10600 *J. Phys. Chem. A* **2000,** *104,* 10600−10602

High-Pressure Electrochemical Promotion of Ammonia Synthesis over an Industrial Iron Catalyst

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Received: June 21, 2000; In Final Form: August 17, 2000

The catalytic reaction of ammonia synthesis is of paramount importance in the chemical industry, mainly for fertilizers production.[1,2] The reaction is equilibrium limited and is favored by low temperatures and high operating pressure. Since the pioneering work of Haber and Bosch the industrial ammonia synthesis is carried out over potassium-promoted Fe catalysts at pressures up to 300 bar. Here we show that the catalytic activity of state-of-the-art fully promoted industrial ammonia synthesis catalysts can be enhanced by up to 1300% by interfacing the catalyst with a proton conductor ($CaIn_{0.1}Zr_{0.9}O_{3-\alpha}$) and electrochemically supplying protons to the catalyst surface. The rate increase is up to 6 times larger than the rate of proton supply to the catalyst. This is the first demonstration of the effect of electrochemical promotion, or non-Faradaic electrochemical modification of catalytic activity (NEMCA)[3−9] using a commercial catalyst and under high (50 bar) pressure. It is also the first demonstration of scale-up of an electrochemically promoted catalytic reactor as 24 electrically connected catalyst pellets were used. The results could in principle lead to a substantial decrease in the operating temperature and pressure of ammonia synthesis reactors.

Of all the century's technological marvels, the Haber−Bosch ammonia synthesis process has made the most difference to our survival.[1,2] The catalyst used until today balances both performance and cost and consists of iron promoted with K_2O, CaO, and Al_2O_3. Today, almost a century later and besides its hazardous operating conditions, the Haber−Bosch process is still used in ammonia plants only in slight variations.[1,2] In an effort to develop alternative ammonia synthesis routes, Marnellos and Stoukides[10] have recently reported measurable ammonia synthesis rates over Pd electrodes at temperatures as high as 570 °C and atmospheric pressure using a high-temperature proton conductor ($SrCe_{0.95}Yb_{0.05}O_3$) in a solid electrolyte cell. Such an electrosynthesis route can, in principle, avoid the thermodynamic limitations of a classical catalytic reactor, provided the electrode surfaces are catalytically inert.[10]

In this study we utilize the effect of electrochemical promotion or nonfaradaic electrochemical modification of catalytic activity (NEMCA effect)[3−9] to show that the catalytic activity of state-of-the-art industrial NH_3 synthesis catalysts can be enhanced by 1300%, or higher, by interfacing the catalyst with $CaIn_{0.1}Zr_{0.9}O_{3-\alpha}$, a proton conductor, and supplying protons to the catalyst via application of a potential (typically −1 V) between the catalyst and a counter electrode.

The electrochemically induced increase in the rate of NH_3 synthesis is up to a factor of 13 higher than the normal catalytic rate and up to a factor of 6 higher than the rate of supply of protons to the catalyst, i.e., from the maximum rate anticipated from Faraday's Law for a purely electrochemical reaction. This is the first demonstration of the effect of electrochemical promotion or NEMCA[3−9] in a high-pressure (50 atm) reactor and also the first demonstration of electrochemical promotion using a fully promoted industrial catalyst. It is also the first successful scale-up of an electrochemical promoted reaction, since 24 catalyst pellets, electrically connected in parallel, were used in the laboratory reactor. Due to the fact that the present process is catalytic rather than faradaic and involves a state-of-the-art industrial catalyst, the NH_3 synthesis rates and rate increases achieved are typically 3−4 orders of magnitude higher than those reported in the pioneering work of Marnellos and Stoukides.[10]

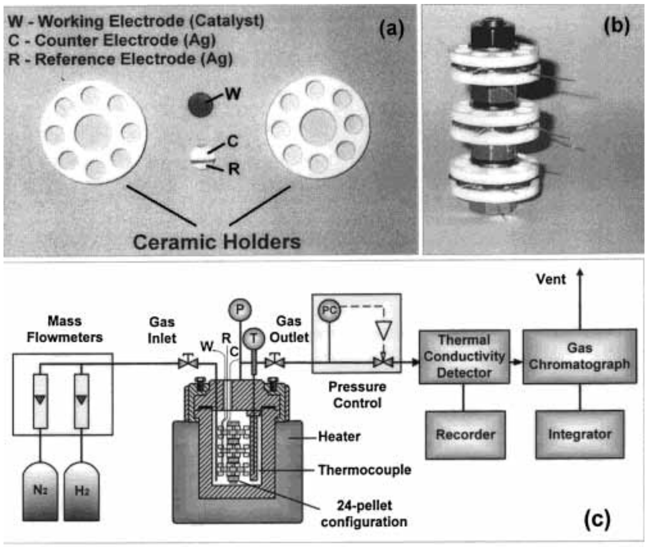

Figure 1. Experimental setup (a) Machinable ceramic holders and two proton-conducting pellets showing the location of catalyst, counter, and reference electrodes. (b) Twenty-four pellet unit. (c) High-pressure reactor, gas feed, and analysis unit.

