

REACTIVITY OF NITROGEN OXIDES TOWARDS SODIUM CARBONATE AND HYDROGENCARBONATE BASED SOLID SORBENTS

Erich LIPPERT, Pavel BACH, Kvetoslava STEJSKALOVA¹, Emerich ERDOS and Karel MOCEK¹

*J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,
182 23 Prague 8, Czech Republic; e-mail: ¹ getastej@jh-inst.cas.cz*

Received May 23, 1996

Accepted September 30, 1996

The reactivity of nitrogen oxides towards sodium carbonate and hydrogencarbonate based solids was measured within a range of variables which is of technological interest. The reactivity is significant at lower temperatures only and is not affected by the presence of carbon dioxide or oxygen. Water vapor acts as a catalyst. Nitrogen dioxide is more reactive than nitrogen monoxide. The reactivity of the solid depends substantially on its origin and way of preparation. As compared with SO_2 or HCl , nitrogen oxides exhibit a lower reactivity, presumably because the solid is blocked by the reaction products.

Key words: Nitrogen oxides; Sodium carbonate; Reactivity.

Heterogeneous chemical reactions between solids and gases encompass a broad spectrum of diverse processes, encountered both in nature and in the technology. Among applications of this type of reactions are technological processes used for the removal of pollutants from waste gases, such as the dry additive limestone process for the removal of SO_2 from combustion gases.

One of the solid substances exhibiting a high reactivity towards acid gaseous pollutants is active sodium carbonate, which has been tested with success for SO_2 both in the laboratory and on a technological scale¹⁻⁵.

Among serious air pollutants present in many waste gases, especially from combustion processes, are nitrogen oxides, NO_x (encompassing nitrogen monoxide and nitrogen dioxide).

The present paper describes a laboratory study of the reactivity of active soda and other solids based on sodium carbonate and hydrogencarbonate towards nitrogen oxides in the absence of any other acid pollutant in the gaseous mixture. In nature such a case can be encountered, e.g., during the combustion of natural gas, where the resulting waste gases contain, besides CO_2 , N_2 , O_2 and H_2O , only nitrogen oxides formed by direct synthesis from nitrogen and oxygen present in the burning mixture.

EXPERIMENTAL

The reactivity was studied within the temperature limits of 25 to 400 °C. The overall NO_x concentration was about 1 000–1 300 ppm (NO_2 concentration varied over the range of 160–210 ppm) with the NO/NO_2 ratio lying largely between 3.0 and 5.5.

The design of the apparatus was based on that of the system used previously for studying the reactivity of active soda towards SO_2 (ref.⁶). The new apparatus differed from the older one basically in three features:

1. The preparation of the gaseous mixture proceeded by continuous mixing of two gas streams, each of which was fed from previously prepared reservoirs, one with a (N_2 , NO) mixture and the other with a (N_2 , O_2 , CO_2 , NO_2) mixture. The detailed procedure has been described in a previous paper⁷.

2. The eudiometrical way of measuring the total gas flow rate was replaced by the use of simple capillary flowmeters.

3. A commercial chemiluminescent NO/NO_x analyzer (Model 138, Chemoprojekt Stalice), adapted for lower gas flow rates (about 100 ml/min), was used for the determination of NO_x including the discrimination between NO and NO_2 .

The evaluation of the kinetic experiments was analogous to the procedure applied previously to SO_2 (refs^{2,6}). A constant flow regime characterized by the parameter M/k (refs^{6,8}) was maintained in each experiment.

The following solid samples were used:

– Commercial sodium hydrogencarbonate of p.a. grade produced by the Solvay company in Belgium.

– Active soda in the form of sodium carbonate monohydrate prepared by fluidized dehydration (drying)⁴ of sodium carbonate decahydrate at a temperature below 32 °C.

– Commercial anhydrous sodium carbonate produced by Tenneco Minerals, U.S.A.

The particle size of the solids was 0.25–0.33 mm. The temperature was varied within two ranges, viz. 25–200 °C (low-temperature series) and 300–400 °C (high-temperature series).

