Hydrogenation of Liquid Styrene by Alumina Supported Nickel Catalysts: Comparison between Classical and Non-Classical Methods

Y. C. Tan, N. H. H. Abu Bakar, W. L. Tan, M. Abu Bakar
School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
E-mail: hana_hanif@usm.my

Abstract. Almina supported Ni catalysts (Ni/Al₂O₃) with different Ni weight percentages (wt%) were prepared via classical and non-classical methods. All samples were prepared via impregnation technique. The samples prepared via non-classical methods were reduced using KBH₄ as the reducing agent. The catalysts were tested for the hydrogenation of styrene in liquid phase. Optimum activation conditions for the hydrogenation reaction were found to be 633 K for 2 hours. Comparison of the catalytic reactivity for all catalysts at these activation conditions showed that catalysts prepared via classical methods exhibited better activity. Furthermore the 7.6wt% Ni-Al₂O₃/C showed enhanced activity when compared to the 5.9wt% and 13.8wt% Ni-Al₂O₃/C catalyst. This phenomenon is mainly attributed to the type of Ni active sites available on the catalyst. The surface properties of the catalysts investigated via H₂-temperature programmed reduction (H₂-TPR), H₂-chemisorption and H₂-temperature programmed desorption (H₂-TPD) confirm this.

1. Introduction

Olefins which are contaminants formed during the cracking process, are especially found in petrochemical and petroleum refining industries [1]. To accelerate the removal of these reactive unsaturated components in the gas stream, catalytic hydrogenation reaction is commonly employed. In laboratory research, the hydrogenation of styrene is frequently used as a catalytic test model to access the performance of hydrogenation catalysts.

Over the years, the hydrogenation of styrene over a series of catalysts consisting of metal particles such as palladium (Pd) [1, 2], nickel (Ni) [3-5], iron (Fe) [6], copper (Cu) [4], cobalt (Co) [4], ruthenium (Ru) [1], rhodium (Rh) [1] and platinum (Pt) [1] has been reported. Amongst these, Ni is the cheapest and is available in abundance. As such, studies on hydrogenation catalysts based on mono-Ni supported alumina [3], silica [4] and sepiolite [5] as well as bimetallic Ni-Pt/alumina [7], Ni-B/MWCNT [8], Ni-Cu/alumina [9] can be found in the literature. The reason behind the numerous studies available is basically because the catalytic hydrogenation of a compound can be affected by several factors such as the metal content, type of support and preparation procedures for the catalysts. As an example, different supports can exert different metal-support interactions which can influence catalytic reactivity. In addition, the method in which the catalysts are prepared can also influence the metal-support interaction differently. In general, catalysts can be synthesized through classical and non-classical methods. Nowadays, the use of non-classical methods have gained popularity as it offers a faster preparation procedure and can prevent aggregation of particles as a result of not needing high
temperature pre-treatments for long durations of time. There are many types of non-classical techniques that have been proposed for the synthesis of supported metal catalysts. Among the various non-classical methods available are those employing reducing agents such as KBH₄ [10] or hydrazine [11] and the sol-gel method [12]. Although this method has its advantages, the classical methods may be a better option as it can remove poisonous elements in a catalyst via calcinations at high temperatures. Notably, many researchers are still employing this method to prepare catalysts.

Hence, in this work, a series of Al₂O₃ supported Ni catalysts have been prepared via both the classical and non-classical methods using the impregnation technique. Here, potassium borohydride, KBH₄ was used as the reducing agent for the catalysts prepared via the non-classical method. The activity of Ni-Al₂O₃ catalysts with different Ni wt% were investigated for hydrogenation of styrene in liquid phase. Catalysts were characterized using imaging and adsorption techniques to understand the phenomenon.

2. Materials And Methods

2.1 Materials

All materials were used as received. Aluminum oxide (Al₂O₃, purity 99.99%) was obtained from Aldrich Chemical Company, Inc., nickel (II)-acetate-4-hydrate, ((CH₃COO)₂Ni·4H₂O, purity 99.998%) was obtained from Merck Sdn Bhd and potassium borohydride, (KBH₄, purity ≥ 96.5%) was acquired from Sigma Aldrich. Ethanol (AR grade, 99.7%) was purchased from Qrec (Asia) Sdn Bhd while Hydrofluoric acid (HF, 40%) was supplied by Univar. Nitric acid (AR grade, HNO₃ 69% Grade) was obtained from Brightchem Sdn Bhd, 1-butanol (AR grade, C₄H₁₀O, purity > 99%) was acquired from Al Ilham Utama Enterprise, styrene, (C₈H₈, purity ≥ 99.6%) was obtained from Merck Schuchardt OHG while acetone (C₃H₆O, purity ≥ 99.5%) was purchased from Intrachem Sdn. Bhd.

