Catalysis Letters 1 (1988) 61–66

ON THE RATE ENHANCEMENT OF AMMONIA SYNTHESIS OVER IRON SINGLE CRYSTALS BY COADSORPTION OF ALUMINUM OXIDE WITH POTASSIUM

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Received 4 December 1987

The behavior of doubly promoted iron catalysts utilized for ammonia synthesis is modelled by the coadsorption of aluminum oxide and potassium on iron single crystal surfaces that were employed in high pressure reaction rate studies. The promoter effect of aluminum oxide is due to its interaction with iron oxide during the preparation stage of the industrial catalyst. After reduction, aluminum oxide stabilizes the most active Fe(111) and Fe(211) crystal surfaces. Potassium does not appear to be involved in the structural promotion but its presence on the active iron surfaces increases the rate of dinitrogen dissociation mostly by lowering the concentration of adsorbed ammonia thus, making more catalytic sites available for dinitrogen dissociation. Co-adsorbed potassium and alumina form a potassium aluminate compound that a) inhibits the aluminum oxide induced restructuring of iron and b) covers up the active iron sites for ammonia synthesis.

1. Introduction

The iron ammonia synthesis catalyst that is utilized in industry is usually mixed with potassium oxide and aluminum oxide additives that further increase the rate of ammonia synthesis. It is found that aluminum oxide additives alone increase the rate of ammonia synthesis by increasing the active surface area of the iron [1]. Potassium addition decreases the iron surface area but it still increases the rate by a factor of three to ten [1]. The doubly "promoted" iron catalyst surface consists of regions where potassium oxide resides alone and areas where it interacts with aluminum oxide [1,2]. Combined high pressure and ultra-high vacuum studies in our laboratory have elucidated the mechanisms by which aluminum oxide [3] or potassium [4] adsorbed alone increases the rates of ammonia synthesis over Fe(111), Fe(100), and Fe(110) single crystal surfaces. In this letter we report the combined effects of coadsorbed potassium and aluminum oxides commonly used in preparing the industrial iron catalyst.

We find that while aluminum oxide can stabilize much more potassium on the iron surface (as compared to the 0.15 monolayers on the clean iron) by probably forming a potassium aluminate compound (i.e. $KAlO_2$) [5], it does not improve the activity of the catalyst any further. This is due in part to the blocking of the active iron surface by potassium aluminate and in part to the inhibiting effect of potassium on the aluminum oxide induced restructuring of iron [3]. It is experimentally shown that the most active ammonia synthesis catalyst is produced by first restructuring iron with water vapor in the presence of aluminum oxide and then adding potassium.

The experiments presented were performed in a combined ultra-high vacuum (UHV)/high pressure apparatus. The stainless steel UHV chamber routinely achieved a base pressure of 1×10^{-9} Torr. The chamber was equipped with a retarding field analyzer (RFA) which would be used for low energy electron diffraction (LEED) or Auger electron spectroscopy (AES). A glancing incidence electron gun provided a primary beam for AES and an ion sputtering gun was present for sample cleaning. The chamber also was equipped with a quadrupole mass spectrometer for temperature programmed desorption (TPD).

The unique part of the chamber was a hydraulically operated high pressure cell. When closed, the cell isolated the iron single crystal sample from the UHV environment and constituted part of a high pressure micro-batch reactor. The cell was pressurized with 15 atm of hydrogen and 5 atm of nitrogen. The sample was resistively heated to 673 K and ammonia formation was monitored by passing samples from the gas phase through a photoionization detector (PID) which was only sensitive to the ammonia concentration. Thus, the PID signal was directly proportional to the ammonia partial pressure in the reaction loop. After reaction, the loop was evacuated and the sample was returned to UHV, where surface sensitive techniques were used to analyze the surface composition and structure.

The preparation of the single crystal samples were carried out by standard metallurgical techniques. The samples were typically 1 cm^2 disks about 1 mm thick. A chromel-alumel thermocouple spot-welded to the edge of the crystal was used to monitor the sample temperature.

Aluminum oxide was deposited from a Knudsen type cell and it was oxidized with water vapor to Al_xO_y in UHV. Surface coverages were determined by CO titration and AES [3,5]. The percentage of iron surface covered by Al_xO_y was taken into account when rates of ammonia synthesis were determined. Potassium was evaporated from a Saes Getter and coverages in monolayers (ML) were determined by AES.

The nitrogen and hydrogen used in this study was research grade. The gases were further purified by passing them through a liquid nitrogen cooled coil and a molecular sieve trap. The ammonia used in this work was obtained from Matheson (99.9%) and it was used without further purification.

