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Research paper

Selective hydrogenation of 1-heptyne on nickel based catalysts

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Abstract : Titania (P-25) supported mono metallic Ni and bimetallic Ni-Cu, Ni-Ag and Ni-Au catalysts were prepared and characterized by Temperature Programmed Reduction, H_2 Temperature Programmed Desorption, X-ray diffraction, Transmission Electron Microscopy, Diffuse Reflectance Spectroscopy and X-ray Photoelectron Spectroscopy techniques. Selective hydrogenation of 1-heptyne (2 % w/w in toluene) to 1-heptene was carried out on all the four catalysts, at atmospheric pressure and in the temperature range 313 – 353 K. Nickel based bimetallic catalysts display higher activity for 1-heptyne conversion and selectivity to 1-heptene, compared to monometallic Ni catalyst. Availability of reactive hydrogen, as revealed by H_2-TPD studies on bimetallic catalysts, is responsible for higher activity. In the case of bimetallic catalysts, XPS data reveal electronic interactions between Ni and promoter elements (Cu, Ag and Au), which increase the electron density around Ni. Such an increase in electron density around Ni facilitates desorption of olefinic species like 1-heptene. Hence higher selectivity towards 1-heptene is observed with bimetallic catalysts.

Keywords : Selective hydrogenation, 1-heptyne, nickel based bimetallic catalysts, charge transfer to Ni, N-H bond strength

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1. Introduction

Selective hydrogenation of alkynes to alkenes is a crucial process step in the synthesis of a number of petrochemicals, polymers, fine chemicals and bio-active chemicals etc. **[1-3]**. The process and the catalysts involved are being extensively investigated from its industrial application and fundamental understanding points of view. Heterogeneous catalysts based on noble metal as well as base metals are used for the selective hydrogenation of alkynes. The main advantages of supported noble catalysts are mild reaction conditions, higher activity, selectivity and long life **[4]**.

Generally, the catalysts are designed for maximum/total selectivity towards alkenes, avoiding total hydrogenation to alkanes. Classical Lindlar catalyst systems **[5]** ($Pd/CaCO_3$ promoted with $Pb(OAc)_2$, for example) have been studied extensively for this application. Since then a number of heterogeneous catalysts have been explored **[6-9]**. Notable amongst them are transition metal based mono metallic and bimetallic supported catalysts, which display excellent characteristics like high activity and selectivity for alkenes in comparison with metal complexes as catalysts, used in homogeneous medium under mild reaction conditions. Some of the model compounds/alkynes investigated over a period of time include, 1-hexyne **[10]**, 1-heptyne **[11]**, 4-octyne **[12]** and phenyl acetylene **[13]**. The major advantage with the supported catalysts is that they can be easily separated from reaction media and the particles size of the active phase could be controlled. Generally the Pd catalysts are used in industrial and academic investigations. In the case of bimetallic catalysts, alloy particles are known to play a key role in the catalytic performance for selective hydrogenation of alkynes.

Prathan et al. **[14]** prepared TiO_2 supported Pd, Au and Pd-Au bi-metallic catalysts and evaluated their catalytic performance for the liquid phase hydrogenation of 1-heptyne at 40 ºC. They showed that the formation of Pd-Au alloy in supported catalysts is responsible for enhanced activity and selective hydrogenation of 1-heptyne to 1-heptene. Monsour et al **[15]** investigated the hydrogenation of 1-heptyne over Pd/Al_2O_3 catalysts and concluded that the performance of the catalysts depended on the influence of solvent used, to obtain fast reaction rate and a high selectivity to 1-heptene. Panpranot et al. **[16]** prepared Pd-Au catalysts by a combination of incipient wetness impregnation and followed by deposition precipitation method. It was observed that the catalytic activity for hydrogenation of 1-heptyne in toluene at 30 °C and selectivity for 1-heptene was determined by the structure of the Pd–Au alloy formed. Chuang Li et al investigated the hydrogenation of phenyl acetylene over glycol stabilized Pt-Ru nano particles supported on CNT and inferred that the catalytic performance depended on the nature of the core component of the alloy that modified the electronic structure and the changed mode of adsorption of phenyl acetylene **[17]**.