All the gases were purchased from Malaysian Oxygen Berhad unless otherwise stated. Purified hydrogen gas (H₂, purity 99.999%), purified argon gas (Ar, purity 99.999%) and diluted hydrogen gas (H₂, 1000 ppm, purity 99.999%) from Air Liquid were used for characterization tests while nitrogen gas (N₂, purity 99.995%) was used for the preparation of catalysts via the non-classical method.

2.2 Methods

2.2.1 Synthesis of Ni/Al₂O₃ Catalysts via Classical Methods (Ni/Al₂O₃-C)

Typically, for the preparation of 7.6 wt% Ni-Al₂O₃/C, 5 g of Al₂O₃ was weighed and added into 17 mL of a 0.5 M Ni(CH₃COO)₂·4H₂O solution. Subsequently, 23 mL of distilled water was added. The solution was left to homogenize for 8 days. The mixture was then dried in an oven overnight at about 60°C. Similar procedures were repeated to prepare other Ni-Al₂O₃/C catalysts however the amount of the Ni salt solution and distill water was varied as in Table 1 to obtain the 13.8 wt% and 5.9 wt% Ni/Al₂O₃/C catalysts.

Upon drying, each sample was calcined. Typically, the sample was heated in air from room temperature to 373 K at the rate of 5 K min⁻¹ then held for 1 hour. Subsequently, the temperature was raised to 873 K while heating at the rate of 10 K min⁻¹. Upon reaching 873 K, the temperature was held for 4 hours.

2.2.2 Synthesis of Ni/Al₂O₃ Catalysts via Non-Classical Methods (Ni/Al₂O₃-NC)

Similar procedures as the classical methods were repeated to synthesize the non-classical catalysts. However 10 mL of 2.5 M KBH₄ (Table 1) was added to the samples after the homogenizing stage. The solution turned dark immediately upon addition of KBH₄. The solution was left to stir for about 15 min before filtering. Catalysts were washed thoroughly with distilled water then dried in a vacuum oven overnight at about 348 K.
Table 1: Precursors for preparing the Ni/Al₂O₃ catalysts and the respective metal compositions.

| Samples Denotation | Volume of Ni Salt Solution (0.5 M), mL | Volume of KBH₄ (2.5 M), mL | Volume of Distilled Water, mL | wt % of Ni |
|--------------------|--------------------------------------|----------------------------|-------------------------------|------------|
| 5.9wt% Ni-Al₂O₃/C  | 8.5                                   | –                         | 31.5                          | 5.9        |
| 7.6wt% Ni-Al₂O₃/C  | 17.0                                  | –                         | 23.0                          | 7.6        |
| 13.8wt% Ni-Al₂O₃/C | 25.6                                  | –                         | 14.4                          | 13.8       |
| 5.0wt% Ni-Al₂O₃/NC | 8.5                                   | 10                        | 31.5                          | 5.0        |
| 8.2wt% Ni-Al₂O₃/NC | 17.0                                  | 10                        | 23.0                          | 8.2        |
| 8.9wt% Ni-Al₂O₃/NC | 25.6                                  | 10                        | 14.4                          | 8.9        |

2.3. Characterization Technique

The real content of the Ni element was determined by atomic absorption spectroscopy (AAS) using a PerkinElmer Analyst 400. An acid mixture (H₂O:HNO₃:HF = 5:3:8) was added to 0.05 g of a sample while heating until the catalyst was dissolved. The solution was filtered then topped up to 50 mL of distilled water.

The morphology of the Ni particles in the catalysts was investigated using scanning electron microscopy (SEM). The catalysts were placed on a carbon tape. Subsequently, samples were sputtered with chromium and then subjected to an FEI Quanta 650 SEM. The samples were viewed using backscattering mode.

