C$_9$-aldehyde hydrogenation over nickel/kieselguhr catalysts in trickle bed reactor

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Abstract

The objective of the present study was to select the optimal catalyst and operating conditions for the manufacture of C$_9$-alcohol, using C$_9$-aldehyde and hydrogen, in a trickle bed reactor. When CaO, Ce$_2$O$_3$ or MgO was added as a promoter to the Ni/kieselguhr catalyst, the BET and Ni surface areas were increased. In the reaction for the manufacture of C$_9$-alcohol, using C$_9$-aldehyde and hydrogen in a batch reactor, a Ni–MgO/kieselguhr catalyst showed the highest activity. In addition, the catalyst using Na$_2$CO$_3$ as a precipitant showed the highest activity. According to the result of an experiment to find the optimal reaction conditions for C$_9$-alcohol synthesis, using C$_9$-aldehyde and hydrogen in a trickle bed reactor loaded with Ni–MgO/kieselguhr catalyst, the highest yield of C$_9$-alcohol was 91.5 wt% at 130 °C, 400 psi and WHSV = 3. The C$_9$-aldehyde hydrogenation performance of the Ni–MgO/kieselguhr catalyst was similar to that of a Cu/ZnO/Al$_2$O$_3$ catalyst, but superior to that of Cu–Ni–Cr–Na/Al$_2$O$_3$ and Ni–Mo/Al$_2$O$_3$ catalysts. In a long-term catalysis test, the Ni–MgO/kieselguhr catalyst showed higher stability than the Cu/ZnO/Al$_2$O$_3$ catalyst.
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Keywords: C$_9$-aldehyde; Hydrogenation; C$_9$-Alcohol; Trickle bed reactor; Catalyst

1. Introduction

The dimerization of *n*-butene produces mixed octene [1,2]. In addition, the hydroformylation of mixed octene and synthesis gas produces C$_9$-aldehyde (isononyl aldehyde) [3,4]. Moreover, C$_9$-alcohol (isononyl alcohol) can be obtained from the hydrogenation of C$_9$-aldehyde. C$_9$-alcohol is used as a plasticizer, detergent and solvent, etc.

The commercial process of aldehyde hydrogenation uses a fixed bed reactor, with the reaction performed at temperatures between 90 and 180 °C and a pressure of 350 psi and between 80–220 °C and 1000–4000 psi in the gas and liquid phase reactions, respectively. Various metals, including Cu, Ni, Mo, Co and Rh, are used as catalysts in aldehyde hydrogenation, and they are sometimes synthesized into 2-, 3- or 4-component metals to be used as catalysts [5–9].

Most commercial applications of aldehyde hydrogenation catalysts are Cu- and Ni-based catalysts. The Cu-based catalyst, Cu/ZnO/Al$_2$O$_3$, has been applied in the manufacture of butanol and 2-ethyl hexanol [10,11], Cu–Ni–Co–Mg/Al$_2$O$_3$ in the manufacture of 2-ethyl hexanol [12,13] and Cu–Ni–Na–Cr/SiO$_2$ in the manufacture of 2-ethyl hexanol [14]. The Ni-based catalyst, Ni–Mo/Al$_2$O$_3$, has been applied in the hydrogenation of nonyl aldehyde for the manufacture C$_9$-alcohol [15,16], but few cases using Ni/kieselguhr catalyst, which is widely used in other hydrogenation processes, have been applied to the hydrogenation of C$_9$-aldehyde.

The objectives of the present study were to establish a method for preparing Ni/kieselguhr catalyst, and establish the operating conditions for the manufacture of alcohol through the hydrogenation of C$_9$-aldehyde produced from the hydroformylation of mixed octene. For this purpose, a catalyst showing optimal performance through the investigation of the effects of the preparation method of the nickel-based catalyst and the promoter on the hydrogenation of C$_9$-aldehyde was selected. In addition, the hydrogenation of aldehyde and the reaction performance of other catalysts were compared using a trickle bed reactor. After establishing the optimal operating conditions of the selected catalyst, the stability of the catalyst was confirmed through a long-term test.