Another exciting possibility is to analyze the effect of addition of second metal to Ni, and studying its influence on activity and selectivity. Addition of second metal to monometallic Ni catalysts resulted in significant improvement in activity, selectivity and stability of a number of reactions **[18]**. Influence of the addition of second metal such as Ag, Cu, Au, Ge, Sn etc to Ni, on different supports like TiO_2, Al_2O_3, Zeolite etc have been reported earlier **[19 - 21]**. Bimetallic catalysts have been explored for several reactions like, methanation, hydrogenaolysis and fuel cell etc. **[22, 23]** However, the intricacies of structure- property relationship have not been understood very well in many cases since the structures of the alloys and core-shell configurations have not been established completely. Presence of a mixture of two different structures complicates the issue further. Gonzalez et al. **[24, 25]** have reported the formation of core-shell structure for Pt-Ru bimetallic particles when prepared by co-impregnation followed by pretreatment with H_2. However, Esteban et al **[26]** reported formation of Pt-Ru particles with core shell type structure with strong interaction between Pt-Ru particles under similar conditions.

In the present work, the structure-performance relationships in the case of titania (P-25) supported Ni based mono metallic and bimetallic catalysts has been investigated. In order to have a systematic study on this aspect, monometallic Ni/TiO_2P25 and Ni based bimetallic catalysts with Cu, Ag and Au as the second metals on the same support have been prepared and characterized by a range of experimental techniques **[27]**. The performance of these catalysts for selective hydrogenation of 1-heptyne in toluene has been evaluated and attempts have been made to correlate the structural and electronic properties of the catalysts with the performance.

2. Experimental methods

Details on the method of preparation of catalysts, experimental techniques, and methods adopted for their characterization and procedures for performance evaluation of the catalysts are described in an earlier publication **[27]**. Briefly, selective hydrogenation of 1-heptyne to 1-heptene in liquid phase was carried out in round bottom flask at 40 ºC, atmospheric pressure, by bubbling hydrogen into toluene (17.32 g) containing 10 mg of catalysts and 0.3464 g of 1-heptyne (1.9 % w/w toluene). Prior to the addition of 1-heptyne, the catalysts were reduced in hydrogen at 40 ºC for 2 h. The product stream was analyzed using Perkin Elmer Clarus-500 GC fitted with ZB-1 capillary column and FID.