The H₂-TPR analysis of the catalysts was carried out using diluted hydrogen gas (a mixture of 1000 ppm H₂/Ar) as reductant with a flow rate 100 mL min⁻¹. As much as 0.2 g of the sample was measured and placed in a U-tube quartz reactor. The samples were heated at a rate of 5 K min⁻¹ from room temperature to 973 K. Hydrogen consumption was measured every 2 minutes with an Agilent G3000A Micro gas chromatograph equipped with a thermal conductivity detector.

The H₂-TPD analysis was conducted on similar apparatus as the H₂-TPR analysis. As much as 0.8 g of a sample was placed in a U-tube quartz reactor. The sample was then activated in pure H₂ with a flow rate of 400 mL min⁻¹ at 633 K for 2 hours. Subsequently, the samples were cooled to room temperature and switched to purified Ar at a flowrate of 100 ml min⁻¹. The sample was then heated from room temperature to 973 K at a heating rate of 5 K min⁻¹, and hydrogen desorption was measured every 2 minutes.

2.4. Hydrogenation of Styrene

The hydrogenation of liquid styrene was carried out to compare the activity of the Ni-Al₂O₃ catalysts prepared via classical and non-classical methods. Typically, as much as 0.2 g of Ni-Al₂O₃ sample was measured and place into a 3-necked round bottom flask. Pure H₂ was flowed into a reaction flask at a flow rate of 100mL min⁻¹. The samples were then activated at 633 K for 2 hours. Other activation conditions such as the temperature (483 to 633 K) and activation time (2 to 4 hours) were also studied to optimize activation of the catalysts.

After activation, the sample was cooled to 373 K. As much as 10 mL 1-butanol followed by 1 mL of styrene was added to the sample. The mixture was homogenized and the extent of hydrogenation was followed using a burette filled with purified hydrogen gas by water displacement. The water level in the burette was recorded every 5 min.

3. Results and Discussion

3.1. Synthesis of Al₂O₃ Supported Ni Catalysts via Classical and Non-Classical Methods

The Al₂O₃ supported Ni catalysts were synthesized via classical as well as chemical reduction method using KBH₄ as the reducing agent. Catalyst denotations including the metal content are presented in Table 1.
The Ni-Al$_2$O$_3$/C catalysts were green in color after drying the mixture of Ni salt with Al$_2$O$_3$. Upon calcinations in air, the samples changed to grayish in color indicating that oxidation of Ni occurred. These samples changed to black in color after activation of the catalysts in pure H$_2$ according to equation (1).

\[ \text{NiO} + \text{H}_2 \rightarrow \text{Ni} + \text{H}_2\text{O} \]  

(1)

For the Ni-Al$_2$O$_3$/NC catalysts, samples were also green in color after homogenizing the Ni salt with Al$_2$O$_3$. However upon reduction with KBH$_4$, the samples changed to black immediately. Bubbles were produced, indicating the release of hydrogen gas according to equation (2) [13].

\[ \text{Ni}^{2+} + \text{KBH}_4 + 4\text{H}_2\text{O} \rightarrow \text{Ni} + \text{KB(OH)}_4 + 3\text{H}_2 + 2\text{H}^+ \]  

(2)

3.2 Hydrogenation of Styrene

The optimum conditions for the hydrogenation of styrene were obtained using the 7.6wt% Ni-Al$_2$O$_3$/C catalyst. The sample was first activated to a temperature of approximately 583 K. Activation was then carried out for various durations to determine the optimum activation time. From Figure 1, it can be seen that activation in pure H$_2$ for 2 hours showed the best results. Generally, the H$_2$ uptake increased steadily for the first 100 min. After that, the uptake of H$_2$ slowed down reaching 60 mL after 400 min. When the sample was activated for 3 hours, the H$_2$ uptake raised steadily also reaching 60 mL at approximately 400 min. In contrast, when the sample was activated for 4 hours, the H$_2$ uptake increased for the first 80 min then slowly came to a constant at 10 ml of H$_2$ uptake. The profiles show that the catalyst activated for 4 hours at 583 K exhibited the lowest hydrogenation of styrene. The low activity may be attributed to the extensive heating times, which may have caused the metal particles to migrate and aggregate. This indirectly may have resulted in a decrease in the surface area of the active phase. Thus, there was low surface area available for catalytic reaction to take place.