2. The effects of coadsorbed potassium and aluminum oxide on the clean, *unrestructured* Fe(100) surface for ammonia synthesis

In these experiments conditions that would induce restructuring of iron (treatment of the Al_xO_y/Fe(100) surface with water vapor at 723 K [3]) were carefully avoided. Thus, the Fe(100) surface structure remained unaltered during these

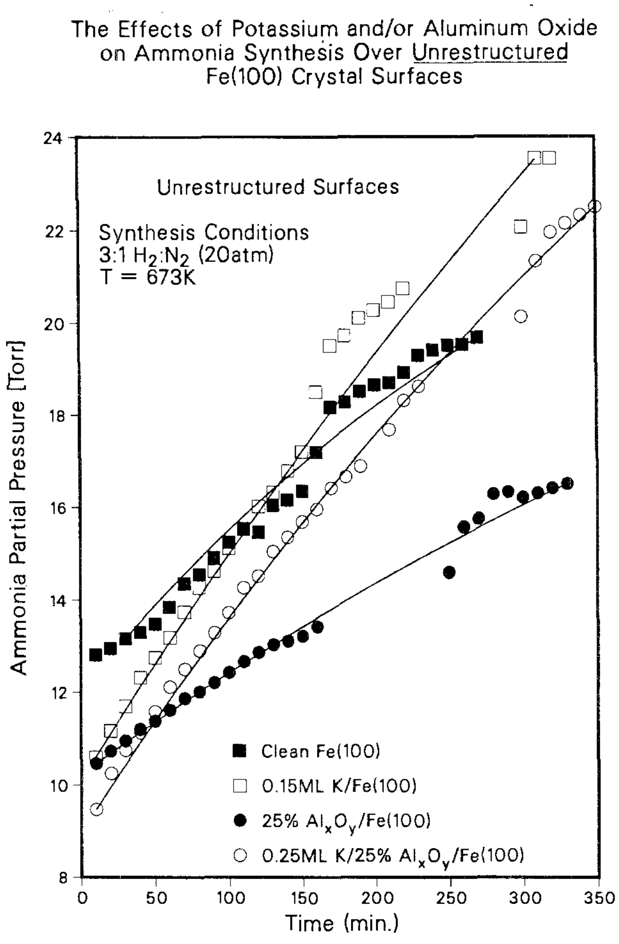

Fig. 1. The amount of ammonia produced in the reaction loop is plotted against time of ammonia synthesis for the 0.15 ML K/Fe(100), clean Fe(100), 0.25 ML K/25% Al_xO_y/Fe(100), and 25% Al_xO_y/Fe(100) surfaces. All the experiments shown were begun with approximately 10–13 Torr of ammonia already in the reactor loop. The non-linearity of the curves is due to gas phase ammonia readsorbing on the catalyst and blocking catalytic sites for the dissociation of dinitrogen. The K/Al_xO_y/Fe(100) surface becomes increasingly more active than the Al_xO_y/Fe(100) surface as the ammonia partial pressure increases in the reactor loop. The rate over the K/Al_xO_y/Fe(100) is about the same as the rate over the 0.15 ML K/Fe(100) surface over the whole range of ammonia partial pressures used in this study. The amount of iron surface covered by Al_xO_y and the surface area of the single crystal is taken into account when rates of ammonia synthesis were determined.

experiments. Figure 1 plots the partial pressure of ammonia in the reaction loop versus time of ammonia synthesis reaction for a clean Fe(100), 0.15 ML K/Fe(100), 0.25 ML K/25%Al_xO_y/Fe(100), and a 25%Al_xO_y/Fe(100) surface. The *initial* rate of ammonia synthesis (0–3 Torr of ammonia is in loop during this time) over the Al_xO_y/Fe(100) and K/Al_xO_y/Fe(100) surfaces have been shown to decrease roughly in proportion to the amount of iron catalyst surface covered by the additives [5]. Thus, potassium aluminate [5] does not increase the activity of the catalyst in this circumstance. As the reaction conversion increases the promoter effect of potassium becomes apparent. Thus, the 0.25 ML K/25%Al_xO_y/Fe(100) surface increasingly becomes more active than the 25%Al_xO_y/Fe(100) surface. This is the same behavior as observed when comparing the reaction rates over the K/Fe(100) and Fe(100) surfaces in the same figure [4]. The addition of potassium reduces the adsorption energy of adsorbed ammonia and leads to a lower surface concentration of ammonia on the catalyst by shifting the equilibrium $NH_{3(ad)} \overset{K_3}{=} NH_{3(g)}$ to the gas phase ammonia side (i.e. the equilibrium constant K_3 increases). With less adsorbed ammonia the number of available sites for the dissociation of dinitrogen, the rate limiting step in ammonia synthesis [6,7], is increased and this causes an increase in the rate of ammonia production. In addition, potassium enhances the rate of dinitrogen dissociation by approximately 30% over Fe(111) and Fe(100) under ammonia synthesis conditions.

It has been shown that the concentration of aluminum oxide and potassium exist in an approximate 1 : 1 ratio under ammonia synthesis conditions [5]. Even though high coverages of potassium can be stabilized with aluminum oxide, the promotional effect never exceeds the effect attained on the 0.15 ML K/Fe(100) surfaces which has been reported on previously [4]. Thus, the potassium that is tied up by the aluminum oxide in a compound ($KAlO_2$) seems to be rendered catalytically inactive. The 0.25 ML K/25%Al_xO_y/Fe(100) surface exhibits roughly the same rate of ammonia synthesis as the 0.15 ML K/Fe(100) surface at all ammonia partial pressures used in this study as indicated by the slopes of the curves in fig. 1. Stabilizing more than 0.25 ML of potassium with Al_xO_y begins to decrease the promoter effect of potassium. One reason for this is that high coverages of potassium block catalytic sites for dinitrogen dissociation [5,8].

