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Abstract

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ISOTOPIC EXCHANGE IN MOLECULAR NITROGEN ON IRON CATALYSTS FOR AMMONIA SYNTHESIS

It has been established ([1-3]) that additions of K_2O and Al_2O_3 to iron catalysts increase their specific activity (activity referred to unit surface area of the catalyst) with respect to the ammonia-synthesis reaction at high pressures. Singly and doubly promoted samples proved to be considerably more active than an unpromoted iron catalyst, with the activating action of K_2O being more pronounced than that of Al_2O_3.

With regard to the effect of these additions on catalyst activity in the case of ammonia synthesis at atmospheric pressure, contradictory data are found in the literature.

A brief communication by A. V. Krylova and S. Z. Roginskii ([4]) was devoted to clarifying the influence of the indicated promoters on the rate of isotopic exchange in molecular nitrogen; they concluded that iron without promoters, in comparison with promoted samples, possesses a higher specific activity. However, in work ([5]) a doubly promoted catalyst proved to be 10 times more active than unpromoted iron.

In connection with this, there arose a need for an additional, broader investigation of isotopic exchange in molecular nitrogen on iron samples with different promoter contents, on which ammonia synthesis had been studied at high pressures ([2,3]).

Experimental Part

The experimental procedure has been described in detail ([5]). The distinctive feature of the present investigation was that all samples, in an amount of 30 g, were reduced with hydrogen in a separate apparatus for 50–55 hr at 500°: for 10 hr at a space velocity of 6000 hr^{-1}, and for the remaining time at a velocity of 3000 hr^{-1}.

After completion of the reduction, the catalysts were passivated at room temperature with nitrogen from a cylinder, using hydrogen purified of oxygen as diluent. The passivated sample was loaded into the apparatus for studying isotopic exchange and treated with hydrogen (activation) at a space velocity of 3000 hr^{-1} at 500° for 10-15 hr.

The true reaction order, i.e., the dependence of the exchange rate on the total gas pressure, was determined in the pressure interval 3-30 mm Hg, and the activation energy in the temperature interval 450–500°.

The specific rate constant of exchange (catalytic activity) was calculated from the equation describing homomolecular isotopic exchange ([5,6]).

Table 1 gives the values of the activation energy, reaction order, and

specific catalytic activity $K(P, t)$ at the corresponding pressure and temperature for the catalyst samples studied.

It should be noted that, in the course of the test, the activity of the catalyst promoted only with K_2O decreased substantially because of partial

Table 1

Kinetic characteristics of isotopic exchange in molecular nitrogen on iron ammonia catalysts

Sample No.	Al_2O_3, %	K_2O, %	S_{sp}, m^2/g	E, kcal/mol	Reaction order	Activity, $cm^3/m^2 \cdot h\ K$ (4.5 mm 500°)	Activity, $cm^3/m^2 \cdot h\ K$ (3.3 mm 500°)
Armco	–	–	0.5	39*	0.9*	$3.8 \cdot 10^{-3}$*	$3.9 \cdot 10^{-3}$
16–55	Impurity	2	1.2–0.6	35	0.75	$4.1—0.8 \cdot 10^{-1}$	
4–55	3.85	2.14	11	44	0.5	$2.6 \cdot 10^{-2}$	
2–55	4.2	Impurity	11.6	43	0.5	$2 \cdot 10^{-1}$	
5–55	1.2	2.6	3.6	41.5	–	$2.6 \cdot 10^{-1}$	

* From Ref. (5).

loss of promoter and a decrease in the surface area of the sample studied. Therefore, for this catalyst the table gives the initial and final activity.

Discussion of the results

From the data in Table 1 one may draw the general conclusion that, in terms of specific activity, promoted catalysts greatly exceed Armco iron (without promoters). This agrees with our results obtained earlier (5).

Consequently, there is a quite definite parallelism in the accelerating action of additives (K_2O and Al_2O_3) on the processes of ammonia synthesis and nitrogen isotopic exchange. This fact is difficult to explain if one accepts (7-9) that, on iron catalysts, the limiting stage in ammonia synthesis is determined by the act of hydrogenation of adsorbed nitrogen.

If it is assumed that isotopic exchange and ammonia synthesis proceed through a common stage—nitrogen adsorption—then one can quantitatively compare the rates of isotopic exchange and ammonia synthesis, taking into account the filling of the catalyst surface with adsorbed nitrogen (5).

Calculation shows that the absolute rates of the reactions of ammonia synthesis and isotopic exchange at identical coverages by adsorbed nitrogen are close in magnitude on singly promoted samples and on Armco iron.*

In the case of the doubly promoted sample (3.85% Al_2O_3 and 2.14% K_2O), the exchange rate is approximately one and a half orders of magnitude lower than the synthesis rate. A similar result was obtained (5) for the catalyst (2% K_2O and 4.5% Al_2O_3). However, a sample with another promoter content (2.6% K_2O and 1.2% Al_2O_3) proved to be very active in exchange (Table 1).

The reduced activity in isotopic exchange of the above-mentioned doubly promoted sample may be due to insufficient mobility of chemisorbed nitrogen atoms on the surface of a catalyst of this composition. It is also possible that ammonia synthesis can proceed on this catalyst through chemisorbed molecular nitrogen.

* For the calculation, experimental data on ammonia synthesis at atmospheric pressure, obtained by N. M. Morozov in the laboratory of Prof. M. I. Temkin, were used.

The kinetics of isotopic exchange on the promoted samples investigated agree quite well with the kinetics of ammonia synthesis. The activation energies of both processes, calculated at constant volatility of adsorbed nitrogen, coincide satisfactorily.

Thus, the experimental data on isotopic exchange on iron ammonia catalysts confirm the Temkin-Pyzhev mechanism[10] for ammonia synthesis.

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