The 24-pellet cell reactor shown in Figure 1 operated at 50 atm. The BASF S6-10RED catalyst was milled and mixed with an Engelhard iron paste OL15/34 (a mixture of 5 g of catalyst in 2 mL of paste). Thin coatings of this medium were applied on one side of high-proton-conductive $CaIn_{0.1}Zr_{0.9}O_{3-\alpha}$ disks (9 mm diameter, 1 mm thickness) and calcined in air at 400 °C

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10.1021/jp002236v CCC: $19.00

for 1 h, successively. The average catalyst loading on each disk was 11.2 mg prior to reduction. Silver reference and counter electrodes were deposited on the other side of the pellets by applying GC Electronics silver followed by drying in air at 120 °C (Figure 1a). Specially built machinable ceramic, Macor, holders were used to support the catalyst pellets. Each holder had eight openings in a circular configuration so that all electrodes were exposed to the gaseous reactant mixture. A screw was passed through a large hole in the middle of the ceramic holders in order to press two holders together and consequently maintain the 8 pellets and the conducting gold electrode rings in contact. The screw was also used to press together the three 8-pellet elements in a 24-pellet unit (Figure 1b). The 24-pellet unit was suspended inside a 300 cm^3-vessel Parr reactor using the configuration shown in Figure 1b. All results were obtained in the experimental setup of Figure 1c at 440 °C and 50 atm using a constant total inlet flow rate of 100 cm^3 STP/min. The gas feed consisted of high-purity N_2 and H_2 mixtures and its flow rate was controlled with high-pressure mass flow meters and controllers. The reactor head was equipped with a transducer gland that fitted three gold wires used to keep all 24 of the working, counter, and reference electrodes, respectively, connected in parallel. By means of these three wires, constant external potentials, U_{WR}, or constant currents, I, could be applied via an AMEL 553 galvanostat−potentiostat. On-line gas chromatography was used to monitor the rate of ammonia production, r_{NH_3}, and therefore the rate, r, of proton consumption computed from $r = 3r_{NH_3}$. A thermal conductivity detector was used to determine stead-state outlet gas conditions after imposed changes in operating conditions. Blank experiments confirmed that only the catalyst contributed to ammonia production.

Figure 2a shows the transient effect of constant potential imposition (potentiostatic transient) on the rate, r, of NH_3 synthesis, expressed throughout in mol H/s, at an inlet $P_{H_2/}P_{N_2}$ ratio of 0.82. Constant potential application ($U_{WR} = -1$ V) causes a steady-state current $I = -11$mA with a concomitant supply of protons to the catalyst or $-I/F = 1.1 \times 10^{-7}$ mol H/s. The rate of NH_3 synthesis increases from its open-circuit value of $r_0 = 6.9 \times 10^{-8}$ mol H/s to a new steady-state value of 1.35×10^{-7} mol H/s. The slow catalytic rate response shown in Figure 2a is due to the long (~150 min) residence time in the reactor. The rate enhancement ratio ρ, defined[3−9] from

$$\rho = r/r_o \tag{1}$$

has thus a value of 2. The Faradaic efficiency, Λ, defined from

$$\Lambda = \Delta r/(-I/F) \tag{2}$$

has thus a value 0.6, i.e., 60% of the protons arriving at the catalyst form ammonia. Thus both faradaic and non-faradaic regimes are observed.

Decreasing the inlet $P_{H_2/}P_{N_2}$ ratio to 0.54 causes non-faradaic rate enhancements, as shown in Figure 2b, which depicts the steady-state effect of electrochemical proton supply to the catalyst, $(-I/F)$, on the rate of NH_3 synthesis. The faradaic efficiency Λ, reaches values of 6 for low negative currents. This means that for each proton supplied to the catalyst surface, six protons react to form NH_3.