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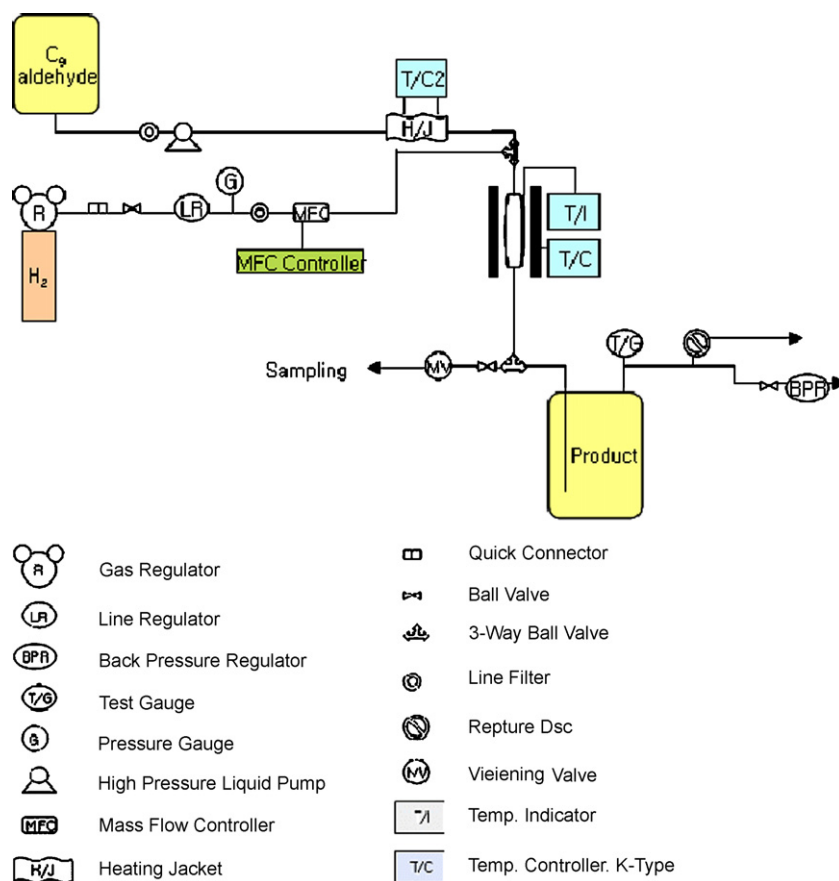*E-mail address:* catalica@uos.ac.kr (Y.-K. Park).

Fig. 1. Schematic diagram of the reaction system.

2. Experimental

2.1. Catalyst synthesis

Ni(NO$_3$)$_2$·6H$_2$O (Junsei), Nickel acetate (Aldrich), Mg(NO$_3$)$_2$·6H$_2$O (Yakuri), Ca(NO$_3$)$_2$·4H$_2$O (Junsei), and Ce(NO$_3$)$_3$·6H$_2$O (Aldrich) were used as precursors, and kieselguhr (Fluka) was used as the support. Na$_2$CO$_3$ (Yakuri), NH$_4$OH (Yakuri) and urea (Aldrich) were used as precipitants. Hydrogen and nitrogen (Matheson, 99.999%) were further purified using a molecular sieve trap.

Catalysts were prepared following the conventional precipitation method described by Suh et al. [17,18]. For the nickel/kieselguhr catalyst, kieselguhr, Ni(NO$_3$)$_2$·6H$_2$O, urea and deionized water were introduced into a 4-neck flask to make a 400 cm^3 aqueous solution. After heating the solution to 90 °C, a precipitant solution was introduced via a metering pump. The final pH of the solution was approximately 8. After filtering and washing, the catalysts were dried overnight in air at 120 °C. After pelletizing the catalyst powder, it was broken into uniform size between 2.0 and 2.8 mm. The prepared catalyst was used after reduction with hydrogen.

2.2. Catalyst characterization

The BET surface area, pore volume and pore size distribution were measured by nitrogen adsorption–desorption at 77 K using a Micromeritics ASAP 2000 instrument. The nickel surface area of the reduced catalyst was estimated from the amount of hydrogen chemisorbed onto the catalyst. This measurement was carried out with a Micromeritics ASAP 2010. The average size of the reduced nickel particles was estimated using an X-ray diffractometer (Rigaku, D/MAX-III, 3 kW) employing Cu Kα radiation. The average nickel particle size was calculated from the width of the peak at 44.6° using Scherrer's equation, which indicated Ni(1 1 1). To avoid contact with air, XRD spectra were obtained using the reduced catalyst impregnated in oil.