3. Results & discussions

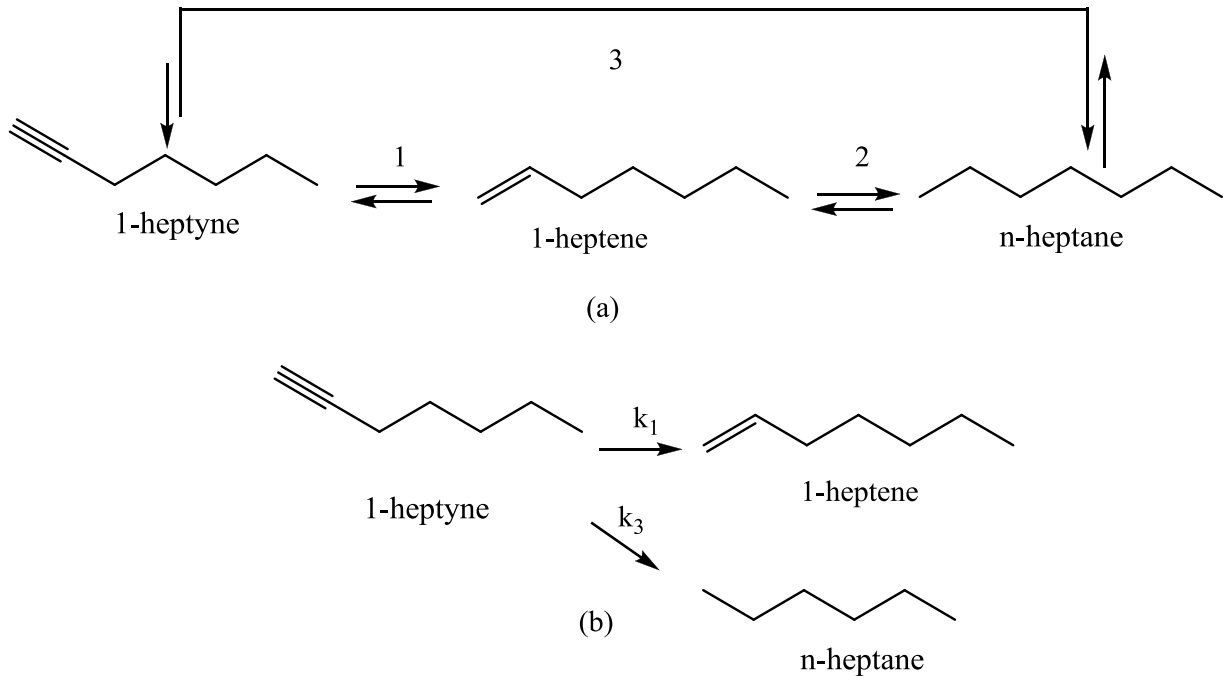
3.1. Characterization of catalysts

Results on the characterization of monometallic Ni/TiO_2 (P-25) and bimetallic catalysts, containing Ni- and Cu/Ag/Au on the same support, by XRD, SEM, TEM, TPR, DRS, H_2 pulse chemisorption, H_2 TPD and XPS techniques and detailed interpretation of the results have been published earlier **[27]**. Highlights of the characterization studies are **[27]**:

- Particle size of the catalysts as measured by X- Ray line broadening analysis (XLBA) and H_2 pulse chemisorption and TEM techniques, are in the range 8-12 nm.
- Based on TPR and DRS studies, it is observed that Ni and Cu form alloy while Ni-Ag and Ni-Au are present as bimetallic nano particles.
- HRTEM studies reveal the formation of hetero junctions in bimetallic catalysts which are in close contact. Such hetero junctions promote electronic interactions between the metals, as evidenced by XPS studies.
- Modifications in the electronic structure of Ni in bimetallic catalysts is revealed by the shifts in XPS binding energy values for Ni $2p_{1/2}$ and Ni $2p_{3/2}$ levels, brought out by the presences of Cu/Ag/Au. These modifications the electronic character of Ni, result in increase in electron density around Ni.
- Ni based bimetallic catalysts desorb H_2 at a lower temperature compared to mono metallic Ni catalyst indicating that Ni-H bond strength is lower in bimetallic catalysts vis-a-vis monometallic catalyst. Availability of labile and active hydrogen could facilitate hydrogenation reactions.

3.2. Selective hydrogenation of 1- heptyne

The catalytic behavior of the titania P25-supported Ni, Ni-Cu, Ni-Ag, and Ni-Au catalysts for the liquid-phase selective hydrogenation of 1-heptyne was evaluated at different temperatures, namely, at 313 K, 333 K and 353 K. The conversion of 1-heptyne and selectivity for 1-heptene formation as a function of reaction time, for mono and bimetallic catalysts, at different temperatures, are shown in Figure (1) to Figure (3). It can be seen from Figure 1(a) to Figure 3(a) that the time taken for 100 % conversion of 1–heptyne is less for bimetallic catalysts, compared to mono metallic Ni/TiO_2, indicating higher activity of bimetallic catalysts. Similar trend is maintained on all bimetallic catalysts and at all three reaction temperatures.



Scheme (1): Reaction schemes for 1-heptyne (a) reversible hydrogenation (b) irreversible hydrogenation. (Reproduced from Ref. **[28]**).

