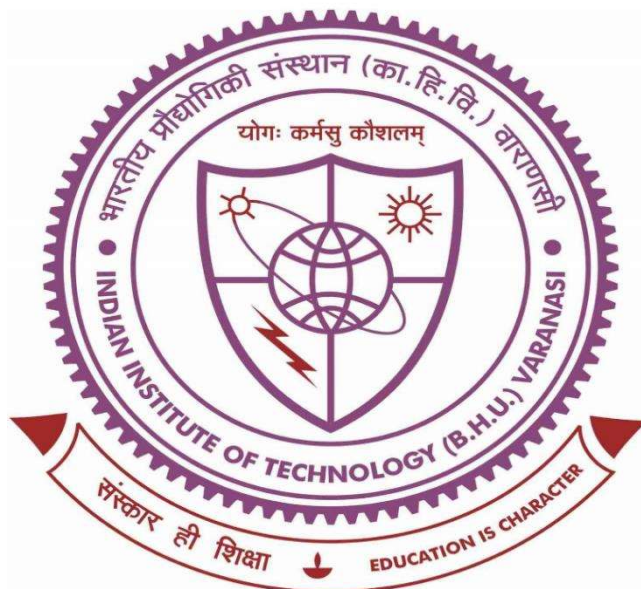


**Studies on Hydrogen Production by Steam Reforming of  
Acetic acid on MOFs derived Nickel Catalysts for  
Utilization of Biomass**



*Thesis submitted in partial fulfilment*

*for the Award of Degree*

**DOCTOR OF PHILOSOPHY**

by

**ANKIT KUMAR**

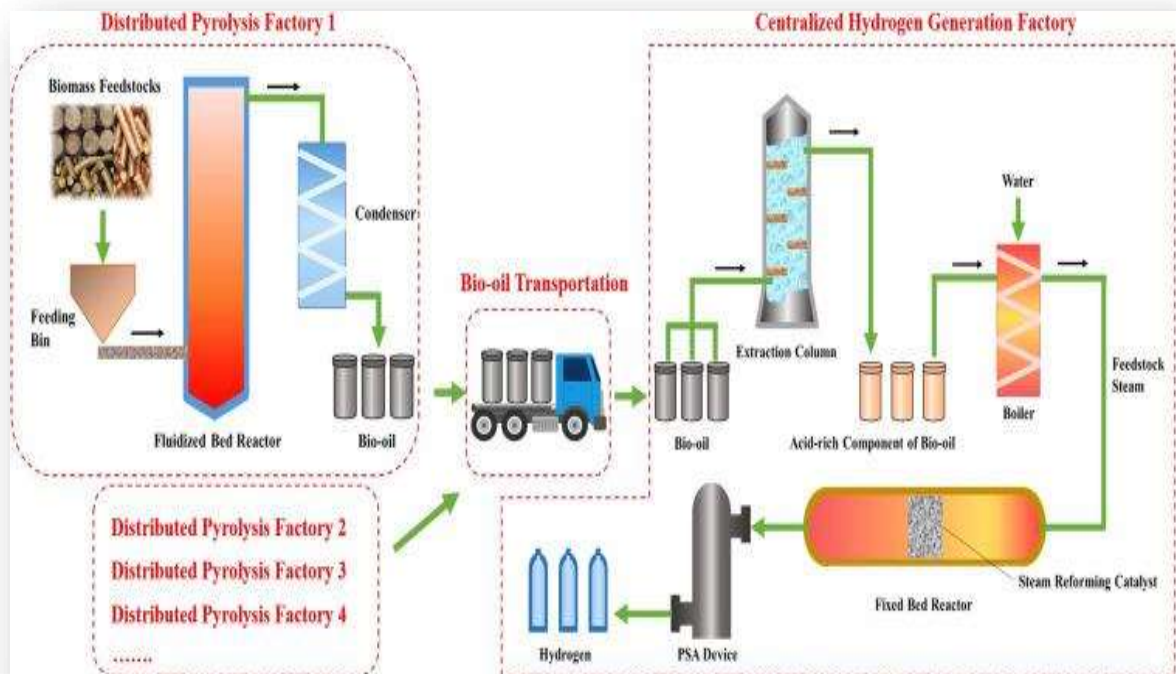
Department of Chemical Engineering & Technology  
Indian Institute of Technology  
(Banaras Hindu University)  
Varanasi – 221005 India