2.3. C$_9$-aldehyde hydrogenation

The hydrogenation reaction was carried out using a batch reactor and a trickle bed reactor. The internal diameter and volume of the batch reactor were 50 mm and 400 ml, respectively. The reactor had a manometer for measuring the hydrogen pressure, a programmable temperature controller for controlling the reaction temperature, an inner cooling coil, a thermocouple and a heating jacket, etc. For storage of the hydrogen to be supplied to the reactor and to measure its consumption, a 1 l hydrogen tank and gas regulator were used, with the hydrogen and nitrogen supplied to the reactor through a manifold with a manometer. In a glove box in a nitrogen atmosphere, 200 g of C$_9$-aldehyde was supplied to the reactor, along with 0.2 g of catalyst, which had been reduced. After installing a heating jacket onto the reactor, air and moisture were purged using nitrogen. Under nitrogen
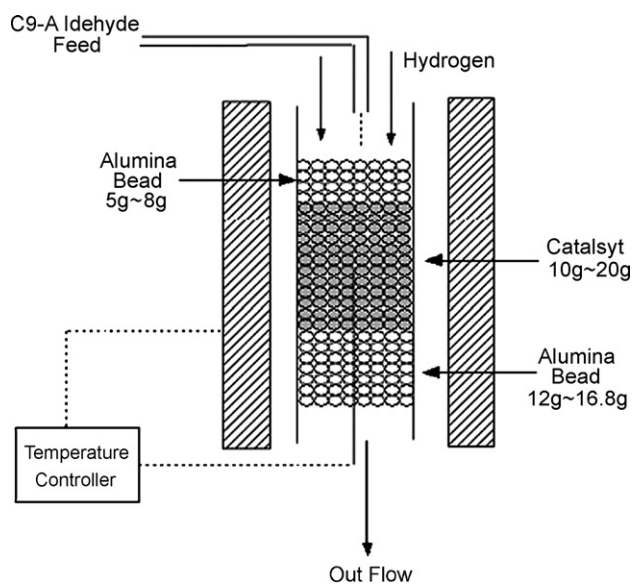
Fig. 2. Trickle bed reactor for isononyl aldehyde hydrogenation.

Fig. 3. Effect of promoters on XRD spectra of the nickel/kieselguhr catalyst after reduction.

gas, the temperature was raised. After the reaction temperature had been reached, hydrogen was infused to 3 atm, and then removed, and the process repeated three times. Again, the reactor was filled with hydrogen to the reaction pressure, and the stirrer rotated. The reaction product was collected at regular intervals, and analyzed using gas chromatography.

Fig. 1 shows the reaction system for the hydrogenation of C_9-aldehyde. A trickle bed reactor (Fig. 2) was used as the reactor, which was made using an 80 cm length of SUS tube with a 0.5-in. outer diameter. The C_9-aldehyde was injected using a high-pressure metering pump, with the flow rate of hydrogen controlled using a mass flow controller (MFC). The temperature of the reactor was controlled using a tubular furnace, with a programmable temperature controller, and the reaction pressure was controlled using a back pressure regulator. Ten grams of catalyst was loaded into the reactor, with the upper and lower parts of the reactor loaded with alumina beads, and the spaces between them filled with catalyst. The catalyst was reduced with hydrogen at normal pressure. When the reaction temperature and pressure were reached, the flow rate of hydrogen was kept constant using an MFC, and C_9-aldehyde fed to the reactor at a constant rate using a metering pump. To monitor changes in the activity of the catalyst according to the reaction time, samples were collected at regular intervals, and analyzed using GC (Agilent 6890). The conversion, selectivity and yield of C_9-aldehyde were calculated from the GC results.

3. Results and discussion

3.1. Effect of promoter on catalyst characteristics

In the previous study, we found that the BET surface area increased due to the increase in microporosity by adding a small amount of magnesium to a kieselguhr-supported nickel catalyst [19]. With the addition of magnesium, the catalysts became more difficult to reduce, but presented higher metallic area. The 4 wt% magnesium-promoted catalyst showed highest activity in triglyceride oil hydrogenation, which appeared to be due to the increase of metallic area as well as maintaining mesoporosity to avoid the effect of diffusion limitation. For the 8 wt% magnesium-promoted catalyst mostly has micropores, which can cause a diffusion limitation. In this regards, the promoter quantity was fixed at 4 wt% in this study.