The nature of the electrochemical effect depends strongly on gaseous composition. Figure 3 shows the effect of inlet H_2/N_2 ratio (=α), on the rate of NH_3 synthesis under open-circuit and closed-circuit (−1.0 V) conditions and on the corresponding Λ and ρ values. The rate vs α dependence shown in Figure 3 suggests competitive adsorption between H and N atoms on the catalyst surface. Under open-circuit conditions a maximum rate of 9.4×10^{-8} mol H·s^{-1} is observed for a H_2/N_2 ratio of 1. When we apply a negative potential of −1.0 V the maximum rate of ammonia synthesis increases to 23.3×10^{-8} mol H·s^{-1} (680% higher than the maximum open-circuit rate) and shifts to a smaller α-value of 0.67. This rat-maximum shift indicates an increase in the coverage of adsorbed H on the catalyst surface upon negative potential application and concomitant H^+ supply to the catalyst. For H_2/N_2 ratios above 1.5 the ammonia synthesis reaction is poisoned by the supply of protons and for $\alpha > 2.3$ the catalytic rate practically disappears, implying that the iron surface is entirely covered with adsorbed H which hinder nitrogen chemisorption. In this region the faradaic efficiency Λ values are negative, i.e., the catalytic rate decreases upon proton supply to the catalyst.

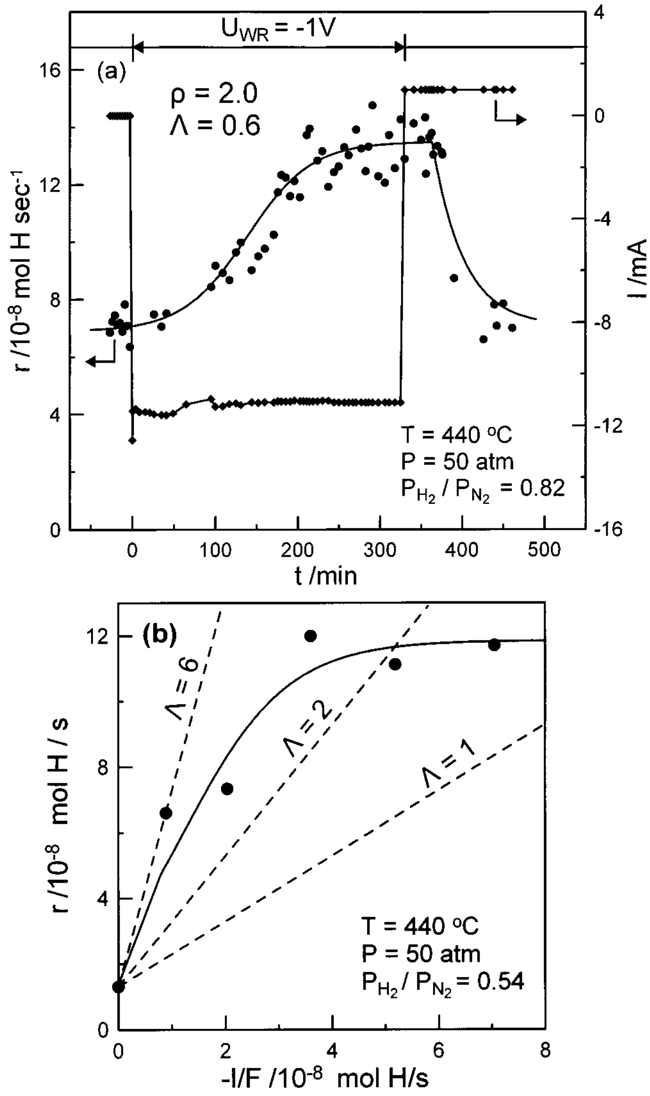

Figure 2. (a) Transient effect of applied potential on the rate of NH_3 synthesis (●) and on cell current (◆). (b) Steady-state effect of applied negative current, i.e., H^+ supply to the catalyst at a rate $-I/F$, on the ammonia synthesis rate increase. Dashed lines are constant faradaic efficiency lines.

Strongly non-faradaic behavior is observed for á-values in the region 0.33 ≥ α ≥ 0.67 with Λ values up to 3 (Figure 3b). Within this region, the largest precisely measurable enhancement ratio ρ was obtained ($\rho = 13$ at $\rho = 0.54$). Even larger ρ values, approaching “infinity”, are obtained at lower α values where under open circuit conditions the NH_3 synthesis rate is im-

