Electrochemical promotion of NO reduction by hydrogen on a platinum/polybenzimidazole catalyst

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The electrochemical promotion of catalytic NO reduction by hydrogen was studied using a (NO, H₂, Ar), Pt polybenzimidazole (PBI)-H₂PO₄/Pt (H₂, Ar) fuel cell at 135°C. A mixture of NO/H₂/Ar was used as the working mixture at one electrode and a mixture of H₂/Ar was used as reference and counter gas at the other electrode. Products of NO reduction (N₂ and H₂O) were analyzed by on-line mass spectrometer. At high NO + H₂ + Ar flow rate (17 mL/min; 17 and 354 mL/min, respectively, at atmospheric pressure) the maximum rate enhancement ratio was 4.65. At low NO + H₂ + Ar flow rate (17 mL/min; 17 and 140 mL/min, respectively), NO reduction increased 20 times even without polarization compared to the high gas flow rate. The electrochemical promotion effect occurs at positive polarization with a maximum increase at approximately 0.08 V and with 1.5 times the zero polarization value. The promotion at the negative polarization can be attributed to the electrochemical production of the promoters. At low gas flow rates, a charge-induced change of the strength of chemisorptive bonds can take place.

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In most previous studies of electrochemical promotion of the catalytic NO reduction, Na was pumped to the surface of the catalyst using electrochemical reduction of Na\(^+\) ions from Na 8\(^-\)-alumina support.\(^1\)-\(^14\) This supply of Na greatly enhanced the reduction of NO on Pt, Pd, Rh, and several other catalytic materials with a reaction rate enhancement as high as two orders of magnitude. Simultaneously the selectivity of production of N\(_2\) against N\(_2\)O increased.\(^24\) As N\(_2\)O is produced by NO dissociation, which is the limiting step of the whole reaction, the electrochemical promotion of NO reduction is equivalent to the effect seen from depositing Na chemically on the catalyst surface. It means that the effect had a pure EPP nature.

The reason for NO reduction being promoted so remarkably is that the supply of Na to the catalytic surface changes the electronic properties of the surface. This happens in a way that strengthens the N-catalyst bond at the expense of the N-O bond, thereby facilitating the dissociation of NO, which is the limiting step of the whole reaction.\(^24\) As N\(_2\)O is produced by NO + N\(_2\)O\(_\text{ads}\) \(\rightarrow\) N\(_2\)O, the fast dissociation of NO diminishes the production of N\(_2\)O.\(^25\)

The electrochemical promotion of NO reduction is increased with the loading of Na until a certain point, where the supply of Na to the catalytic surface changes the electronic nature. This happens in a way that strengthens the N-catalyst bond at the expense of the N-O bond, thereby facilitating the dissociation of NO, which is the limiting step of the whole reaction.\(^24\) As N\(_2\)O is produced by NO + N\(_2\)O\(_\text{ads}\) \(\rightarrow\) N\(_2\)O, the fast dissociation of NO diminishes the production of N\(_2\)O.

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The mixture of NO and hydrogen, diluted by Ar (NO/H\(_2\)/Ar = 17 mL/min; 17 and 354 mL/min; or 17 mL/min; 17 and 140 mL/min, respectively, at atmospheric pressure) was used as a working mixture at one electrode and hydrogen/argon mixture (H\(_2\)/Ar was 17 and 371 mL/min or 17 and 140 mL/min, respectively) was used as a reference and a counter gas at the other electrode. The temperature was 135-137°C.

Commercial gases NO (99.9%), H\(_2\) (99.9%, \(\leq\)10 ppm of O\(_2\), \(\leq\)15 ppm of H\(_2\)O), and Ar (\(\leq\)40 ppm O\(_2\) + H\(_2\)O) were used.

An EG&G Instrument (Princeton Applied Research) 283 potentiostat/galvanostat controlled by 352 SoftCorr\TM III Software was used for electrode polarization and steady-state voltammetric measurements. The initial (at zero polarization) catalytic activity was measured after the yield of gas products had stabilized, i.e., under steady-state conditions. For each value of polarization the measurements were performed after stabilization of the yield of gas products (1-1.5 h). NO conversion vs. polarization curves were reproduced for each studied product and temperature. The open-circuit potential of the working electrode was approximately 0.14 V.

**Results and Discussion**

The results of the investigation of the electrochemical promotion of the catalytic NO reduction are given in Fig. 2–5. The presented data has been obtained at high and low gas flow rates to create the conditions where there are, respectively, an underproduction and an overproduction of the Pt-H\(_\text{ads}\) and Pt-H\(^+\)\_\text{ads} sites at the catalyst-gas interface through the chemical reaction.

Data in Fig. 2 and 3 were obtained at high gas flow rate after the catalyst was first polarized 0.1 V positively and then negatively to
-0.3 V. Nitrogen and water are the NO reduction products. Without polarization the NO conversion was 2% (Fig. 2). The reaction is assumed to be

\[ 2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \quad [6] \]

Dependence of the NO conversion on polarization is given in Fig. 2. It can be seen that Reaction 6 can be electrochemically promoted at negative polarization and exhibits a clear "volcano"-type promotion behavior.\(^6\) This means that there is a maximum promotion effect (9.3% NO conversion) at a polarization of approximately \(-0.15\) V, or \(-0.01\) V catalyst potential vs. the reversible hydrogen electrode, RHE. The catalytic rate enhancement ratio at this maximum is 4.65. Figure 2 shows no NO conversion at a polarization \(\leq 0.1\) and \(\leq -0.3\) V.