Table 1 shows changes in the physical properties of the catalyst when either CaO, MgO or Ce_2O_3 was added as a promoter, at 4 wt%, to the Ni/kieselguhr catalyst. The BET surface area of the Ni/kieselguhr catalyst was 107 m^2/g, but if CaO, MgO or Ce_2O_3 was added as a promoter, the BET surface area increased to 122, 153 or 149 m^2/g, respectively. In addition, the pore size

Table 1
Effect of promoter on physical properties of Ni/kieselguhr catalysts

Catalyst[a]	BET surface area (m^3/g)	Average pore diameter (Å)	Ni particle size (Å)
Ni/kieselguhr	107	56	47
Ni–CaO//kieselguhr	122	52	34
Ni–MgO/kieselguhr	153	41	29
Ni–Ce₂O₃/kieselguhr	149	40	29

[a] Ni 40 wt%, promoter 4 wt%.

Table 2
Effect of precipitant on physical properties of catalysts (catalyst: Ni–MgO/kieselguhr)

Precipitant	BET surface area (m^3/g)	Average pore diameter (Å)	Ni particle size (Å)
Na_2CO_3 + urea	153	41	29
NH_4OH + urea	36	141	20
Na_2CO_3	180	48	28
$NaHCO_3$	161	50	34
$(NH_4)_2CO_3$	153	52	34

Fig. 4. Effect of precipitant on pore size distribution of catalysts.

Table 3
Effect of reduction condition on Ni particle size over Ni–MgO/kieselguhr

Calcination	Reduction temperature (°C)	Flow rate of hydrogen (ml/min)	Ni particle size (Å)
–	400	100	23
–	450	100	29
–	500	100	30
–	450	50	24
300 °C, 4 h	450	100	29

Ni–MgO/kieselguhr catalysts prepared using Na_2CO_3 + urea, NH_4OH + urea, Na_2CO_3, $NaHCO_3$ or $(NH_4)_2CO_3$ as the precipitant. In the case of the catalyst prepared using NH_4OH + urea as a precipitant, the size of the nickel particles was the smallest, but most were 100–1000 Å large macropores, with relatively fewer mesopores and, as a consequence, the BET surface area was very small. In addition, the average pore size was around 140 Å, much larger than that of other catalysts. The catalysts prepared using Na_2CO_3 + urea, Na_2CO_3, $NaHCO_3$ or $(NH_4)_2CO_3$ as the precipitant showed similar pore size distribution patterns, with a large portion of 40 Å large mesopores; also, the size of the nickel particles was similar. The BET surface area was the largest in the catalyst prepared using Na_2CO_3 as the precipitant (Table 2). The effects of the reduction conditions of the Ni–MgO/kieselguhr catalyst were also investigated. Table 3 shows the effects of the reduction temperature and hydrogen flow rate. Fig. 6 shows the effect of reduction condition on XRD spectra of the Ni–MgO/kieselguhr catalyst. When the reduction temperature was raised from 400 to 500 °C, the size of Ni particles increased from 23 to 30 Å. The high hydrogen flow rate also enlarged the size of the Ni particles. Conversely, when comparing the catalyst reduced through 4 h

3.2. Effect of catalyst preparation method on catalyst characteristics

When preparing a catalyst using the precipitation method, various kinds of alkali compounds are used as precipitants. The present study used common precipitants, such as Na_2CO_3, Na_2CO_3 + urea, NH_4OH + urea, $NaHCO_3$ and $(NH_4)_2CO_3$, to examine their effects on the characteristics of the catalyst. Table 2 and Fig. 4 show changes in the characteristics of the catalyst according to the precipitant used in preparing the Ni–MgO/kieselguhr catalyst. Fig. 5 shows XRD spectra of the
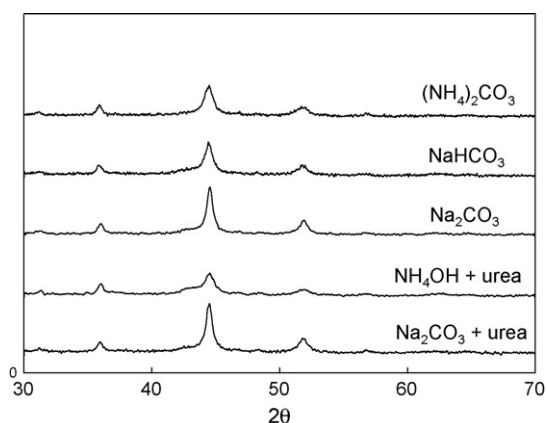
of the Ni/kieselguhr catalyst was reduced from 56 Å to 52, 41 and 40 Å. Fig. 3 shows XRD spectra of the nickel/kieselguhr catalysts with the promoter. The peak of nickel decreases with the addition of CaO, MgO or Ce_2O_3. The size of the Ni particle of the Ni/kieselguhr catalyst calculated from the width of the peak at 44.6° using Scherrer's equation was 47 Å, but if CaO, MgO or Ce_2O_3 was added as a promoter, size of the Ni particle decreased to 34, 29 and 28 Å, respectively.