RESULTS AND DISCUSSION

Low-Temperature Series (25–200 °C)

An attempt was made to perform the kinetic runs in approximately differential conditions. A sufficient condition for this is that the M/k parameter equals approximately $1.23 \cdot 10^5 \text{ Pa s}$, which corresponds to a gas–solid contact time of about 0.02 s. The kinetic runs were performed at a constant concentration of oxygen (5 vol.%) and a water vapour content of 2 vol.% or 5 vol.% in the presence of carbon dioxide (about 10 vol.%) or in its absence. The NO_2 and NO concentrations usually varied over the regions of 160–200 ppm and 800–1 100 ppm, respectively, the rest was nitrogen. In the experimental conditions used, the extent of the possible homogeneous oxidation of NO to NO_2 has been estimated⁹ to be 5–10 rel.%.

The results for the Solvay NaHCO_3 are shown in Fig. 1. The course of the reaction of nitrogen oxides with active soda prepared from the decahydrate was similar but the reactivity of this form of sodium carbonate was appreciably lower.

The results can be summarized as follows:

a) Both samples (Solvay NaHCO_3 and active soda) exhibit a significant temperature dependence of reactivity within the range of 50–150 °C, with a marked monotonous reactivity decrease with increasing temperature, whereas within the range of 25–50 °C the reactivity remains nearly constant.

b) The character of this temperature dependence is not affected by the presence of carbon dioxide in concentrations about 10 vol.%, but the absolute value of the reaction rate is about 20% lower.

c) The presence of oxygen in the gaseous mixture at concentrations above 5 vol.% has no effect on the reactivity of the two solids.

d) The reactivity of the two samples towards NO_x is affected significantly by the presence of water vapour. In fact, the reaction does not proceed if no water vapour is present.

e) The reactivity of active soda prepared from sodium carbonate decahydrate is 35–50% lower (in terms of the conversion degree at $W = 1$) than that of the sample prepared from the Solvay NaHCO_3 .

The influence of the parameter M/k was studied at 100 °C for the Solvay NaHCO_3 and at 150 °C for the active soda. When this parameter was increased from $1.13 \cdot 10^5$ to $3.92 \cdot 10^5$ Pa s (i.e. by a factor of 3.5) at 100 °C, the conversion degree (x_1)_g (conversion degree of sodium carbonate at the stoichiometric loading $W = 1$ calculated from the composition of the gas phase) increased from 0.10 to 0.185, whereas an increase in the parameter from $1.13 \cdot 10^5$ to $2.89 \cdot 10^5$ Pa s (by a factor of 2.6) at 150 °C brought about no detectable change in reactivity.

The reactivity was also compared for a series of sodium carbonate and hydrogencarbonate samples differing in their origin and way of preparation. The results are given in Table I.

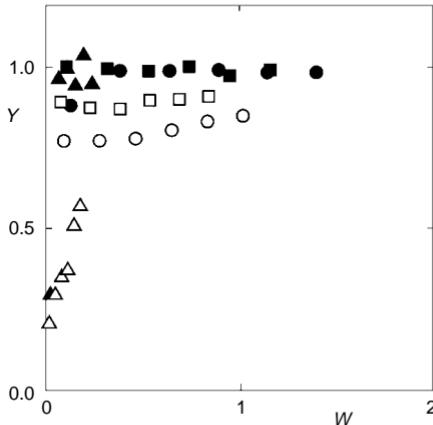


FIG. 1

Break-through curves of NO_x (○, ●), NO (□, ■), and NO_2 (Δ, ▲) for sample prepared from NaHCO_3 ; $M/k = 1.13 \cdot 10^5$ Pa s, $P_{\text{NO}_2} = 18$ Pa, $P_{\text{NO}} = 90$ Pa, 50 °C (open symbols), 200 °C (full symbols)

High-Temperature Series (300–400 °C)

The conditions were basically the same as in the low-temperature measurements. The following conclusions can be drawn from the results:

a) The reactivity of both samples (Solvay NaHCO_3 and active soda) is relatively very low, comparable with that observed at 200 °C, and decreases slightly if the temperature is additionally increased.

b) Carbon dioxide was found to have no effect on the reactivity of the two solids.

c) At temperatures above 300 °C, the reactivity of the two solids is very low, with conversion degrees of the solid amounting to a few per cent even if the M/k value is increased by a factor of three.

d) Increase in the water vapour concentration from 2 vol.% to 5 vol.% has no effect on the reactivity at 300 °C.