Roll No: 13041501

2020

# Chapter: 5

## Conclusions & Future Recommendations



## Conclusions and Future Recommendations

---

This thesis focused and provided an overview of the development of active and selective catalysts via MOFs process for acetic acid steam reforming to produce hydrogen. Therefore, based on the results and discussion presented in the previous chapter, the thesis conclusions are described below section-wise.

### Section I:

In this work, Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts impregnated with La<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> have been prepared from two different methods (i) via MOF and (ii) wet impregnation method. Their catalytic activity and stability were evaluated in AASR for hydrogen production at different temperatures ranging from 300 to 650 °C, with fixed S/C ratio = 6.5 and weight hour space velocity (WHSV) 1.05 h<sup>-1</sup> and time on stream (TOS). The stability test for acetic acid conversion and product distribution were observed for 36 h of TOS for both catalysts. The yield of H<sub>2</sub> was found to be approx. 90%, i.e., close to the theoretical stoichiometric limit. Very low CH<sub>4</sub> selectivity was observed in both catalysts at high temperatures. The results showed that the catalyst prepared using the MOF process showed a better yield towards hydrogen production and stability against coke deposition due to porous three-dimensional framework and available high surface area of the catalyst and the availability of large number of free nickel particles more Ce<sup>3+</sup> vacancies on the support surface. Catalyst synthesized via MOFs precursor exhibited high crystalline slightly high surface area and smaller pore sizes distribution capered to nickel formate precursor due to the regular arranged ordered pore size and porosity and coordinating bonding of catalyst, which improved the movement of reactants and catalytic activity.

The better activity and yields for H<sub>2</sub> in the case of catalyst 2 are due to MOF-derived nano-nickel particles form a porous three-dimensional framework, and available high surface area of the catalyst and availability of a large number of free nickel particles and more Ce<sup>3+</sup> vacancies on the support surface a large number of free nickel particles and more Ce<sup>3+</sup> vacancies on the support surface resulting in high catalytic activity and stability. In addition, amorphous-like carbon and filamentous-like carbon were observed over spent catalysts after the stability test. Therefore, catalyst synthesized via MOF process showed better catalytic activity since it showed less coke deposition and high H<sub>2</sub> yield.

## **Section II:**

Further, catalytic activity and stability and coke deposition behavior of the catalysts synthesized via MOFs precursors were tested for acetic acid steam reforming with different Ni loading x% Ni (x = 10, 15 and 20 wt%) at fixed operating conditions (S/C = 6.5, WHSV = 1.05 h<sup>-1</sup> and,) with varying temperatures from 400 to 650 °C. Results suggested that metal-support interaction with the support varied with the nickel loadings and showed weak to medium interaction and increased the growth of Ni particles. All the catalysts exhibited almost complete acetic acid (AcOH) conversion into H<sub>2</sub> and various C1 products (CO, CH<sub>4</sub>, and CO<sub>2</sub>). Moreover, the La<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> solid solution phase formation in all Ni-Comp/ALC catalysts promoted oxygen vacancies beneficial to oxygen transfer in carbon gasification. As a result, deactivation by carbon deposition and sintering was restrained.

On the other hand, the increase of Ni loading increases the particle sizes of nickel and decreases the dispersion resulting in catalyst deactivation by coke deposition, which decreases the catalytic activity as well as stability. The characterization results indicate that 15 wt% Ni-Comp/ALC catalyst has more free Ni particles, better dispersion as shown in TEM analysis and high active surface area because of possesses the majority of pores

in the  $< 20 \text{ \AA}$  diameter size range. All these properties resulted in better catalytic activity with an  $\text{H}_2$  yield of 91.3%. An increase of Ni loadings from 10 to 15 wt% significantly enhanced conversion and  $\text{H}_2$  yield, while further increase in Ni loading markedly increase the particle sizes of metallic Ni.