Fig. 5. Effect of precipitant on XRD spectra of the Ni–MgO/kieselguhr catalyst after reduction.
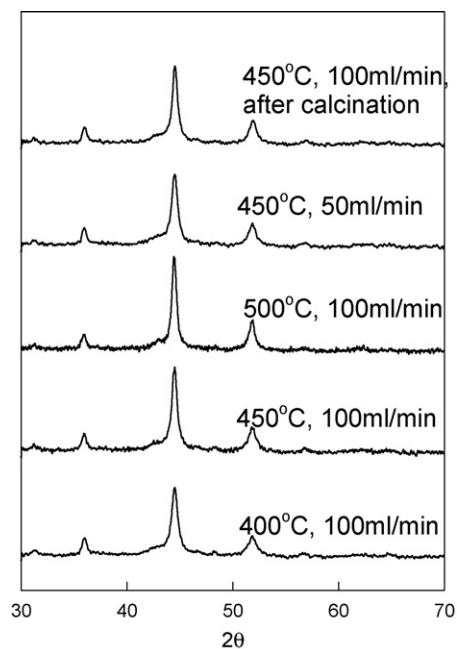

Fig. 6. Effect of reduction condition on XRD spectra of the Ni–MgO/kieselguhr catalyst.

Table 4
Effect of reaction condition on activity and selectivity (catalyst: Ni–MgO/kieselguhr)

Temperature (°C)	Pressure (psi)	Feed flow rate (cm³/min)	Conversion (%)	Selectivity (%)	Yield (%)
130	400	0.2	97.5	91.0	88.7
130	400	0.6	98.9	92.5	91.5
130	600	0.2	98.1	88.8	87.1
130	800	0.2	91.0	88.9	80.9
130	800	0.6	67.9	79.0	53.6
175	400	0.2	99.8	59.0	58.9
175	400	0.6	99.1	71.3	70.7
175	800	0.2	99.9	62.6	62.5
175	800	0.6	98.0	69.5	68.1

calcinations at 300 °C, with that reduced without calcinations, almost no difference was observed in the size of the Ni particles.

3.3. C9-aldehyde hydrogenation in a batch reactor

Fig. 7 shows the result of C9-aldehyde hydrogenation in the batch reactor at 120 °C and 100 bar using the Ni/kieselguhr catalyst, to which 4 wt% CaO, MgO or Ce₂O₃ was added as a promoter. During the initial 60 min of the reaction, the catalysts with CaO, MgO or Ce₂O₃ showed higher reaction activities than that without the promoter, with the catalyst containing MgO showing the highest activity.

This result can be explained by changes in the catalyst characteristics. The addition of the promoters MgO, CaO or Ce₂O₃ increase the BET surface area, reduce the pore size down to around 40 Å and decrease the size of the Ni particles. If the pores of catalyst are too small, it will affect the diffusion resistance. As the pore size is reduced by the addition of a promoter, the BET surface area increases, but most pores are mesopores, with an average size of 40 Å, which prevents the increase in the diffusion resistance. In addition, the decrease in the size of the Ni particles increases the surface area of Ni, which explains the increase in the reaction activity. If the size of the nickel particles decreases, a large number of Ni atoms will exist on the surface; that is, as there are many active sites where reaction takes place, the reaction rate will be accelerated.
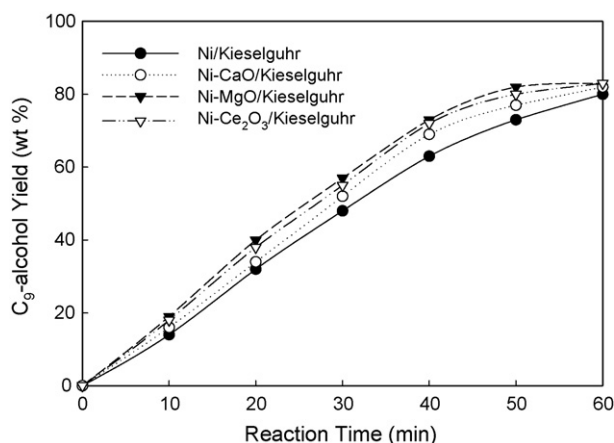
Fig. 8 shows the results of a hydrogenation experiment according to the precipitant used. The catalyst prepared using Na₂CO₃ showed the highest reaction activity. As shown in Table 2, the catalyst using NH₄OH as the precipitant showed the lowest reaction activity due to its significantly smaller surface area.

