Catalytic decomposition of ethanol over bimetallic NiCo catalysts for carbon nanotube synthesis

Anand Kumar, Anchu Ashok
Department of Chemical Engineering
Qatar University, P O Box - 2713, Doha, Qatar; email: akumar@qu.edu.qa

كلية الهندسة
College of Engineering
QATAR UNIVERSITY جامعة قطر

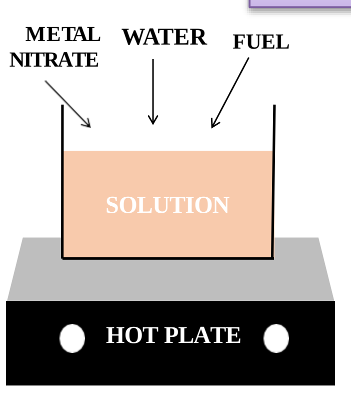
Faculty and PostDoc, Science and Engineering

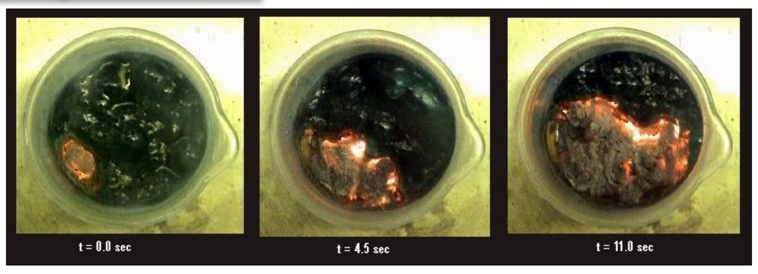
Abstract: Here we report the results of catalytic decomposition of ethanol over a porous mixed metal oxide of NiCo ($NiCoO_2$) and analyze the effect of Ni incorporation in Co_3O_4 lattice on the activity and hydrogen selectivity from ethanol decomposition reaction. In-situ FTIR analysis was conducted between 50 °C to 400 °C for both, Co_3O_4 and $NiCoO_2$, catalysts to understand the reaction mechanism leading to gas phase product distribution. On cobalt surface the reaction pathway proceeds via the formation of surface ethoxy intermediate that subsequently transforms to aldehyde and acetate intermediates before decomposing to release CO_2, H_2 and CH_4 gases at high temperature. HRTEM-STEM shows the simultaneous growth of carbon nanofibers (CNFs) and multiwalled carbon nanotubes (MWCNTs) that were favored by larger and smaller crystallites respectively

Introduction

- ✓ Hydrogen generation from ethanol gained much research attention due to its potential for on-site H2 generation for fuel cell and other applications.
- ✓ Researchers proposed many techniques such as steam reforming, decomposition, auto reforming, and partial oxidation to produce H2 from light alcoho
- ✓ Ethanol decomposition (ED) is an endothermic reaction but require less energy compared to the highly endothermic ethanol steam reforming (ESR) reaction.
- ✓ Sintering and coke deposition during decomposition reaction significantly reduces the activity of the catalysts at higher temperature by blocking the active sites.
- ✓ During ethanol decomposition reaction, the cleavage of CeC bond produces adsorbed *CH4 and *CO species that further decompose to form carbonaceous compounds.
- ✓ The carbonaceous species thus formed are reported to be of varying types such as carbide, amorphous, graphitic, filamentous, nanotubes, sheets and shell types, where the amount and the activity are highly influenced by preparation method, structure, reaction condition and the support used.

Catalyst Preparation





Combustion front movement

Key features: Molecular level homogenization ,high temperature (~1000 ˚C), short process time, evolution of gases, porous and high surface area