![Figure 1: The effect of activation time on the hydrogenation of styrene.](image-url)
Considering that the 7.6wt% Ni-Al₂O₃/C showed better catalytic activity when activated for duration of 2 hours, this activation time was employed to study the effect of activation temperature. From Figure 2, it can be seen that the catalyst activated at 663 K showed better H₂ uptake compared to catalysts activated at other temperatures. The H₂ uptake increased steadily until reaching 100 mL in approximately 150 min. After this, the uptake continues however at a much slower rate until reaching a maximum of 110 mL. The H₂ uptake for catalysts activated at 583 K and 483 K were also compared. It is seen that activation at 583 K showed a better H₂ uptake than catalysts activated at 483 K. This maybe because when the sample was heated at the temperature of 483 K, the temperature is insufficient to totally reduce the NiO particles. Here, only reduction of oxides on the surface of the Ni species occurred. When the temperature was increased to 583 K, activity was better because at higher temperature more NiO particles can be reduced. Catalysts which were activated at 663 K had the best activity because the temperature is sufficient to reduce both the surface and bulk oxides of the particles. Therefore, it has been shown that in the temperature and time range investigated, the optimum activation condition for this hydrogenation test is 583 K for 2 hours.

![Figure 2](image_url)

Figure 2: The effect activation temperature for the hydrogenation of styrene.

These conditions were applied to all the classical and non-classical catalysts. Results are presented in Figure 3. From Figure 3, it is obvious that the 7.6wt% Ni-Al₂O₃/C catalyst demonstrated the best catalytic activity. This is followed by the 13.8wt% and 5.9wt% Ni-Al₂O₃/C catalysts. The 13.8wt% and 5.9wt% Ni-Al₂O₃/C showed similar maximum activity whereby maximum H₂ uptake is 35 mL. However, the 5.9wt% Ni-Al₂O₃/C took a longer time to reach the maximum activity, which was at approximately 200 min while 13.8wt% reached the maximum activity at approximately 80 min. Among the samples prepared via the non-classical method, 8.2wt% Ni-Al₂O₃/NC showed the best catalytic activity. For this catalyst, H₂ uptake reached 40 mL. Other catalysts prepared via non-classical methods were almost inactive. Hence as an overall, the graph showed that the classical method had a much better catalytic activity than the non-classical method. In general, this may be due to the fact that in classical method, all samples were calcined. As a result, this removes any impurities which may poison and indirectly affect the catalysts. In contrast, catalysts prepared via non-classical methods were reduced using KBH₄. Even traces of boron left in the catalyst may have poisoned the catalysts, resulting in the extremely low activity observed.
3.3 Characterization of Ni-Al₂O₃/C Catalysts

To understand the factors which contributed to the enhanced activity demonstrated by the catalysts prepared via classical methods, this series of catalysts were characterized to gain knowledge on the morphology of the active phase and its surface properties.

The SEM analysis were conducted for the 5.9 wt%, 7.6 wt%, 13.8wt% Ni-Al₂O₃/C catalysts. The images are shown in Figure 4. The Al₂O₃ support appears as greyish particles while the Ni species are evidenced by the white particles. It can be seen that very few particles attributed to Ni species are observed in the 5.9wt% Ni-Al₂O₃/C catalyst. Furthermore the sizes of the particles seem to be very small. In contrast, larger Ni species are available in the 7.6 wt% and 13.8wt% Ni-Al₂O₃/C catalysts. In the case of the 13.8wt% Ni-Al₂O₃/C catalyst, aggregation of the Ni species was also observed. Thus this indicates that the 13.8wt% Ni-Al₂O₃/C may give rise to a lower surface area for the active phase when compared to the 5.9 wt% and 7.6wt% Ni-Al₂O₃/C catalyst.