3. The effects of coadsorbed potassium and aluminum oxide on the *restructured* Fe(100) surface for ammonia synthesis

Figure 2 plots ammonia accumulation as a function of time for the clean Fe(100), for 25%Al_xO_y/Fe(100) that was restructured by 20 Torr of water vapor at 723 K and for 0.25 ML K/25%Al_xO_y/Fe(100) that was restructured first in the presence of aluminum oxide alone before adding the potassium. Our studies [3]

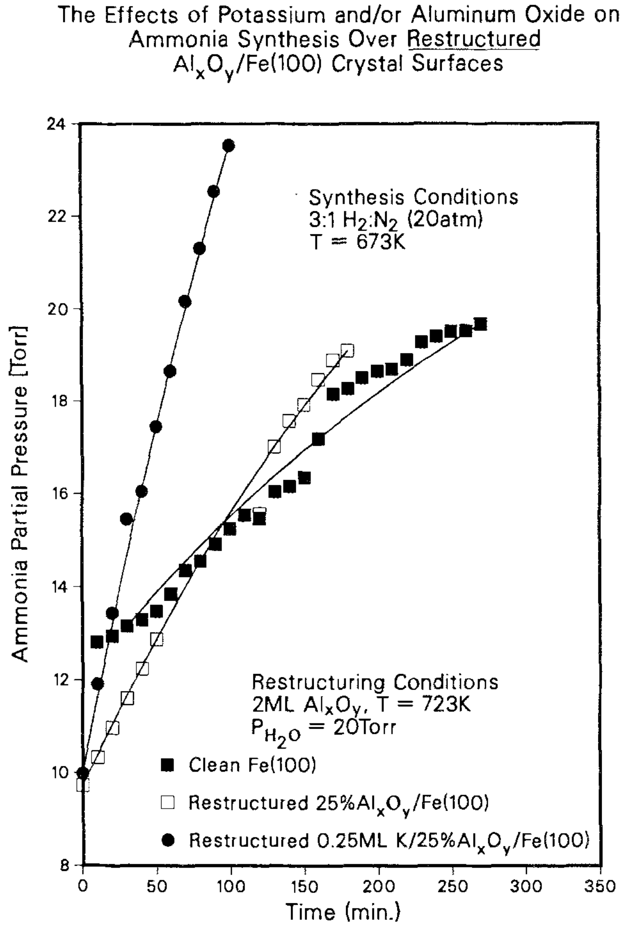

Fig. 2. Ammonia accumulation in the reaction loop is plotted against time for the clean Fe(100), restructured Al_xO_y/Fe(100) and for a 0.25 ML K/Al_xO_y/Fe(100) which had been restructured before the addition of potassium. Restructuring conditions are given in the figure. The 0.25 ML K/Al_xO_y/Fe(100) is the most active surface in this study. It has approximately the same activity as the 0.15 ML K/Fe(111) surface [4]. To fully obtain the promotional effects of both aluminum oxide and potassium restructuring must be performed with aluminum oxide alone and potassium should be added afterwards. This is because potassium inhibits the aluminum oxide restructuring process on the iron single crystal surfaces.

suggest that aluminum oxide catalyzes restructuring to crystal faces, such as Fe(111) and Fe(211), which are about an order of magnitude more active than the Fe(100) face [9]. Potassium addition to the restructured surface further enhances the rate of the restructured iron, that becomes predominant at high ammonia conversions. In this way the promotional effects of both aluminum oxide and potassium can be fully realized. It should be noted that if both aluminum oxide and potassium are added before restructuring in water vapor the extent of surface restructuring (Fe(100) → Fe(111) and Fe(211)) is decreased. The potassium aluminate that forms on the surface seems to prevent the aluminum oxide-iron interaction needed for reconstruction of the iron surface morphology.

The motivation behind the work done in this laboratory has been to understand the promotional effects of aluminum oxide and potassium in the industrial catalyst. By using model iron single crystal surfaces as catalysts, it has been shown that the promoter effect of aluminum oxide results from the interaction with iron oxide during the preparation stage of the industrial catalyst [3]. After the activation of the catalyst (i.e. reduction in N_2 and H_2), aluminum oxide stabilizes the iron in active orientations for ammonia synthesis, such as Fe(111) and Fe(211) [3,9]. Potassium does not seem to be involved in this structural promotion [3] but its presence on the catalyst surface promotes ammonia synthesis on these active crystal orientations by increasing the rate of dinitrogen dissociation and by lowering the concentration of adsorbed ammonia, making more catalytic sites available for dinitrogen dissociation [4].

Acknowledgement

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under contract DE-AC03-76SF00098. The authors gratefully acknowledge I.C.I. for partial support of this research.

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