It is clear from Fig. 1 that the main reacting component in the mixture of NO and NO_2 with anhydrous active soda is NO_2 , for which the purification degree reaches 50 to 80% during the initial stages of the reaction. Subsequently, this reaction rate (for NO_2) decreases sharply with increasing W . For NO the reaction patterns are somewhat different: the reaction rate is relatively low during the initial stages of the heterogeneous reaction but it does not change markedly across the entire region of W values.

Table II gives a comparison of the reactivity of active soda (prepared by thermal decomposition of NaHCO_3) towards SO_2 , HCl and NO_x , where the conversion degree

TABLE I

Degree of conversion (x_1)_g of sodium carbonate and hydrogencarbonate samples in reaction with nitrogen oxides in dependence on their origin and way of preparation; $t = 25$ °C, $M/k = 1 \cdot 10^5$ Pa s

Na_2CO_3^a	NaHCO_3^b	Na_2CO_3^c	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}^d$	Na_2CO_3^e
0.005	0.025	0.226	0.067	0.167

^a Tenneco Minerals; ^b Solvay, Belgium; ^c obtained by decomposition of commercial NaHCO_3 at 150 °C;

^d obtained by fluidized drying of $\text{Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O}$ at a temperature below 32 °C; ^e obtained by decomposition of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}^d$ prepared by fluidized drying at 150 °C.

TABLE II

Comparison of reactivity of anhydrous sodium carbonate prepared by thermal decomposition of sodium hydrogencarbonate (at 150 °C) towards SO_2 , HCl and NO_x at 150 °C

Gas mixture component	SO_2	HCl	NO_x
(x_1) _g at $W = 1$	0.90–0.95	0.44–0.60	0.02–0.07

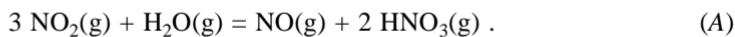
of the solid attained at the moment when the stoichiometric amount of the reacting gas had passed the bed was chosen as a criterion. The relevant conversion degrees are illustrated as a range, where the effect of the changes in the M/k parameter and in the partial pressure of the reacting gaseous components is taken into account. It is clear that, at 150 °C, nitrogen oxides (NO_x) are less reactive than SO_2 or HCl . The results presented in Table II apply to gas mixtures containing only one of the components mentioned.

The lower reactivity of NO_x towards active sodium carbonate can be explained in terms of the difference between the molar volumes of the reacting and formed chemical species in relation to the stoichiometry of the reaction. One mole of sodium carbonate yields two moles of nitrite or nitrate or of a mixture of both nitrite and nitrate. The resulting total volume is 52–79% larger, in dependence on the products formed (the two limiting values of this range refer to the formation of nitrite solely and nitrate solely, respectively). Owing to this, the surface layers of the reacting solid particles can be gradually, as the reaction proceeds, covered by an impermeable layer of nitrate or and nitrite and thus prevent access of the reacting gases (NO and NO_2) to the core of the particles.

The reactivity of sodium carbonate and hydrogencarbonate based sorbents towards nitrogen oxides is strongly dependent on the way of preparation of the reacting sodium carbonate. Commercially available samples of anhydrous sodium carbonate are almost non-reactive even in the most favourable conditions, i.e. at temperatures of 25–50 °C and with NO_2 prevailing in the gas mixture. In such conditions, no significant reactivity is observed either for the two direct precursors of anhydrous active sodium carbonate, viz. commercial sodium hydrogencarbonate and sodium carbonate monohydrate.