The H₂-TPR analysis was conducted to determine the reducibility of the oxide particles and to give an idea on the size of the particles in the Ni-Al₂O₃/C catalysts. The H₂-TPR profiles are presented in Figure 5. It can be seen that the 13.8wt% Ni-Al₂O₃/C exhibits a strong peak at 400 K. According to Kim and co-workers [14], this peak can be attributed to bulk oxides which do not interact with the support. The availability of higher Ni content in this catalyst enabled the growth of the particles, which increased the size of particles [14,15]. This can result in a weaker interaction between the oxide particles with the support. Therefore, this gave rise to the sharp peak observed in the 13.8wt% Ni-Al₂O₃/C. Observation of the 5.9 wt% and 7.6wt% Ni-Al₂O₃/C catalysts on the other hand does not show a peak in this region. This may be due to the low Ni content as compared to the 13.8wt% Ni-Al₂O₃/C. Further inspection of the H₂-TPR profiles reveal that all the Ni-Al₂O₃/C catalysts showed one broad peak from 600 - 811 K and a sharp peak at around 900 K. It seems that the intensity of the broad peak is significantly lower for the 7.6wt% Ni-Al₂O₃ when compared to the 5.9 wt% and 13.8wt% Ni-Al₂O₃/C catalysts. This depicts that metal-support interaction occurs to a greater extent in the later catalysts, which reduces the capability of the Ni²⁺ ions to decrease to metallic form. In contrast, the sharp peak at higher temperatures of about 900 K can be assigned to Ni²⁺ ions in strong interaction with the alumina support.
Figure 4: SEM images of (a) 5.9wt% (b) 7.6wt% and (c) 13.8wt% Ni-Al₂O₃/C.

Subsequently, another interesting observation is that the 7.6wt% Ni-Al₂O₃ catalysts showed an additional prominent peak at 592 K. This peak is only observed in this catalyst and indicates some additional characteristic of the catalyst. The availability of this peak depicts that Ni species are in weaker interaction with the support or smaller NiO aggregates exists in the catalyst when compared to the 5.9 wt% and 13.8wt% Ni-Al₂O₃.
H$_2$ - chemisorption studies of the Ni-Al$_2$O$_3$/C catalysts revealed that the 5.9wt%, 7.6wt% and 13.8wt% Ni-Al$_2$O$_3$ catalysts adsorbed as much as $2.74 \times 10^{-6}$ mol g$_{cat}$$^{-1}$, $1.80 \times 10^{-6}$ mol g$_{cat}$$^{-1}$ and $2.15 \times 10^{-6}$ mol g$_{cat}$$^{-1}$ of H$_2$ correspondingly. This gives a total metallic surface area of 21.47 m$^2$ g$_{cat}$$^{-1}$, 14.11 m$^2$ g$_{cat}$$^{-1}$ and 16.85 m$^2$ g$_{cat}$$^{-1}$ for each of the catalysts respectively. The results show that the 7.6 wt% Ni-Al$_2$O$_3$/C gives rise to the lowest amount of H$_2$ adsorbed and lowest metallic surface area. This does not correlate with the high activity demonstrated by this catalyst and reveals that the catalytic activity is not directly influenced by the surface area of the active phase.

H$_2$-TPD analyses were also carried out for this series of catalysts to gain an understanding of the strength of H$_2$ adsorption on the metal phase. Profiles of the catalysts are presented in Figure 6. As can be seen, the 5.9wt% Ni-Al$_2$O$_3$/C gives rise to three main peaks positioned at 385 K, 442 K and 709 K respectively. Previous work has shown that the peaks at lower temperatures of 385 K and 442 K are attributed to H$_2$ weakly adsorbed onto Ni active sites [9]. In contrast, the peak arising at 709 K can be assigned to several factors such as H$_2$ strongly bonded to the Ni particles, hydrogen retained at the metal-support interphase or H$_2$ spillover [16]. In contrast to the 5.9wt% Ni-Al$_2$O$_3$/C, the 7.6 wt% Ni-Al$_2$O$_3$/C exhibits only two H$_2$ desorption peaks. The peaks have maximum temperatures at approximately 401 K and 506 K. As such, only H$_2$ weakly adsorbed onto the Ni active sites exists in this catalyst. Finally, the 13.6 wt% Ni-Al$_2$O$_3$/C catalyst exhibits a strong desorption peak at 414 K with a shoulder at lower temperatures of about 346 K as well as a H$_2$ desorption tail ranging from 435 to 780 K. Similarly to the catalysts with low Ni contents, the high desorption at low temperatures is attributed to H$_2$ weakly bonded to the Ni particles. Even so, the desorption tail towards higher temperatures indicates the availability of H$_2$ which are moderately and strongly adsorb onto the Ni active sites, hydrogen at the metal-support interphase or hydrogen spillover. Based on these results, it is obvious that the 5.9wt% and 13.6 wt% Ni-Al$_2$O$_3$/C show similar characteristics whereby H$_2$ desorption is seen at higher temperatures of more than 550 K. The availability of these active sites may have resulted in the lower catalytic activity observed when compared to the 7.6 wt% Ni-Al$_2$O$_3$/C where only low temperature desorption is observed. This correlates well with the H$_2$-TPR findings. Another interesting observation is that the 13.6 wt% Ni-Al$_2$O$_3$/C exhibits very high H$_2$ desorption ($3.044 \times 10^{-4}$ mol g$_{cat}$$^{-1}$) in the temperature range of 300 to 435 K. This phenomenon may have contributed to the initial rapid H$_2$ uptake during the hydrogenation of styrene when compared to the 5.9wt% Ni-Al$_2$O$_3$/C.
4. Conclusion

