generation: ○ SO_2, ● NO_x, the active soda of the 2nd generation: ☐ SO_2, ■ NO_x

From Fig. 1 and especially from Table I it can be seen that the reactivity of active soda of the first generation is significantly higher than in the case of the second generation one. A smaller increase of the reactivity of active soda of the second generation takes place at temperature 180 °C.

A detailed reactivity study of the active sodium carbonate of the first and the second generation in the isolated desulfurization[6] and denoxification[8] reactions revealed that the reactivity of the AKSO (active soda) of the second generation is by about 30% lower than that of the AKSO of the first generation in both isolated reactions.

If we assume the multiplication effect of decrease of both isolated reactions the total reactivity decrease of active soda of the second generation towards the mixture SO_2 + NO_x should be about 50%. With the exception of temperature 180 °C and the ratio of $SO_2/NO_x = 0.5$ the total decrease by about 50% is mostly achieved.

From comparison of the reactivity of both active sodium carbonates towards gaseous mixture SO_2 + NO_x the most important conclusion follows: The active sodium carbonate of the first generation is much more promising substance for simultaneous removal of SO_2 and NO_x.

TABLE II
Effects of O_2 content and of CO_2 content on the reactivity of the active soda of the first generation toward gaseous mixture SO_2 + NO_x; temperature 150 °C, $SO_2/NO_x \approx 2.1$, NO/NO_2 4.2–7.8, τ_g = 0.03–0.05 s, 5 vol.% of water vapour content

CO_2, %	O_2, %	x_1	E_{SO_2}	E_{NO_x}
0	5	0.62	0.73	0.40
0	20	0.63	0.77	0.30[a]
9.0	0	0.49	0.60	0.34
9.2	5	0.61	0.73	0.44[b]
10.5	10.5	0.53	0.68	0.38
9.4	14.1	0.57	0.72	0.37
0	5	0.62	0.73	0.40
9.2	5	0.61	0.73	0.44[b]
4.3	17	0.61	0.70	0.32
11.6	17	0.52	0.55	0.38
0	20	0.63	0.77	0.30[a]
4.7	18.9	0.54	0.60	0.37

[a] Lower value $NO/NO_2 = 4.4$ (ref.[6]); [b] higher value $NO/NO_2 = 8.5$ (ref.[6]).

Effect of Oxygen and of Carbon Dioxide on the Reactivity of Active Soda of the First Generation

These effects have been examined at temperature of 150 °C, SO_2/NO_x ratio in the range of 4.2–7.8 and hydrodynamic regime of the reactor M/k corresponding to the contact time of the gas with the solid $\tau_g = 0.03–0.05$ s. All experiments were performed with 5 vol.% of water vapour.

The effect of oxygen has been measured at three levels of carbon dioxide content (0, 5, 10 vol.%). The effect of carbon dioxide has been examined at six levels of oxygen (0, 5, 10, 14, 17, 20 vol.%). The results of reactivity measurements are summarized in Table II.

In absence of CO_2 there is no effect of O_2 on the degree of solid conversion x_1, SO_2 removal E_{SO_2} and NO_x removal E_{NO_x} in the range of oxygen contents of 5–20 vol.%. In presence of CO_2 the distinct adverse effect takes place in absence of oxygen (the worst case). With increasing content of O_2, the maximum values of x_1, E_{SO_2} and E_{NO_x} are achieved at 5–6 vol.% of oxygen. At higher oxygen and carbon dioxide contents (over 10%) a slight decrease of the reactivity has been observed. In general no expressive changes in the reactivity take place at low oxygen (<6 vol.%) and carbon dioxide content (<10 vol.%). Fortunately these oxygen and carbon dioxide contents are most common in waste gases of various origin.

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