

was increased. In these cases further reaction could not be observed at temperatures up to 180°C.

From our results we may conclude that the decomposition of N₂O at room temperature is an adequate method for the determination of specific copper surface areas.

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The Influence of Oxygen on the Catalytic Reduction of Nitric Oxide by Ammonia

Investigations on the heterogeneous catalytic reduction of nitric oxide, especially by means of hydrogen and carbon monoxide, have already been treated in a series of papers. Only a few authors (1-4), however, have studied the catalytic reaction of nitric oxide with ammonia, and their papers, moreover, present only qualitative conclusions.

Only Mikhailova (5) has investigated in some detail the course of the reaction of nitric oxide with ammonia on a platinum filament as a catalyst. The experiments were performed in a static apparatus with a circulating gas mixture at a total pressure of 10-20 torr and at temperatures of 500-530°K. Evaluating the results of her measurements, the author formulated the hypothesis that the reaction proceeds, in the absence of oxygen, between molecules of ammonia and nitric oxide adsorbed on adjacent active centers of the catalyst. From the fact that the original activity of the Pt filament is reduced by heating in an

oxygen atmosphere or in air the author concluded—not quite exactly—that the reaction is inhibited by oxygen.

The influence of the presence of oxygen on the catalytic reaction of nitric oxide with ammonia has not been studied yet, though the reaction also has some practical importance. It is, however, commonly known that from a mixture of nitrogen oxides (NO + NO₂) with oxygen the nitrogen oxides are reduced by ammonia preferentially, i.e., that ammonia reacts selectively.

To be able to explain this phenomenon and the influence of oxygen in the reaction mentioned the authors of the present note investigated the course of the reaction of ammonia with nitric oxide alone, as well as that of the reaction in the presence of oxygen.

EXPERIMENTAL

The investigations on the reaction NH₃ + NO → N₂ + H₂O were performed on Pt-

Al_2O_3 catalyst in an integral flow reactor at atmospheric pressure. The catalyst was prepared by the impregnation of alumina (preheated to 750°C) with a solution of chloroplatinic acid. The concentration of the solution was chosen so that the catalyst after reduction contained 1% Pt. The reduction of the catalyst was carried out directly in the reactor by hydrogen at 350°C for 3 hr. The total surface of the catalyst was $145\text{ m}^2/\text{g}$, as determined by the BET method by adsorption of nitrogen at the temperature of its boiling point. The composition of the gas mixture entering the reactor was 0.4% NO and 0.4% NH_3 , or, 0.4% NO, 0.4% NH_3 and 3% O_2 (the rest was always nitrogen), the output was 30 l (STP) of the mixture/g of the catalyst/hour. Oxygen was introduced into the mixture immediately before the inlet into the reactor, to prevent oxidation of the nitric oxide.

In the gas outflow the total amount of nitrogen oxides was determined after the removal of the ammonia not consumed in the reaction by sorption on anhydrous $\text{Mg}(\text{ClO}_4)_2$ by titration, utilizing a modified method according to Johnson (6).

RESULTS AND DISCUSSION

The results obtained are shown in Fig. 1 in the form of the dependence of nitric oxide conversion (i.e., the portion of the original amount of NO which entered the

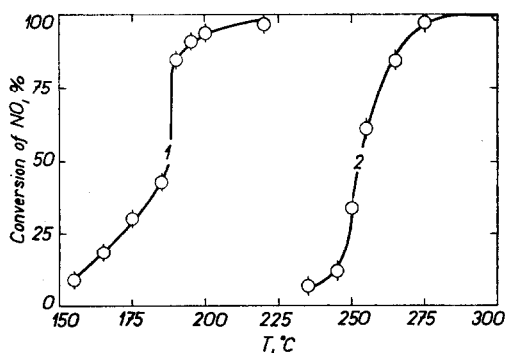
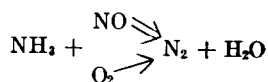


Fig. 1. Dependence of nitric oxide conversion on the reaction temperature: 1, reaction performed in the presence of O_2 ; 2, reaction performed in the absence of O_2 .

reaction, expressed in %) on the reaction temperature. It follows from the figure that in the presence of oxygen the same conversion values were attained at appreciably lower temperatures than in a reaction of mere nitric oxide with ammonia, i.e., that oxygen enhances the reaction rate.

This interesting fact might perhaps be explained by the following mechanism, provisionally assumed by the authors.

Nitric oxide and ammonia molecules are preferentially adsorbed on the surface of the catalyst. The adsorbed ammonia dissociates according to current views on the catalytic effect of platinum (7) to the fragments H, NH_2 , and eventually NH. Oxygen accelerates the overall reaction by its reaction with one of these fragments, thus the rate of the reaction between the remaining fragments and nitric oxide is enhanced too. Thus, under the conditions mentioned above two side reactions influencing one another occur



Corresponding with this working hypothesis, the actual amount of ammonia consumed in the reaction is greater than that assumed from the stoichiometrically reduced portion of nitric oxide.

A more detailed explanation of the role of oxygen in the catalytic reduction of nitric oxide by means of ammonia forms the subject of our further investigations.

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Application of the Halsey Form Correlation to Nitrogen Adsorption on Metal and Supported Metal Substrates

It has been shown (1) that porous structure can significantly affect the apparent relationship between adsorbed multilayer thickness and relative pressure in the nitrogen isotherm technique for determining volume-area distributions. Studies based on adsorption-desorption isotherms for nitrogen on a number of alumina samples with widely differing pore shapes, sizes, and specific surface areas (2) have demonstrated that structural effects on multilayer adsorption are very well correlated by an expression of the form:

$$\ln(N) = (1/n) \ln[\ln(X_M)/\ln(X)] + \ln(a') \quad (1)$$

in which N is the number of adsorbed monolayers, X the relative pressure, X_M the relative pressure at monolayer coverage, and n and a' constants which can be related to properties characteristic of a given porous structure. Equation (1) derives from a form originally proposed by Halsey (3).

Since there is obvious application to a large range of supported catalysts and materials other than alumina, it is the purpose of this note to examine application of the proposed correlation to such materials. In Table 1 are listed properties of four representative samples selected for the wide range in surface area, porosity, and composition involved. Sample I is a high surface area, gelatinous boehmite reported by de Boer and Lippens under the

designation of A-120. Sample II is an alumina-supported Co-Mo catalyst of moderate surface area; the composition of this material (approximately 10% Mo, 5% Co) is such that the adsorbent surface is only partially covered by these metals. Sample III is an alumina-supported chromium catalyst of low surface area, 15% by weight Cr. In this sample proportionately more of the surface is covered by the metal than in II; however, complete coverage is unlikely since the catalyst is composed of a mechanical mixture of Cr_2O_3 and gamma alumina. Sample IV is a pure copper catalyst of low surface area. The pore structures of these samples also differ considerably, as indicated by the $\bar{r}_{S_{BET}}$ data of Table 1, and by the shapes of the nitrogen isotherms reported or measured for the degassed materials in a flow system at liquid nitrogen temperature (Samples II-IV), as shown in Fig. 1.

These data establish the diversity of structure and surface composition of the test materials. The adsorbed layer thickness correlation is evaluated on the basis of the consistency of results of volume-area distribution computations and comparison with those obtained employing alternative (4, 5, 6) correlations. A major part of this comparison and consistency test follows from the observation that for extremes of porous structure types the surface area computed from nitrogen *desorption* isotherm data cannot be smaller than S_{BET} , but may be larger. An additional important con-