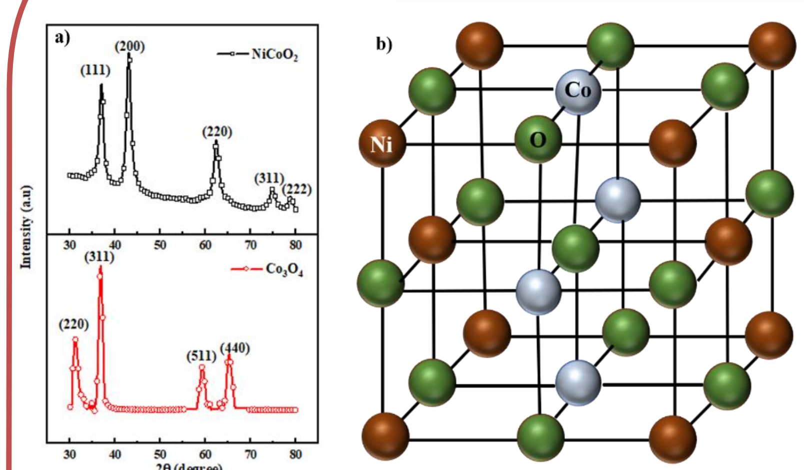
Fuel: e.g. glycine, urea, hydrazine etc.

$$Me^{v}(NO_3)_v + \frac{5}{9}v\varphi NH_2CH_2COOH + \frac{5}{4}v(\varphi-1)O_2 \rightarrow MeO_{\frac{v}{2}} + \frac{10}{9}v\varphi CO_2 + \frac{25}{18}v\varphi H_2O + \left(\frac{5\varphi+9}{18}\right)vN_2$$

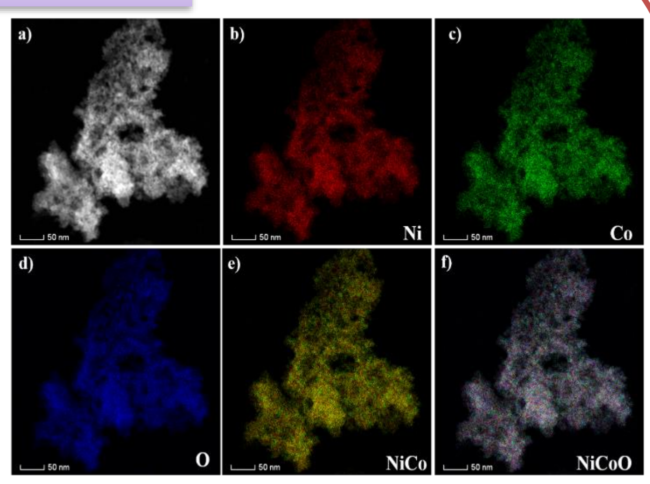
Metal Oxide — Gas Phase Products

Where φ is fuel to oxidizer ratio
φ = 1, Stoichiometric mixture
φ > 1, Fuel rich
φ < 1, Fuel lean

