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Ethanol decomposition on transition metal catalysts - synthesis, deactivation and coking mechanism

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1. Introduction

Catalytic production of hydrogen from hydrogen rich compounds of biomass is an interesting topic of research. Biomass derived products, such as ethanol, methanol etc. are considered renewable sources of hydrogen for sustainable and clean energy applications. Out of this ethanol has received a great attention due to having a high hydrogen content, being non-toxic, and safe for storage and easy handling. Researchers have investigated many techniques such as steam reforming (SR), decomposition (ED), auto reforming, and partial oxidation (POx) to produce hydrogen along with other by-products from ethanol. The highly endothermic SR reaction requires high temperature and continuous flow of steam from an external source to sustain the reaction. POx is an exothermic reaction that releases energy during the reaction, however with lower selectivity for hydrogen, whereas ED is an endothermic reaction but requires less energy when compared to the highly endothermic ESR reaction and provides better hydrogen selectivity than POx.

In this work, we investigate the use of NiCo bimetal/oxide as catalyst for hydrogen production from ethanol, with a focus on the deactivation pattern and the nature of the observed carbon deposition [1, 2]. It is well known that sintering and coke deposition during decomposition reaction significantly reduces the activity of the catalysts at higher temperature, by blocking the active sites of the catalysts. During ethanol decomposition reaction, the cleavage of C-C bond produces adsorbed *CH₄ and *CO species that further decompose to form carbonaceous compounds [3].

2. Methods

NiCo and NiCoO₂ were synthesized using combustion technique by adding nickel nitrate (Ni(NO₃)₂·6H₂O), cobalt nitrate (Co(NO₃)₂·6H₂O) and glycine (C₂H₅NO₂) with 1:1 ratio of metal nitrates, and maintaining a fuel to metal nitrate ratio as 0.5:1. The measured precursors were dissolved in 25 ml of deionized water and heated at 300°C until the water gets evaporated and ignition starts followed by combustion to produce the desired nanoparticles. DRIFT studies were carried out, to understand the reaction mechanism, using a Thermo Nicolet 6700 FTIR with a DRIFT reaction chamber and a praying mantis optical assembly. The ethanol conversion and selectivity study was performed in a customized tubular quartz flow reactor with an internal diameter of 10.5 mm and 35 cm in length. The catalyst was placed inside the reactor using silica wool as an inert material to hold it in place, a thermo couple touching the catalyst surface was used to measure the bed temperature. The catalyst was reduced at 300°C in presence of H₂ for 1 h at a flow rate of 30 sccm. Once reduced, the two-way gas flow was changed from H₂ to N₂ to remove all the excess residual H₂ while cooling down to room temperature. The ethanol was introduced to the catalyst surface by passing 100 sccm of N₂ through an ethanol bubbler. The gaseous product from the outlet of the reactor was connected to a gas chromatography (GC) to analyze the output of the tubular reactor.

3. Results and discussion

In this study, we report the ethanol decomposition over NiCo (and NiCoO₂ oxide) along with the oxide of cobalt (Co₃O₄) catalyst. FTIR in-situ analysis was conducted between 50 to 400°C for all the catalysts to understand the reaction mechanism and product selectivity. Cobalt was found to be selective for aldehyde and acetate, whereas bimetallic Ni-Co was selective for the formation of CO at 400°C along with aldehyde. Complete conversion of ethanol was observed at 350°C and 420°C for NiCo and Cobalt respectively indicating an improvement in the rate of conversion when Ni was added to cobalt. The crystallinity, morphology and particle analysis of the used catalyst after reaction were studied using XRD, SEM and TEM respectively. The XRD shows the complete phase change of porous NiCoO₂ to NiCo alloy and SEM indicates the presence of fibrous structure on the surface with 91.7 % of carbon while keeping 1:1 ratio of Ni and Co after the reaction. The detailed analysis of carbon structure using HRTEM-STEM shows the simultaneous growth of carbon nano fibers (CNFs) and multiwalled carbon nanotubes (MWCNTs) that were favored on larger and smaller crystallites respectively. Analysis of carbon formation on individual Co catalyst and bimetallic NiCo catalyst shows a clear difference in the initiation patter of carbon deposition. Metallic Co nanopartiles was found to be more mobile where Co disperses along the catalysts surface, whereas NiCo nanoparticles were relatively less mobile, and maintained their structure.

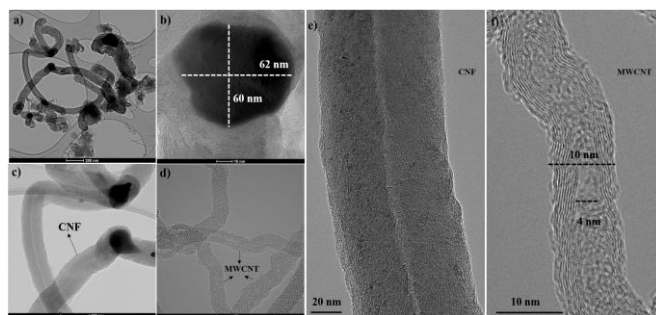


Figure 1: TEM/HRTEM image of carbonaceous deposit over the used catalyst

4. Conclusions

Mixed oxide of NiCo (NiCoO₂) and cobalt oxide (Co₃O₄) were successfully synthesized using a single step solution combustion synthesis technique to evaluate their performance for ethanol decomposition reaction and to understand the coking mechanism. The reaction proceeds via the formation of surface aldehyde and acetate on cobalt surface that further decompose to release gaseous H₂, CO₂ and H₂O, along with some CH₄ at higher temperature (400°C). While the incorporation of Ni in Co lattice initially follows a similar reaction pathway but decomposes surface acetaldehyde to release CO and only small fraction of surface aldehyde is converted to acetate that subsequently decomposes releasing relatively small amount of CO₂ at high temperature. A detailed analysis of NiCo catalysts surface indicates the formation of filamentous carbon nanofibers (CNF) and multi-walled carbon nanotubes (MWCNT). CNF is found to be the primary form of carbon along with smaller amount of MWCNTs. TEM analysis reveals a good correlation between the structure of carbon and the size of catalyst nanoparticles, with smaller particles favoring MWCNT formation and the larger particles generating CNF.

References

- [1] Ashok, A., Kumar, A., Ponraj, J., Mansour, S.A. and Tarlochan, F Applied Catalysis B: Environmental, 254 (2019) 300-311.
- [2] Ashok, A., Kumar, A., Bhosale, R., Saad, M.A.S., AlMomani, F. and Tarlochan, F. International Journal of Hydrogen Energy, 42 (2017) 23464-23473.
- [3] Perez-Cabero, M., Rodriguez-Ramos, I. and Guerrero-Ruiz, A. Journal of catalysis, 215 (2003) 305-316.