There are obvious anodic and cathodic faradaic reactions inside this potential region (presence of the voltammetric waves, Fig. 3). The anodic current at the potential of maximum effect was \(0.2\) mA/cm\(^2\). The value of \(\Lambda\) calculated for the maximum promotion effect was \(1.26 \times 10^3\), \(i.e.\), \(\Lambda \gg 1\). This means that this effect has an EPP nature.\(^2\)

The closest published example of an electrochemically promoted catalytic reaction is the catalytic oxidation of CO by \(\text{O}_2\) at the Pt catalyst on YSZ support.\(^{19}\) According to Belyaev et al., this catalytic reaction is promoted by \(\text{ZO}_2\) oxygen species which are the products of the interaction between electrochemically produced \(\text{ZO}\) species and chemically adsorbed oxygen species \(\text{Z}_\text{O}\text{O}\) (where \(\text{Z}\) are the catalyst active sites at the catalyst-support-gas interface and \(\text{Z}_\text{O}\) are the catalyst active sites at the catalyst-gas interface). We can assume here that both electrochemically produced \(\text{ZH}\) and chemically produced \(\text{ZH}\) species, and also the possible product of their interaction with \(\text{H}^+\), \(\text{ZH}^+\), can promote the NO catalytic reduction. The reaction

\[ \text{ZH} = \text{Z} + \text{H}^+ + e \quad [7] \]

takes place in the potential range between 0 and 0.4 V vs. RHE,\(^{25}\) \(i.e.\), at the potentials of the electrochemical promotion of NO reduction (Fig. 2). The nature of promotion of NO reduction by the adsorbed hydrogen species is probably the same as the nature of the promotion of the same reaction by the adsorbed Na atoms.\(^{1,14}\) It has been shown that the rate-determining step of the catalytic NO reduction at a Pt catalyst is dissociative chemisorption of NO because Pt is relatively ineffective at this step.\(^{24}\) Adsorbed hydrogen species can act to increase the adsorption strength of electronegative adsorbates (NO) and weaken the N-O bond in the adsorbed molecule and therefore promote NO dissociation.\(^{13}\)

Data in Fig. 4 and 5 were obtained at low gas flow rate after the catalyst was first polarized \(-0.3\) V negatively and then positively to 0.2 V. It can be seen from comparison of Fig. 2 and 4 that NO reduction is increased 20 times even without polarization. Moreover, under these conditions negative polarization decreased the rate of NO reduction (\(i.e.\), an opposite effect to what was found at high gas flow rates). It can also be seen that the electrochemical promotion effect did occur at a positive polarization with maximum increase at approximately 0.08 V polarization and with 1.5 times the zero polarization value.

The steady-state voltammetric behavior of the catalyst at a low gas flow rate is shown in Fig. 5. It is obvious from Fig. 5 that in the potential range of the promotion effect faradaic current is absent.
This means that the promotion effect has a CI nature. Increase of the NO conversion under open-circuit conditions and changes in the nature of the promotion effect can be explained by a high concentration of Pt-H sites at the low gas flow rates. The increased number of the adsorbed hydrogen species (as in the NO promotion with Na) can complicate the NO (electronegative adsorbate) chemisorption, especially at negative polarization. At positive polarization, however, the charge-induced change of the strength of chemisorptive bonds can take place (CI effect).

Conclusions

The possibility of the electrochemical promotion of the catalytic NO reduction by hydrogen at the Pt-PBI(H2PO4)-gas boundary has been demonstrated. It has also been shown that the nature of this promotion effect can vary depending on the flow rate of the NO/H2/Ar gas mixture. At high NO + H2 + Ar flow rate (17 mL/min; 17 and 354 mL/min, respectively, at atmospheric pressure), it has been found that NO reduction can be electrochemically promoted at negative polarization with maximum at approximately −0.15 V, i.e., close to the potential found for the maximum promotion of CH4 oxidation at the same catalyst. The maximum rate enhancement ratio was 4.65. The value of Λ calculated for maximum promotion effect conditions was 1.26 × 10³, i.e., Λ ≈ 1. This means that this effect has an EPP nature, the catalytic reaction was promoted by the electrochemically produced adsorbed hydrogen species.

At low NO + H2 + Ar flow rate (17 mL/min; 17 and 140 mL/min, respectively, at atmospheric pressure), NO reduction increased 20 times even without polarization. Moreover, under these conditions, negative polarization decreased the rate of NO reduction (i.e., an opposite effect to what was found at high gas flow rates). However, the electrochemical promotion effect did occur at positive polarization with maximum increase at approximately 0.08 V and with 1.5 times the zero polarization value. In the potential range of the promotion effect, faradaic current is absent. It means that the promotion effect has a CI nature. This means that the effect was caused by the charge-induced change of the strength of chemisorptive bonds.

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References