Active sites for the electrocatalytic direct NH_3 synthesis from N_2 and H_2O at ambient temperature and pressure

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Abstract: We report here the NH_3 electrocatalytic synthesis on iron nanoparticles supported over carbon nanotubes (CNTs), showing in particular the difference in the nature of active sites and reaction mechanism with respect to that present in iron catalysts for conventional high temperature/ pressure catalytic synthesis of ammonia. The active sites are located at carbon defective sites at the interface with the iron-oxide particles, likely responsible for a non-dissociative N_2 reduction via multielectron transfer.

Keywords: Ammonia direct synthesis, Fe_2O_3/CNT, Electrocatalysis.

1. Introduction

Ammonia synthesis, produced on an over 150 Mt world-scale in a multi-step process starting mainly from natural gas, is the largest-scale chemical process and top largest chemical process in terms of energy consumption, with about 2.5 EJ use on a world scale and between 1,8-2.1 t_{CO2} emitted per t_{NH3} produced, depending on plant efficiency. Therefore, over 300 Mt CO_2 emissions are associated to ammonia production. This value could be decreased by over 90% in a direct electrocatalytic process using N_2, H_2O and renewable energy as input sources. We showed earlier[1,2] the possibility to use electrocatalysis for the direct NH_3 synthesis from N_2 + H_2O at conditions close to ambient temperature and pressure in a flow electrochemical cell characterized from a gas-diffusion layer type electrode to operate electrocatalysis virtually under gas phase conditions, to allow a low-energy ammonia recovery from the gas stream leaving the reactor. This approach allows also the development of a distributed production of fertilizers.

Iron nanoparticles supported on carbon nanotubes (Fe/CNT), which were found to be an effective and stable electrocatalysts in this process, were utilized in the NH_3 synthesis hemicell.[1,2] A 30 wt % iron-oxide loading was found to be optimal, but with the performances greatly depending on the cell design, where the possibility of ammonia crossover through the membrane has to be inhibited.[2] Being iron also the industrial catalyst used in the high temperature/pressure (T/P) process (even if not supported on CNTs), the general question is whether the nature of the active sites and the reaction mechanism are the same in the low T/P electrocatalytic and high T/P catalytic processes, with the potential applied in the electrocatalytic processes providing just only the driven force to operate at much milder conditions, or rather a different mechanism and nature of the active sites is present in the two cases. While still debate exists on high T/P ammonia synthesis reaction mechanism, it is somewhat established that at typical industrial operating conditions a N_2 dissociative mechanism is present (i.e. that dissociative chemisorption of dinitrogen is the first step)[3], with subsurface diffusion of nitrogen to form surface iron-nitride or other Fe-N species. Metallic iron is the catalyst for high T/P industrial synthesis of ammonia (about 400-450°C and 10-30 MPa).[4]

We will show here that the active state of iron nanoparticles in Fe/CNTs electrocatalysts for ambient temperature/pressure ammonia direct synthesis from N_2+H_2O is an oxidized form, by comparing the behavior of Fe, Fe_2N and Fe_2O_3 nanoparticles supported on CNTs (functionalized by oxidative treatment). The results evidence that the active state of the iron in the electrocatalytic reduction of N_2 to ammonia is different from that present at high temperature/pressure in the catalytic process, and as a consequence the mechanisms of reaction is different. The analysis of the in-situ activation provides evidences that the active sites for the reaction are located at

2. Experimental

The 30% Fe_2O_3/CNT were prepared by i) first functionalization of CNT (Pyrograph®-III, CNT PR-24XT) by oxidative treatment (conc. HNO_3, washing and drying at 80°C) (o-CNT) and then ii) adding iron by impregnation with an iron-nitrate in ethanol solution. Samples were dried and calcined at 400°C. XRD, TEM and SEM/EDX characterizations shows the presence of Fe_2O_3 nanoparticles (about 1 nm size) well dispersed over o-CNT. The sample was reduced in H_2 at 500°C to form Fe/CNT, after TPR tests to determine the optimal reduction conditions. Fe_2N/CNT was formed by treatment of Fe_2O_3/CNT in an NH_3 flow at 500°C, after determining optimal conditions in NH_3-TPR tests.