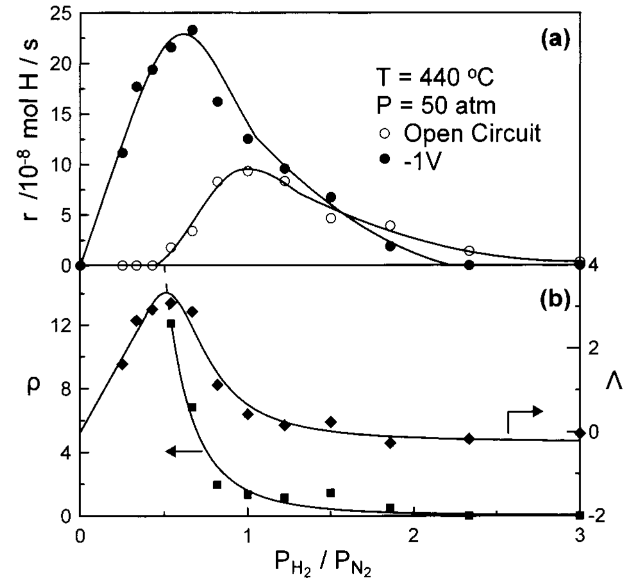

Figure 3. (a) Effect of inlet H_2/N_2 ratio (=α) on the rate of NH_3 synthesis under open-circuit (○) and for U_{WR} = −1.0 V (●). (b) Corresponding ρ (■) and Λ (◆) values.

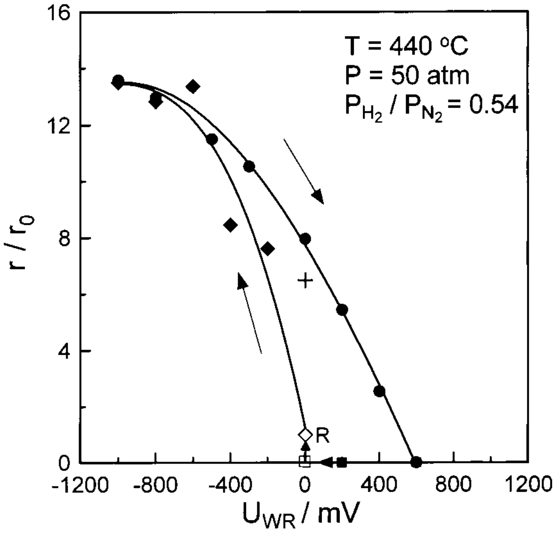

Figure 4. Steady-state effect of catalyst potential on the rate of NH_3 synthesis. Arrows indicate the sequence of measurements. Open symbols correspond to open-circuit conditions; $r_o = 10^{-8}$ mol H/s.

measurably low (Figure 3a) (exit NH_3 mol fraction below 80 ppm). The actual ρ-values in this area must be much greater than the maximum precisely measurable value of 13 at $\alpha = 0.54$. These large increases in rate (>1300%) are not in conflict with thermodynamics. In fact, the data shown in Figure 3 are considerably far from thermodynamic equilibrium as the largest hydrogen conversion is below 1% while at equilibrium it would be 8% ($k_a = 7.76 \times 10^{-3}$ at 440 °C).

Figure 4 shows the effect of catalyst potential, U_{WR}, on the ammonia synthesis rate. The reaction exhibits strong electrophilic behavior, i.e., the catalyst rate is significantly promoted with negative potentials and significantly poisoned with positive ones. As shown in Figure 4, hysteresis phenomena are also observed and prolonged (3−4 h) positive potential application leads to an irreversible loss of catalytic activity. This type of "permanent NEMCA" effect has been recently reported by Comninellis and co-workers.[8] We found that the initial catalytic activity could be restored only after prolonged (12 h) catalyst treatment in H_2 (arrow labeled R in Figure 4).

The observed, pronounced enhancement of catalytic activity with negative potentials can be explained by taking into account two synergetic factors commonly used to rationalize electrochemical promotion. First, the enhanced supply of protons onto the catalyst surface, and, second the enhanced chemisorptive binding energy and sticking coefficient of nitrogen (an electron acceptor) on the catalyst surface with decreasing potential and work function. The change in chemisorptive binding energies is strongly manifest by the fact that the maximum catalytic rate obtained with decreased potential and work function greatly exceeds the maximum value obtained under open-circuit conditions (Figure 3). The present results show that electrochemical promotion acts synergistically with classical chemical promotion and thus can be used to dramatically enhance the performance of even the best fully promoted state-of-the-art catalysts. This enhanced catalyst activity permits catalyst and reactor operation under conditions (e.g., low H_2/N_2 ratios) where the catalytic rate is otherwise negligibly small. Even taking the conservative limit of 13-fold catalytic rate enhancement, one can estimate a 50 °C reduction in operating temperature or a 30% reduction in operating pressure if electrochemical promotion were applied in an industrial ammonia synthesis reactor.

Acknowledgment. Financial support by the Electric Power Research Institute (EPRI) and by BASF is gratefully acknoledged. The authors thank Dr. F. Kalhammer of EPRI and Dr. H. Pütter of BASF for numerous helpful discussions.

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