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Abstract

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ISOTOPIC EXCHANGE OF CO_2 CHEMISORBED ON AN IRON CATALYST FOR AMMONIA SYNTHESIS

The catalytic synthesis of ammonia from nitrogen and hydrogen on an iron catalyst with additions of aluminum and potassium has been the subject of a large number of studies; however, the nature of the promoting action of these additives still remains unclear.

In a work by one of us ([2]), among possible applications of isotopes to the study of catalysts, the use of measurements of the rates of isotopic exchange of surface atoms with gases was emphasized. In comparison with the differential isotope method proposed earlier for studying heterogeneity ([1], [3]-[5]), the kinetic isotope method has a number of advantages, since when it is applied the probability of redistribution of molecules is reduced and, what is very important, all measurements are carried out at an unchanged surface coverage.

The first study of the rate of isotopic exchange of chemisorbed carbon monoxide on the surface of an iron catalyst for ammonia synthesis was carried out by Aischens ([6]). In his experiments the rate constant for exchange of chemisorbed $C^{14}O$ with $C^{12}O$ of the gas phase gradually decreased, which cannot be explained by the influence of interaction, in view of the constancy of the coverage under the experimental conditions. The author comes to the conclusion that the sites chemisorbing CO are heterogeneous. Similar results were obtained by N. P. Keier ([7]), who studied the isotopic exchange of acetylene over a nickel catalyst. The exchange kinetics satisfy bilogarithmic dependences characteristic of broadly heterogeneous surfaces with an exponential distribution of sites with respect to activation energies.

In the present work the kinetics of isotopic exchange of CO_2 were investigated on a doubly promoted iron catalyst for ammonia synthesis.

Experimental Part

The work was carried out on a doubly promoted iron catalyst for ammonia synthesis at 21°, reduced and passivated outside the reaction system*. The

Fig. 1. Simplified diagram of the experimental apparatus; 1 —reactor, 2 and 4 —counting chambers with end-window counters, 3 —magnetic circulation pump, 5 —flasks for storing gases

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composition of the catalyst (in percent): FeO 27.3; Al_2O_3 3.94; K_2O 1.82; CaO 0.084; MgO 0.021; SO_3 0.017; SiO_2 0.16.

According to V. N. Shishkova, the surface area of the catalyst, determined by BET, is 13 m^2/g.

The passivated catalyst was placed in the reaction vessel and further reduced in a stream of pure hydrogen for 2 hr at 500° at a space velocity of 15,000.

Active carbon dioxide was obtained from $BaC^{14}O_3$ and 96% H_2SO_4. The resulting gas was frozen out in a trap with liquid nitrogen, and the noncondensed gases were pumped off to 10^{-4} mm Hg. The purification system consisted of columns with silica gel, traps with "dry ice," and P_2O_5.

* Passivation of the catalyst was carried out by the method described by M. I. Temkin.

Inactive carbon dioxide was obtained by pyrolytic decomposition of sodium bicarbonate and was subjected to the same purification.

The scheme of the experimental apparatus is shown in Fig. 1. The essential part of the apparatus consisted of a quartz reactor **1**, into which a definite weighed portion of catalyst (4.1 g) was placed, a counting chamber **2**, and a magnetic circulation pump **3**.

Fig. 1. Simplified diagram of the experimental apparatus; **1** —reactor, **2** and **4** —counting chambers with end-window counters, **3** —magnetic circulation pump, **5** —flasks for storing gases.

The work was carried out as follows. Into a previously calibrated volume, onto a trained contact, a portion of active $C^{14}O_2$ was admitted. After equilibrium had been established (after 20 min), the unabsorbed $C^{14}O_2$ was frozen out from the circulation loop with liquid nitrogen. Preliminary experiments had established that the adsorption capacity of the sample for CO_2 was 3.24 ml (NTP). Then a portion of inactive CO_2 was admitted into the loop to a pressure of 100 mm Hg (41 ml), and the circulation pump was switched on. The change in the isotopic composition of the gas phase was recorded with an MST-17 end-window counter built into the counting chamber. To prevent the mica window of the counter from being pressed into the vacuum (window thickness 4.5 mg/cm^2), special glass grids were used. A correction for self-absorption in the gas phase was introduced into the counter readings, and, in the case of high activities, a

Fig. 2

Figure 2: Fig. 2

correction for the resolving time of the apparatus was also introduced.

The direct and continuous measurement of the isotopic composition of the gas phase used in the present work has an advantage over the method of sampling followed by conversion into an active precipitate of $BaC^{14}O_3$. In our work it is possible to carry out measurements at short time intervals and with greater accuracy. In the future it is intended to record the readings automatically, using for this purpose an integrating count-rate meter.