An increased reactivity towards NO_x , however, is found for anhydrous sodium carbonate prepared from the precursors by thermal decomposition or dehydration. It is noteworthy that sodium carbonate prepared by thermal decomposition of NaHCO_3 and active soda formed by dehydration of $\text{Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O}$ to the monohydrate and consecutively to the anhydrous form⁴ have approximately the same specific surface area, viz. roughly $10 \text{ m}^2/\text{g}$ (ref.¹⁰). The bulk density of the two forms of Na_2CO_3 is about 0.4 g/cm^3 . The total pore volume of active soda is $0.8 \text{ cm}^3/\text{g}$. On the other hand, the specific surface area of the nearly non-reactive commercial anhydrous Na_2CO_3 is lower than $1 \text{ m}^2/\text{g}$ (ref.¹⁰).

Of interest is the catalytic effect of water vapour present in the gaseous mixture on the course of the reaction, which is similar to the effect on the reaction of active soda with sulfur dioxide, but is not so marked. One of the possible explanations of the catalytic effect of water vapour consists in the formation of HNO_3 in the gas phase¹¹ by the reaction



For the experimental conditions used, the equilibrium constant of reaction (A) and the equilibrium partial pressure of HNO_3 have been evaluated to be $K_A = 0.1369$ and $P_{\text{HNO}_3} = 0.47 \text{ Pa}$, respectively. In our experiments, the partial pressure of nitrogen dioxide at the inlet was usually $P_{\text{NO}_2} = 20 \text{ Pa}$. When reaction (A) is in its equilibrium, the maximum degree of conversion reaches 2.3%.

SYMBOLS

M/k parameter characterizing the flow regime of the integral fix bed reactor defined by the equation

$$M = kPn_s/F = kp_{0n_s}/F_g, \quad (I)$$

where k is the effective rate constant ($1/\text{Pa s}$), P is the total pressure (Pa), n_s is the amount of reacting solid in the reactor (mol), p_0 is the partial pressure of the reacting gas component at the reactor inlet (Pa), F is the total gas feed rate (mol/s), and F_g is the feed rate of the reacting gas component (mol/s)

W degree of stoichiometric loading of the bed of the solid (Na_2CO_3) defined as $\dot{n}_{\text{NO}_x}^0 t/2n_s$, where $\dot{n}_{\text{NO}_x}^0$ is the feed rate of nitrogen oxides (mol/s), and t is time (s)

$(x_1)_g$ degree of conversion of the solid (Na_2CO_3) calculated from the gas phase analysis at the stoichiometric loading $W = 1$

Y relative concentration of the reacting gaseous component (NO , NO_2 or NO_x) at the outlet of the reactor, $Y = c_{\text{outlet}}/c_{\text{inlet}}$

The authors wish to thank the Grant Agency of the Czech Republic (Grant No. 104/95/0298) for financial support.

REFERENCES

1. Erdos E., Bares J.: *Proceedings of the 5th International Symposium on the Reactivity of Solids, Munich 1964*, p. 677. Elsevier, Amsterdam 1965.
2. Erdos E., Bares J., Marecek J., Mocek K. in: *Festkorperchemie-Beitrage aus Forschung und Praxis* (V. Boldyrev and K. Mayer, Eds) p. 478. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1973.
3. Erdos E., Mocek K., Lippert E., Uchytlova V., Neuzil L., Bejcek V.: J. Air Waste Management Assoc. 39, 1206 (1989).
4. Mocek K., Erdos E., Lippert E., Beruto D.: Czech. 265828 (1989); Chem. Abstr. 110, 41434 (1989).
5. Mocek K., Lippert E., Erdos E.: Collect. Czech. Chem. Commun. 57, 2302 (1992).
6. Marecek J., Mocek K., Erdos E.: Collect. Czech. Chem. Commun. 35, 154 (1970).
7. Lippert E., Bach P., Stejskalova K., Mocek K.: Chem. Listy 88, 60 (1994).
8. Erdos E.: Collect. Czech. Chem. Commun. 32, 1653 (1967).
9. Solc M.: Chem. Listy 57, 673 (1963).
10. Mocek K., Beruto D.: Mater. Chem. Phys. 14, 219 (1986).
11. England Ch., Corcoran W. H.: Ind. Eng. Chem. Fundam. 13, 373 (1974).