3.4. C9-aldehyde hydrogenation in a trickle bed reactor

In order to find the optimal reaction conditions, C9-aldehyde hydrogenation reactions were performed in the trickle bed reactor with the Ni–MgO/kieselguhr catalyst (Figs. 1 and 2). While changing the reaction temperature and pressure and the flow rate of the reactant C9-aldehyde, changes in the yield of C9-alcohol, which is an indicator of the catalyst activity, were measured. As shown in Table 4, the reaction temperature was changed from 130 to 175 °C, the reaction pressure from 400 to 600 psi and 800 psi, and the space velocity of the reactant C9-aldehyde from 1 to 3 h⁻¹. Here, the flow rate of hydrogen was changed from 30 to 90 cm³/min, along with the change in the flow rate of C9-aldehyde. First, with respect to the change in the reaction activity caused by the reaction temperature, the alcohol yield was increased by 10–20% at 130 °C compared to 175 °C when the reaction pressure and flow rate of C9-aldehyde were kept constant. Compared to 130 °C, the octene content of the product at a reaction temperature of 175 °C was 24–29% higher. This
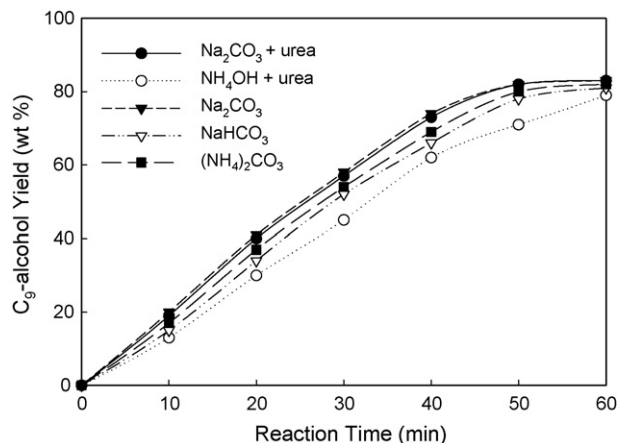

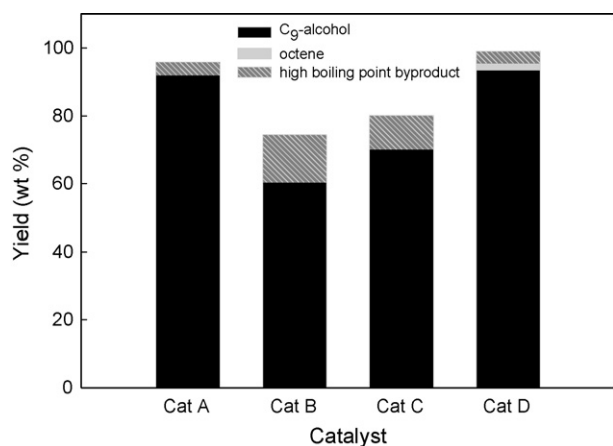Fig. 7. Effect of promoter on C9-alcohol yield over Ni/kieselguhr catalyst in a batch reactor (120 °C, 100 bar).

Fig. 8. Effect of precipitant on C9-alcohol yield over Ni/kieselguhr catalyst in a batch reactor (120 °C, 100 bar).