The lower curves show that the absorbed CO_2 is not desorbed in an atmosphere of CO, H_2, or Ar at a pressure of 500 mm Hg. If, however, CO_2 is admitted into the apparatus, a rapid increase in activity is observed in the gas phase. As can be seen from the curves, 75% of the equilibrium activity appears during the first 3-4 min, after which the increase in activity is very slight, and after approximately 20-25 h no noticeable change in activity (A_{I}) in the gas phase can be recorded. After equilibrium had been established, the CO_2 was frozen out into a calibrated vessel (**4**) with an MST-17 counter, and its total activity (A_{I}) was determined. It was found that A_{I} is of the order of 40-50% of the total amount of absorbed $C^{14}O_2$. After this, the same portion of inactive CO_2 was again admitted onto the catalyst. The activity (A_{II}) in the gas phase increased only slightly. This operation was repeated once more. No increase in activity (A_{III}) in the gas phase could be detected. Then the reactor was heated to a temperature of 475°. Heating causes activity (A_{IV}) to appear in the gas phase, amounting to approximately 20% of the total activity absorbed by the contact. Only the introduction of hydrogen into the circulation loop at a temperature of 475° makes it possible to remove the remaining part of the activity. It has not yet been possible to establish the chemical composition of the gases evolved after heating and during treatment of the catalyst with hydrogen at a temperature of 475-500°.

The stages of the kinetic experiment just described are shown in Fig. 2. Similar experiments were repeated many times, and the character of the changes was well reproduced.

In another series, the experiments were carried out as follows. On the pretreated catalyst, a definite portion of inactive CO_2 (1.64 cm^3 at N.T.P.) was first absorbed, and then a strictly measured portion (0.82 cm^3 at N.T.P.) of active $C^{14}O_2$ was absorbed, after which the usual kinetic experiment was carried out. In another experiment, the same portion (0.82 cm^3 at N.T.P.) of active $C^{14}O_2$ was absorbed by the catalyst immediately after pretreatment, followed by recording of the isotope-exchange curve (Fig. 3).

Fig. 2. Transfer into the gas phase of chemisorbed CO_2 under various conditions. 1, 2, and 3—treatment of the catalyst with three successive portions of inactive

Fig. 3

Figure 3: Fig. 3

Fig. 4. Dependences of the rate of isotopic exchange on the degree of preliminary filling of the surface with inactive CO_2.

Figure 4: Fig. 4. Dependences of the rate of isotopic exchange on the degree of preliminary filling of the surface with inactive CO_2.

CO_2; 4—heating of the catalyst at a temperature of 475°; 5 and 6—two successive treatments of the catalyst with hydrogen at a temperature of 475°.

Fig. 3. Dependence of the rate of isotope exchange on the order in which the catalyst surface is filled. 1—first, 1.64 ml of inactive CO_2 was absorbed, and then 0.82 ml of active $C^{14}O_2$; 2—active $C^{14}O_2$ was absorbed directly onto the pretreated catalyst.

As is evident from Fig. 3, the percentage of exchange depends on the sequence of absorption: if active $C^{14}O_2$ is absorbed first, the exchange fraction is 15-20% lower than with the reverse sequence.

The fraction of exchangeable CO_2 depends not only on the sequence of absorption, but also on the degree of filling of the active sites.

Figure 4 presents the results of measuring the rate of exchange of CO_2 for experiments in which 2.85 cm^3 of inactive CO_2 and only 0.42 ml of active $C^{14}O_2$ had previously been deposited on the catalyst. In this case the fraction of exchange is about 60-65%. The data presented indicate the presence of two regions, sharply different in their properties, characterizing the alkaline part of the catalyst surface. Apparently, we are dealing either with the existence of at least two chemically different forms of the alkaline promoter, or with the presence of a set of sites sharply differing in their activity. A broad investigation of a large number of ammonia-synthesis catalysts, promoted in different ways, will make it possible to approach more deeply the question of the promoting action of the alkaline additive and of the role of CO_2 as a catalytic poison.

Fig. 4. Dependences of the rate of isotopic exchange on the degree of preliminary filling of the surface with inactive CO_2.

The absence of a change in activity during prolonged circulation in an atmosphere of CO, H_2, and Ar, and rapid exchange in the presence of CO_2 in the gas phase, indicate that the exchange mechanism in the case investigated is apparently close to the CO_2 exchange process proposed by some authors[8] on carbonates of alkali and alkaline-earth elements. According to this scheme, the first stage is adsorption of the gas on the carbonate surface with formation of a surface compound of adsorbed carbon dioxide with the carbonate anion

$$[C^{14}O_3^{2-} \cdot C^{12}O_2] \rightleftarrows [C^{12}O_3 \cdot C^{14}O_2]$$

with subsequent desorption of $C^{14}O_2$ into the volume, i.e., a double exchange occurs with formation of an intermediate complex, and not dissociative exchange through the gas phase.

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CITED LITERATURE

1. S. Roginskii, O. Todes, *Acta Physicochim. URSS*, **21**, 519 (1946).
2. S. Z. Roginskii, *Izv. AN SSSR, ser. fiz.*, **3**, No. 2, 350 (1940).
3. S. Z. Roginskii, *Theoretical Foundations of Isotopic Methods for Studying Chemical Reactions*, 1956.
4. N. P. Keier, S. Z. Roginskii, *DAN*, **57**, 157 (1947).
5. J. T. Kummer, P. H. Emmett, *J. Am. Chem. Soc.*, **73**, 2811 (1951).
6. R. P. Eischens, *J. Am. Chem. Soc.*, **74**, 6167 (1925).
7. N. P. Keier, Abstracts of the Conference on the Application of Isotopes in Catalysis, Moscow, 1956, p. 61.
8. V. A. Shushunov, B. G. Zaitsev, *ZhFKh*, **30**, No. 2, 321 (1956).

Note: Figure translations are in progress. See original paper for figures.