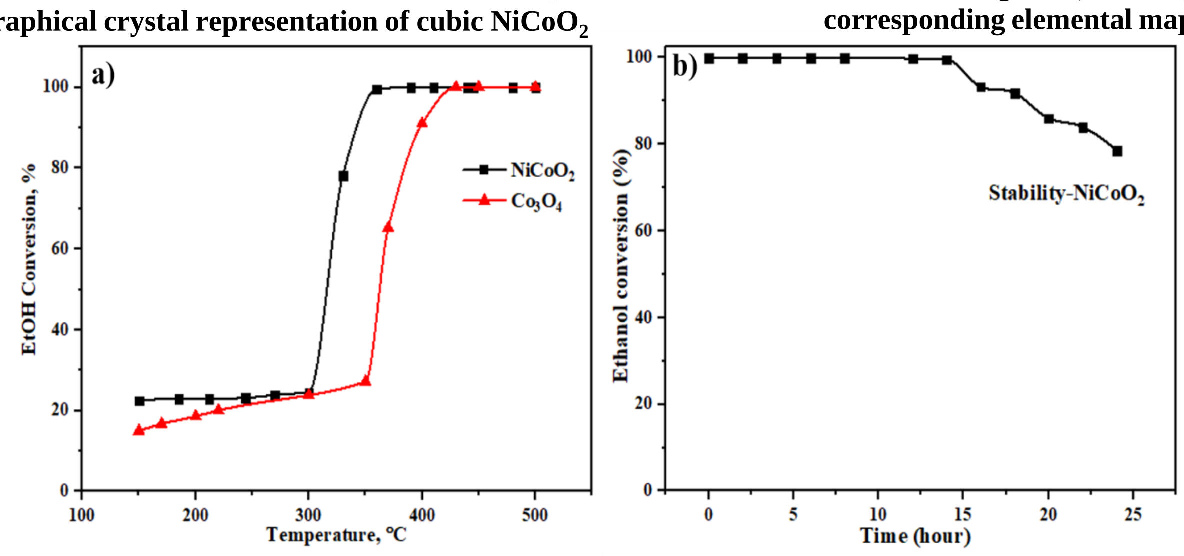
Catalyst Characterization



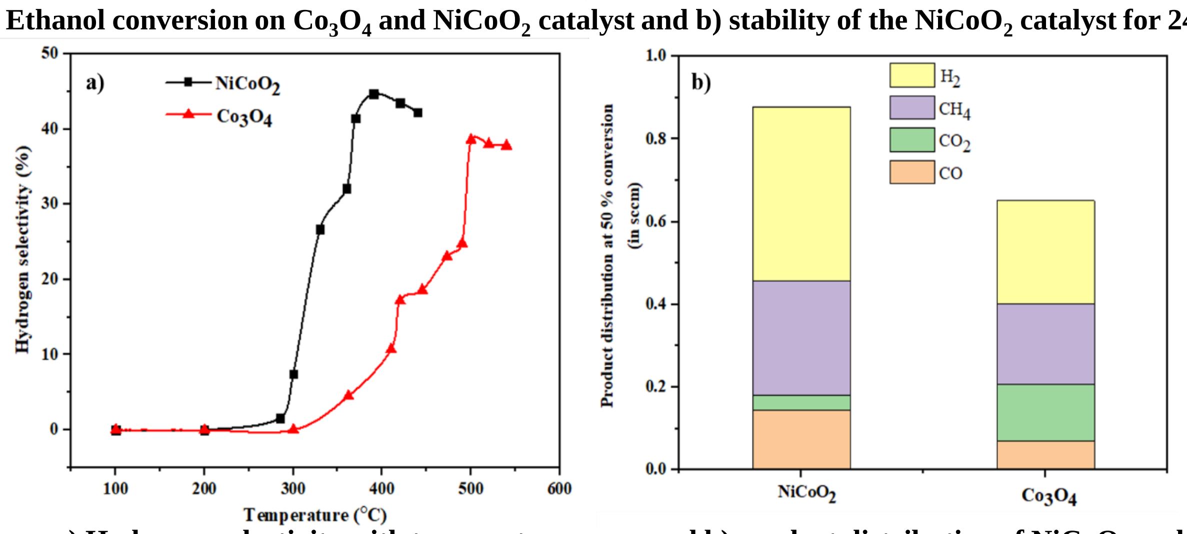
XRD profile of as-synthesized a) $NiCoO_2$ and Co_3O_4 and b) 3D graphical crystal representation of cubic $NiCoO_2$



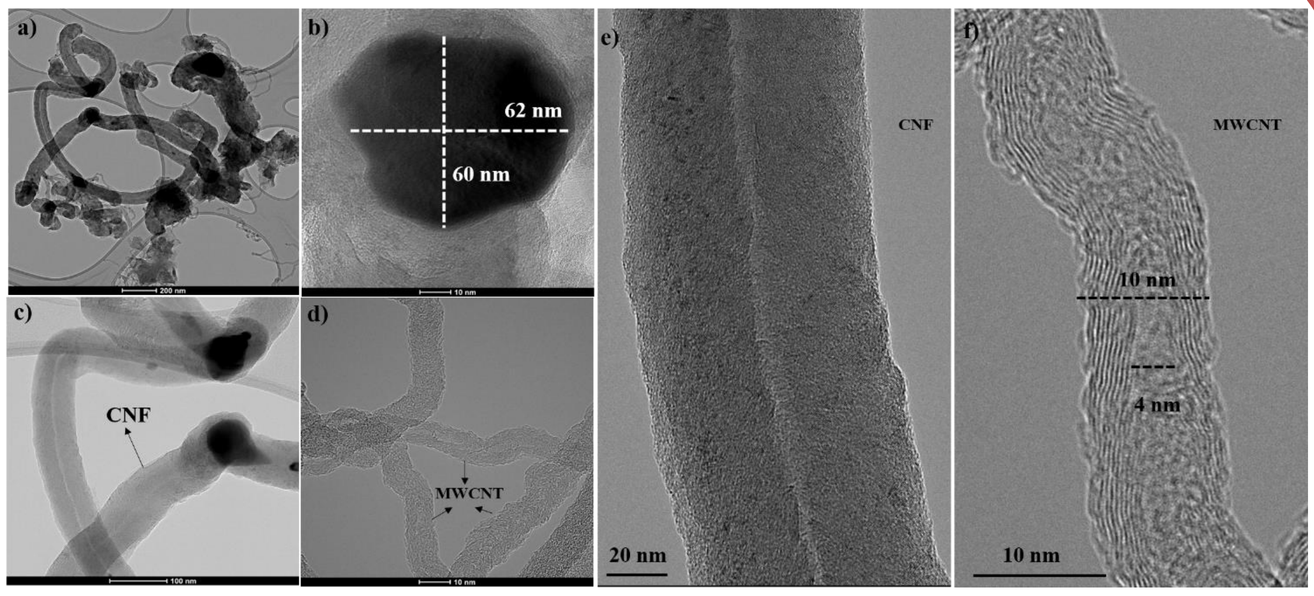
HAADF-STEM image of a) $NiCoO_2$ and b-f) its corresponding elemental mapping.