Consequently, lower down the conversion as well as  $\text{H}_2$  yield. The above results showed that x% Ni-Comp/ALC (x =10 to 20 wt%) catalysts catalytic activity strongly depended on the Ni particles' size. This is because the Ni species present over the catalysts are the active sites in the SR reaction, which is well dispersed on the support. Therefore, the active Ni species interacting with support also plays a significant role in catalytic performance.

### **Section III:**

We have also investigated that 15% Ni loading is the best for catalytic activity and  $\text{H}_2$  yield. Keeping in mind, here we report a detailed study on the performance of this 15% Ni-complex/ALC catalyst for AASR. Effects of operating conditions such as temperatures (400 - 650 °C), steam to carbon molar ratio (S/C, 0 to 6.5) and WHSV (0.6 to 2.35  $\text{h}^{-1}$ ) were evaluated and optimized. Results showed excellent activity for AASR at the molar ratio S/C = 6.5, WHSV = 1.05  $\text{h}^{-1}$  and 600 °C with almost total conversion and more than 90% of  $\text{H}_2$  yield. The ordered porous structure of embedded nickel-supported catalyst promotes excellent steam reforming activity and water gas shift reaction even at low temperatures, which leads to good stable behavior up to 36 h of TOS. The coke formation was also significantly suppressed by ALC support. Catalyst regenerated by passing oxygen at 500 °C and followed by reduction in hydrogen also shows a good activity. At constant operating conditions (S/C = 6.5, WHSV = 1.05  $\text{h}^{-1}$ ), the increase in the temperature range from 400 - 650 °C conversion increases while in the case of  $\text{H}_2$  yield it increases up to 600 °C and then slightly decreases after 600 °C due to RWGS reaction dominating at high temperature. The

results showed that during the AASR, H<sub>2</sub>, CO, CH<sub>4</sub>, and CO<sub>2</sub> were the main product gases, whereas a maximum hydrogen yield of 91.3% was obtained at temperature 600 °C. The temperatures and S/C ratio were observed to be the key parameters, while the space velocity of the AcOH/H<sub>2</sub>O mixture showed only a marginal effect during AASR. The catalyst was deactivated by coke deposition. Amorphous and graphitic types of coke were found to get deposited on the surface of the deactivated catalyst. Deactivated catalyst had lower surface area and pores of larger diameter compared to those of fresh catalyst. The deactivation studies of Ni-Complex/ALC catalyst showed excellent stability up to 36 h TOS. Catalyst regeneration of the spent catalyst was achieved by flowing oxygen over the catalyst at 500 °C, followed by reduction by H<sub>2</sub> gas. Regenerated catalyst regained the surface area, pore-volume, and nearly the same activity as a fresh catalyst. The sintering of Ni particles was not significant. It has been attributed to the existence of nickel-support interaction. The lower performance of regenerated catalyst compared to fresh catalyst may be due to the increase of Ni crystallite size (from 37 to 40 nm) and structural change in the support as observed in pore size analysis (Refer Table 6.1 & 6.2). The SEM analysis also showed that only marginal coke deposition occurred over the catalyst surface, showing the high stability of both fresh and regenerated catalysts.

#### **Recommendations for Future Work**

1. Catalytic steam reforming of other model bio-oil compounds such as glucose, levoglucosan, alcohols, phenol should be further investigated in detail.
2. Catalyst development is required for enhancing hydrogen production via steam reforming of bio-oil. A catalyst with high C-C and C-H bond scission activity, high WGS reaction, but low activity towards methanation would be desirable.

3. There is inadequate information on the kinetics of bio-oil reforming in literature; hence in-depth information on reaction mechanism and kinetics should be investigated to design a reactor.
4. Improved catalysts can be prepared by various ways, such as using promoters, using newer preparation techniques and using high surface area supports.
5. Further, the MOFs method can prepare a Heterometallic catalyst to improve catalytic activity and suppressed coking.
6. Detail study on catalyst characterization and catalyst development and the use of similar feedstock should be done.