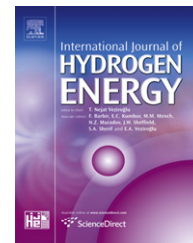


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Effect of preparation methods on the performance of Ni/Al₂O₃ catalysts for aqueous-phase reforming of ethanol: Part I-catalytic activity

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ABSTRACT

The effect of preparation method on the performance of Ni/Al₂O₃ catalysts for aqueous-phase reforming of ethanol (EtOH) has been investigated. The first catalyst was prepared by a sol-gel (SG) method and for the second one the Al₂O₃ support was made by a solution combustion synthesis (SCS) route and then the metal was loaded by standard wet impregnation. The catalytic activity of these catalysts of different Ni loading was compared with a commercial Al₂O₃ supported Ni catalyst [CM (10%)] at different temperatures, pressures, feed flow rates, and feed concentrations. Based on the product distribution, the proposed reaction pathway is a mixture of dehydrogenation of EtOH to CH₃CHO followed by C–C bond breaking to produce CO + CH₄ and oxidation of CH₃CHO to CH₃COOH followed by decarbonylation to CO₂ + CH₄. CH₄ (C₂H₆ and C₃H₈) also can form via Fischer–Tropsch reactions of CO/CO₂ with H₂. The CH₄ (C₂H₆ and C₃H₈) reacts to form hydrogen and carbon monoxide through steam reforming, while CO converts to CO₂ mostly through the water–gas shift reaction (WGS). SG catalysts showed poorer WGS activity than the SCS catalysts. The activation energies for H₂ and CO₂ production were 153, 155 and 167 kJ/mol and 158, 160 and 169 kJ/mol for SCS (10%), SG (10%), and CM (10%) samples, respectively.

Primarily, the difference in the metal particle size distribution governed by the preparation method appeared to be the key factor controlling catalytic efficiency. The SCS samples (with smaller Ni particle size) turned out to be superior for EtOH conversion, selectivity for H₂ & CO₂, and TOF values of H₂ and CO₂ to the corresponding SG (10%), SG (5%) and CM (10%) samples of bigger Ni particles size irrespective of the reaction conditions. For the SG catalysts, the selectivity to CO increased with temperature, while SCS catalysts produced no CO. While the particle sizes of SCS (10%) and SG (2%) are almost the same and their selectivity to H₂ and CO₂ are close, the TOF values to H₂ and CO₂ production for the SG (2%) catalyst are 2–3 times lower than that of the SCS (10%) catalyst. Similarly, the Ni particle size on SCS (10%) is 2.5 times larger than that on SCS (2%), but their selectivity to H₂ and CO₂ are almost the same. These anomalous results can be explained

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by the microstructural and phase compositional differences of the catalysts imposed by the variation of the preparation methods and will be discussed in detail in part II of this paper.

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1. Introduction

Hydrogen can be used as a feedstock in the ammonia and fertilizer industries, as a fuel source in PEM fuel cells, for producing fungible liquid fuel by hydrodeoxygenating large oxygenates, etc. Hydrogen, produced from renewable biomass, instead of non-renewable fossil fuel sources is an alternative source of environmentally clean energy [1]. Aqueous-phase reforming (APR) is a single step and low temperature (≤ 500 K) energy efficient process, which produces hydrogen from water-diluted oxygenated hydrocarbons obtained directly from fermentation, eliminating the energy intensive distillation of EtOH/water mixtures [2]. The typical operating pressure and low temperature for APR can be helpful for the separation of H_2 and CO_2 from other products that are volatile at atmospheric pressure. Additionally, APR is useful for producing fuel cell grade H_2 with small amounts of CO in a single chemical reactor as a consequence of the water–gas shift (WGS) reaction being thermodynamically favored at lower temperature reaction condition [3,4].