Ethanol conversion on Co_3O_4 and $NiCoO_2$ catalyst and b) stability of the $NiCoO_2$ catalyst for 24 hr

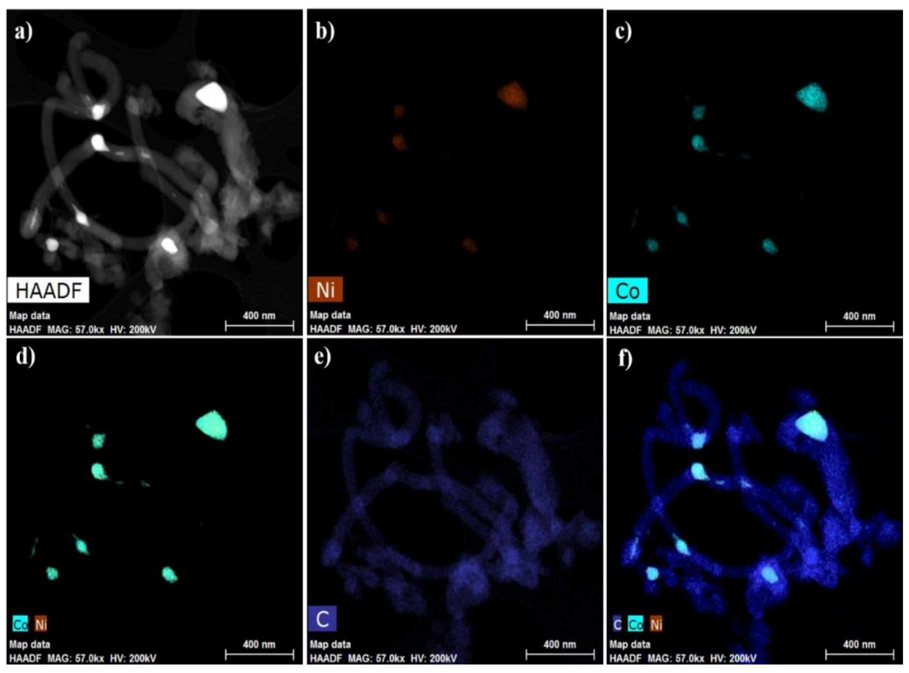


a) Hydrogen selectivity with temperature ramp and b) product distribution of $NiCoO_2$ and Co_3O_4 catalyst at 50 % conversion.