Besides that by XRD, TEM and SEM, samples were characterized before and after catalytic tests, by XPS. The electrocatalytic tests were made in a flow electrocatalytic cells, where the hemicell, where NH_3 synthesis occurs, operates in the gas-phase mode, i.e. virtually without a liquid electrolyte, by using a gas-diffusion type electrode joint to a Nafion membrane. H_2O electrolysis occurs in the other hemicell.

3. Results and discussion

The behavior of the different electrocatalysts, studied as a function of time on stream and different voltage applied, indicates that: i) under electrocatalytic conditions, the formation of NH_3 from N_2 and H_2O is significantly larger than the catalytic activity of the same samples, i.e. when N_2 + H_2 is send to the electrocatalytic cell, without application of a potential, ii) the virtual meal-free electrocatalysts (o-CNT) is active in NH_3 synthesis, although the activity of Fe_2O_3/CNT is better; iii) there is a maximum activity for 30% wt. loading of Fe_2O_3, but the activity of Fe_2O_3 alone is lower than that of o-CNT, iv) the activity of Fe_2O_3/CNT is larger than that of Fe/CNT and Fe_2N/CNT in all range of potential. XPS characterization (O 1s) shows the presence of four components: i) O1 (Fe-O-Fe, 530.5±0.1 eV), related to O^{2-} in Fe_2O_3 or FeOOH species; ii) O2 (Fe-O-H, 531.8±0.1 eV), related to FeOOH species; iii) O3 (C-O-C, 532.4±0.1 eV), related to ether functional groups of carbons substrate; iv) O4 (C-O-H, 533.8±0.1 eV), related to OH and COOH functional groups of carbons substrate. The first O1 species was observed to correlate linearly with the ammonia initial rate of formation in iron/CNTs samples with the same iron loading (Fig. 1, bottom). An in-situ activation was present in the Fe_2O_3/CNT sample during electrocatalytic tests. The analysis of the change of Fe_2O_3/CNT samples during this activation phase under application of a -2V indicates that defect carbon sites are present at the interface between the iron-oxide nanoparticles and the CNT support, and that these sites largely increase during the activation phase. Operando EXAFS data indicate that a ferrihydrate (FeOOH) is present rather than a Fe_2O_3 phase under working conditions, but that increasing the potential reduction occurs with an in increase in side reaction of H_2 formation. All these results indicate that the active sites are located at carbon defective sites at the interface with the iron-oxide particles, likely responsible for a non-dissociative N_2 reduction via multielectron transfer.

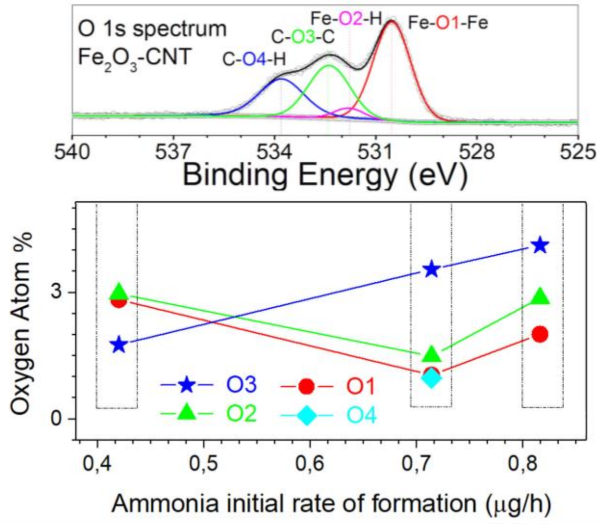

Figure 1. O1s XPS spectrum of Fe_2O_3/CNT samples (top) and relation of the intensity of the different oxygen components with the ammonia initial rate of formation

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