A series of studies was conducted to investigate the optimum activation conditions for the hydrogenation of liquid styrene. The optimum conditions in the range of this study were determined to be 360°C for 2 hours. The effect of classical and non-classical preparation methods were studied at these conditions. The Ni-Al₂O₃/C catalysts demonstrated better catalytic activity when compared to the Ni-Al₂O₃/NC catalysts. The 7.6wt% Ni-Al₂O₃ classical catalyst gave rise to the best activity because it exhibited weaker H₂ adsorption on the Ni particles when compared to the 5.9wt% and 13.8wt% Ni-Al₂O₃/C catalysts. Furthermore, results show that the activity of this catalyst is largely dependent on the type of active site available and not the surface area of the catalyst.

Acknowledgements

The authors would like to show their gratitude to the Malaysian Ministry of Higher Education for the financial support in the form of the Fundamental Research Grant Scheme (FRGS) grant (203/PKIMIA/6711419).

References

1. Badano J M, Quiroga M, Bettì C, Vera C, Canavese S and Coloma-Pascual F 2010 Catal. Lett. 137 35
2. Harraz F A, El-Hout S E, Killa H M and Ibrahim IA 2012 J. Catal. 286 184
3. Nijhuis T A, Dautzenberg F M, Mouljina J A 2003 Chem. Eng. Sci. 58 1113
4. Corvaisier F, Schuurman Y, Fecant A, Thomazeau C, Raybaud P, Toulhoat H and Farrusseng D 2013 J. Catal. 307 352
5. Anderson J A, Daza L, Damyanova S, Fierro J L G and Rodrigo MT 1994 Appl. Catal. A 113 75
6. Pa’rvulescu V I, Filoti G, Pa’rvulescu V, Grecu N, Angelescu E and Nicolescu L V 1994 J. Mol. Catal. 89 267
7. Betti C, Badano J, Maccarrone M J, Mazzieri V, Vera C, Quiroga M 2012 *Appl. Catal. A* **435-436** 181
8. Liu Z, Li Z, Wang F, Liu J, Ji J, Park K C and Endo M 2012 *Mater. Res. Bull.* **47** 338
9. Muhammad S, Tan W L, Abu Bakar N H H, Abu Bakar M and Bettahar M M 2016 *Reac. Kinet. Mech. Cat.* (DOI 10.1007/s11144-016-0980-2)
10. Yu W, Xu J, Ma H, Chen C, Zhao J, Miao H and Song Q 2010 *Catal. Comm.* **11** 493
11. Hussain M S and Haque K A 2010 *J. Sci. Res.* **2** 313
12. Gronchi P, Kaddouri A, Centola P and Del Rosso R 2003 *J. Sol-Gel Sci. Tech.* **26** 843
13. Büchner W, Niederprüm H, Bayer A G, Leverkusen, and W. Germany. Pure & Appl. Chem. 49 (1977) 733-743.
14. Kim P, Joo J B, Kim H, Kim W, Kim Y, Song I K and Yi J 2005 *Catal. Lett.* **104** 181
15. Wen G, Xu Y, Xu Z and Tian Z 2009 *Catal. Lett.* **129** 250
16. Chettibi S, Wojcieszak R, Boudjennad E H, Belloni J, Bettahar M M and Keghouche N 2006 *Catal. Today* **113** 157