Rate of hydrogenation increases with the reaction time and tends to slow down, as 1-heptyne is consumed. Similarly, selectivity values (Figure 1(b) to Figure 3(b)) are higher in the initial stages and when the concentration of 1-heptene is low. Further hydrogenation of 1-heptene to heptanes occurs as the concentration of 1-heptene increases, resulting in loss of selectivity. The reaction scheme proposed by Crespo-Quesada et al. **[28]** is operative in this case (Scheme, 1-a)

It can be noted that the conversion of 1-heptyne increased with increase of reaction temperatures, accompanied by a decrease in selectivity for 1-heptene. Among the all catalysts, the best conversion and selectivity were achieved in Ni-Au/P25 Catalyst. The catalytic activity decreases the order: Ni-Au> Ni-Ag> Ni-Cu> Ni for 1-heptyne hydrogenation.

At any given temperature, 1-heptene selectivity is higher on all bimetallic catalysts, Figure 1(b) to Figure 3(b), compared to mono metallic catalyst, Ni/TiO_2. Among the three bimetallic catalysts, Ni-Au displays maximum selectivity for 1-heptene and selectivity decreases in the order Ni-Au>Ni-Ag>Ni-Cu>Ni

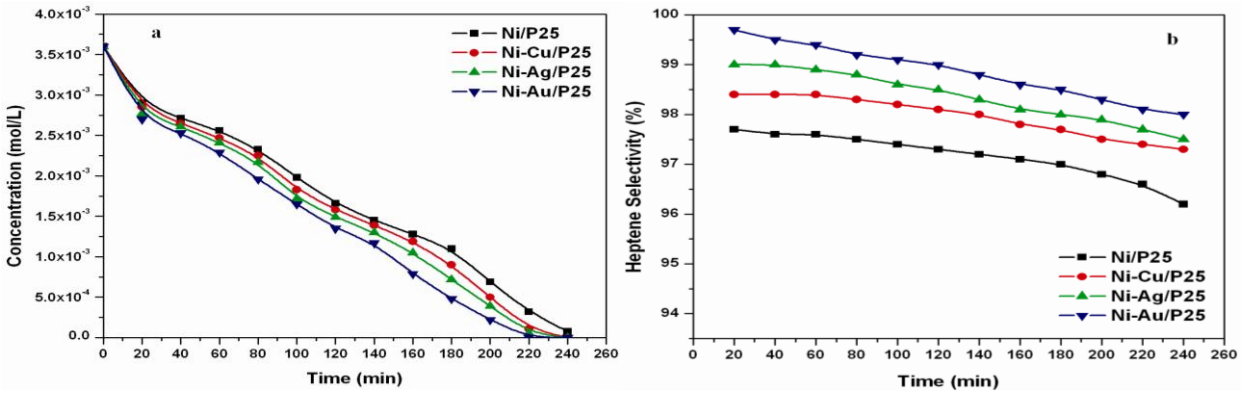


Figure (1): (a) Conversion of 1-Heptyne and (b) Selectivity to 1-Heptene at 313K.