In order to achieve high H_2 selectivity on a metallic catalyst for the APR of an oxygenated hydrocarbon, low acidic nature supports are required. Other important beneficial factors are that the catalysts should have a high C–C bond breaking rate, a low C–O breaking rate, and a low methanation reaction rate. Monometallic noble catalysts, such as Pt, depending on the support could demonstrate high H_2 selectivity for aqueous-phase reforming of ethylene glycol at low temperatures (≤ 500 K). However, the high cost of Pt makes it economically infeasible to use. Huber and Dumesic reported that in terms of overall catalytic activity of APR of ethylene glycol (as measured by the rate of CO_2 production per active surface metal site) over silica supported metallic catalysts, performance of Ni is comparable to Pt, and better than Ru, Rh, Pd, and Ir [5]. According to Sinfelt [6], Grenoble, et al. [7], and Vannice [8] compared to Co, Pt, Pd, Fe, Ir, and Rh catalysts, Ni has higher rate of C–C bond breakage rate, reasonably good water gas shift activity, and moderate methanation reaction capacity. These traits make Ni a potential catalyst for APR.

High specific surface area-to-volume ratio, homogeneous dispersion of metals, and precise design of mesopore structure (large pore volume and narrow pore size distribution) combined with proper control of acidity/basicity of the support oxides are other important factors for high catalytic performance. There are many different ways of preparing nano metal/ Al_2O_3 based catalysts; such as sol–gel, aerosol, coprecipitation, solution combustion synthesis, etc. [9–14]. While, reportedly, the sol–gel method has many scientific and technical advantages, such as, homogeneity at the molecular level, high dispersion of metal, easy introduction of dopants, resistance toward sintering, etc., the solution combustion

synthesis method (SCS) has not been explored for APR. SCS is a fast, simple, and energy efficient technique for the preparation of pure, porous, and small-particle size ceramics generally used as catalysts, phosphors, pigments, etc. [15–17]. Bera et al., reported combustion synthesis of nanometal (Pt, Pd, Ag and Au) particles supported on α - Al_2O_3 and their use as catalysts for gas phase CO oxidation and NO reduction [18]. Chen et al prepared Ni/ Al_2O_3 catalyst by a solution combustion route and used it for partial oxidation of methane to syngas [11].

In SCS, the exothermic characteristics of the redox (reduction–oxidation or electron transfer) reactions between mixtures of metal nitrates (oxidizers) and fuel (carbohydrazide, glycine, urea, etc.) are utilized in producing self-sustaining spontaneous combustion under heating. The resulting material consists of a powder of microscopic particles composed of fine particles of submicron to nano-scale. This phenomenon can be attributed to the evolution of large amounts of gases (NH_3 , CO_2 , H_2O , N_2) from the exothermic reaction, which help in dissipating the heat, preventing the oxides from sintering, and forming a foam like porous structure. Other special features, such as high temperature, fast heating rate, and short reaction time, in general, make SCS a very effective approach for producing technologically useful materials at low cost compared to other conventional materials processing techniques [19].

In this paper, we present a study of the effect of preparation methods on the performance of Ni/ Al_2O_3 catalysts for aqueous-phase reforming of EtOH. The first catalyst was prepared by a sol-gel (SG) method and for the second one the Al_2O_3 support was made by a solution combustion synthesis (SCS) route and then the metal was loaded by standard wet impregnation. The catalytic activity of these catalysts of different Ni loading was compared with a commercial Al_2O_3 supported Ni catalyst [CM (10%)] at different temperatures, pressures, feed flow rates, and feed concentrations. Here we propose a possible pathway of reaction in order to explain the catalytic activities. The detail of microstructural and phase compositional experiments and analysis interpreting these catalytic activities will be presented in the next part of this paper.

2. Material and methods

2.1. Preparation of catalysts

The first group of Ni (2 wt%, 5 wt%, and 10 wt %) loaded Al_2O_3 catalysts were prepared by a sol–gel method. For the second group, the Al_2O_3 support was made by a solution combustion method (SCS) and then the metal (2 wt%, 5 wt%, and 10 wt %

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