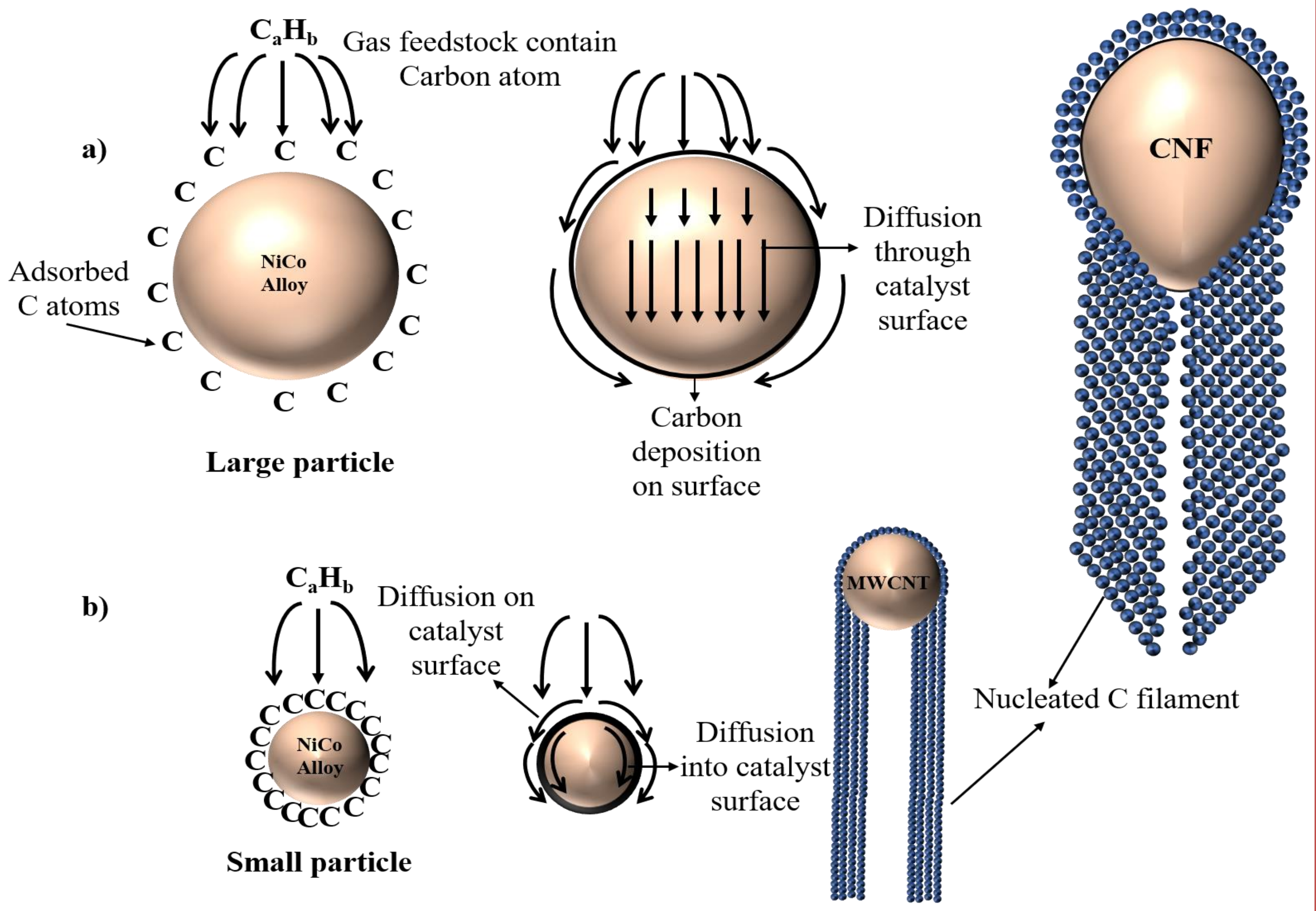


TEM image of carbonaceous deposit over the catalyst and the characteristics of filaments formed

- Diameter of the alloyed particles are like the diameter of the carbon filaments formed.
- NiCo alloy is supported with the carbon layer



- ➢ Larger Particle : **Bigger sized CNFs (80 – 100 nm)**
- ➢ Smaller Particle : **Smaller sized MWCNTs (10 – 15 nm)**



Schematic diagram of catalyzed growth of a) CNF and b) MWCNT during the ethanol decomposition reaction

Conclusion

- ❖ Mixed oxide of **NiCo ($NiCoO_2$) and cobalt oxide (Co_3O_4)** were successfully synthesized using a single step solution combustion synthesis technique.
- ❖ The incorporation of Ni in Co lattice favors the formation of **CO, aldehyde and acetates.**
- ❖ NiCo catalysts surface indicates the formation of **filamentous carbon nanofibers (CNF)** and **multi-walled carbon nanotubes (MWCNT).**
- ❖ 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:

Ashok, A., Kumar, A., Ponraj, J., Mansour, S.A. and Tarlochan, F., 2019. *Applied Catalysis B: Environmental*, *254*, pp.300-311.

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