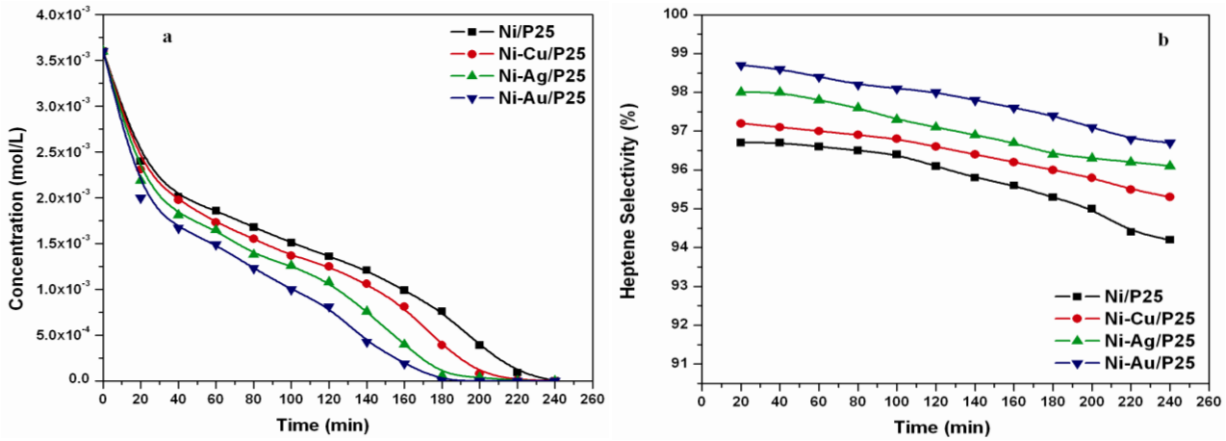


Figure (2): (a) Conversion of 1-Heptyne and (b) Selectivity to 1-Heptene at 333K.

As the temperature increases, the selectivity decreases, since the hydrogenation of 1-heptene to 1-heptane is catalyzed. Selectivity for 1-heptene in the case of monometallic Ni decreases with time and with increase in 1-1-heptyne conversion. However, bimetallic catalysts display stable selectivity towards 1-heptene even at higher conversions.

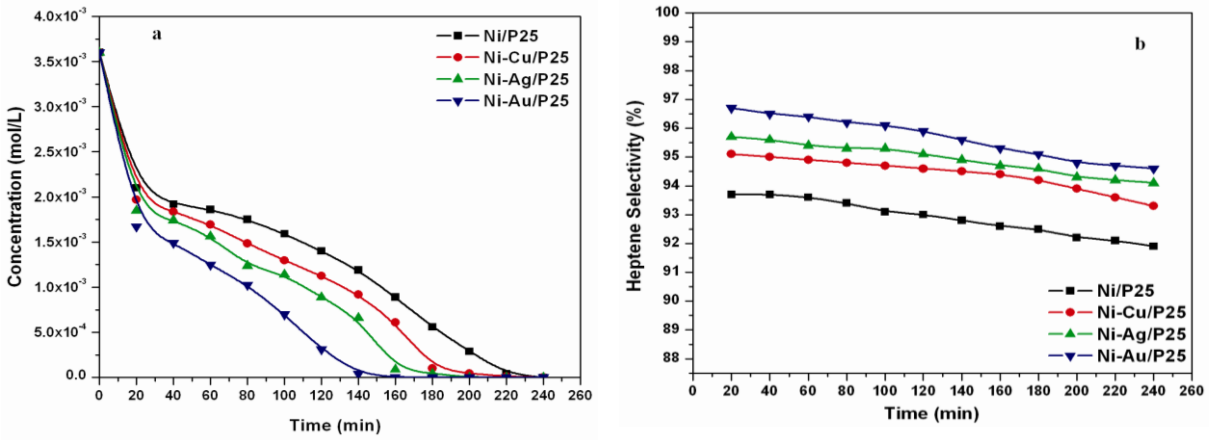


Figure (3): (a) Conversion of 1-Heptyne and (b) Selectivity to 1-Heptene at 353 K.

As revealed by H_2TPD studies [27], Ni-H bonds strength in Ni based bimetallic catalysts are weaker compared to that on mono metallic catalyst. Availability of active hydrogen is responsible for the increase in heptyne conversion observed for bimetallic catalysts. Besides, XPS data for bimetallic catalysts indicate increase in electron density around Ni due to charge transfer from Cu/Ag/Au to Ni. Increase in electron density around the Ni metal does not favor adsorption of olefin. This facilitates desorption of olefins (heptene), thus leading higher selectivity for heptene.

4. Conclusions

Bimetallic Ni-Cu, Ni-Ag and Ni-Au catalysts supported on TiO_2 P-25 display higher activity for 1-heptyne conversion compared to monometallic Ni catalyst. Availability of reactive hydrogen on bimetallic catalysts is responsible for higher activity. Electronic interactions between Ni and promoter elements (Cu, Ag and Au) cause an increase in electron density around Ni in the case of bimetallic catalysts, which in turn facilitates desorption of olefinic species like 1-heptene. Hence higher selectivity towards 1-heptene is observed with bimetallic catalysts.

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