Catalytic Ammonia Decomposition: Cobalt-Molybdenum Molar Ratio Effect on Hydrogen Production

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Abstract : Catalytic ammonia decomposition represents an attractive alternative due to its high H_2 content (17.8% w/w), a product stream free of CO_x, among others; however, challenges need to be addressed for its consolidation as an H_2 chemical storage technology, especially, those focused on the synthesis of efficient bimetallic catalytic systems, as an alternative to the price and scarcity of ruthenium, the most active catalyst reported. In this sense, from the perspective of rational catalyst design, adjusting the main catalytic activity descriptor, a screening of supported catalysts with different compositional settings of cobalt-molybdenum metals is presented to evaluate their effect on the catalytic decomposition rate of ammonia. Subsequently, a kinetic study on the supported monometallic Co and Mo catalysts, as well as on the bimetallic CoMo catalyst with the highest activity is shown. The synthesis of catalysts supported on γ-alumina was carried out using the Charge Enhanced Dry Impregnation (CEDI) method, all with a 5% w/w loading metal. Seeking to maintain uniform dispersion, the catalysts were oxidized and activated (In-situ activation) using a flow of anhydrous air and hydrogen, respectively, under the same conditions: 40 ml min^{-1} and 5 °C min^{-1} from room temperature to 600 °C. Catalytic tests were carried out in a fixed-bed reactor, confirming the absence of transport limitations, as well as an Approach to equilibrium ($< 1 \times 10^{-4}$). The reaction rate on all catalysts was measured between 400 and 500 ºC at 53.09 kPa NH3. The synergy theoretically (DFT) reported for bimetallic catalysts was confirmed experimentally. Specifically, it was observed that the catalyst composed mainly of 75 mol% cobalt proved to be the most active in the experiments, followed by the monometallic cobalt and molybdenum catalysts, in this order of activity as referred to in the literature. A kinetic study was performed at 10.13 – 101.32 kPa NH3 and at four equidistant temperatures between 437 and 475 °C the data were adjusted to an LHHW-type model, which considered the desorption of nitrogen atoms from the active phase surface as the rate determining step (RDS). The regression analysis were carried out under an integral regime, using a minimization algorithm based on SLSQP. The physical meaning of the parameters adjusted in the kinetic model, such as the RDS rate constant (k_5) and the lumped adsorption constant of the quasi-equilibrated steps (α) was confirmed through their Arrhenius and Van't Hoff-type behavior ($R^2 > 0.98$), respectively. From an energetic perspective, the activation energy for cobalt, cobalt-molybdenum, and molybdenum was 115.2, 106.8, and 177.5 kJ mol^{-1}, respectively. With this evidence and considering the volcano shape described by the ammonia decomposition rate in relation to the metal composition ratio, the synergistic behavior of the system is clearly observed. However, since characterizations by XRD and TEM were inconclusive, the formation of intermetallic compounds should be still verified using HRTEM-EDS. From this point onwards, our objective is to incorporate parameters into the kinetic expressions that consider both compositional and structural elements and explore how these can maximize or influence H_2 production.

Keywords : CEDI, hydrogen carrier, LHHW, RDS

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