Fig. 9. Comparison of C_9-aldehyde hydrogenation over various catalysts [Cat A: $CuO/ZnO/Al_2O_3$ (60:30:10); Cat B: $Cu–Ni–Cr–Na/Al_2O_3$ (Cu 0.3%, Ni 4.5%, Cr 0.07%, Na 0.03%); Cat C: $Ni–Mo/Al_2O_3$ (NiO 4.0%, MoO_3 20.0%); Cat D: $Ni–MgO/kieselguhr$ (Ni 60%)].

Fig. 10. Long-term performance in a trickle bed reactor (reaction temperature: 130 °C; reaction pressure: 400 psi).

was probably because, in the case using the Ni–MgO/kieselguhr catalyst, a high reaction temperature decomposes the reactant C_9-aldehyde into the octene and, as a result, the selectivity of C_9-alcohol decreases, despite the high conversion; the yield of C_9-alcohol was also lower at a higher temperature.

Next, with respect to the effect of reaction pressure, when the pressure was raised from 400 to 800 psi, the yield of C_9-alcohol generally decreased at each temperature. At the low temperature of 130 °C, no significant change in the activity was observed until 600 psi, but as the pressure was raised to 800 psi, the conversion and selectivity of C_9-aldehyde decreased and, as a result, the catalyst activity was considerably reduced. This trend was more noticeable when the flow rate of C_9-aldehyde was high. The quantity of high-boiling-point by-products (HBPBP) also increased at the higher pressure of 800 psi. Conversely, at the higher temperature of 175 °C, no remarkable decrease was observed in relation to the reaction pressure. The effect of the C_9-aldehyde flow rate on the catalyst activity was less than that of the reaction temperature and pressure. However, at a low temperature and high pressure (130 °C, 800 psi), as well as at a high temperature and low pressure (175 °C, 400 psi), the yield of C_9-alcohol changed rapidly, by around 10–23%, in relation to the C_9-aldehyde flow rate. In the case of Ni–MgO/kieselguhr, the change in activity according to reaction temperature was the most remarkable. To some degree, with a pressure increase at a low temperature the activity was reduced, but was only slightly affected by the flow rate of reactant C_9-aldehyde.

Conversely, as mentioned in Section 1, the catalysts reported for the hydrogenation of aldehyde include $Cu–Ni–Cr–Na/Al_2O_3$, $Ni–Mo/Al_2O_3$ and $Cu/ZnO/Al_2O_3$ [10–16]. Fig. 9 shows the result of C_9-aldehyde hydrogenation in a trickle bed reactor using these catalysts. In the conversion of C_9-aldehyde, $Cu/ZnO/Al_2O_3$ and Ni–MgO/kieselguhr showed similar activities. In addition, the yield of high-boiling-point by-products was 3.8% with $Cu/ZnO/Al_2O_3$ and 4.0% with Ni–MgO/kieselguhr, which were both lower than the 14.7 and 10.2% recorded for $Cu–Ni–Cr–Na/Al_2O_3$ and $Ni–Mo/Al_2O_3$, respectively. Accordingly, the C_9-alcohol
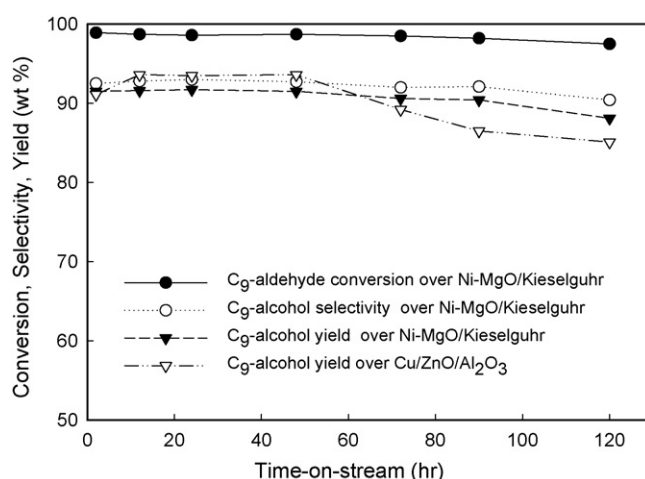
yield with Ni–MgO/kieselguhr was similar to that with $Cu/ZnO/Al_2O_3$, but higher than that with $Cu–Ni–Cr–Na/Al_2O_3$ and $Ni–Mo/Al_2O_3$.

Using the result of the experiment for establishing the optimal reaction conditions, the stability of the catalyst was tested in a long-term operation. The trickle bed reactor was filled with 10 g Ni–MgO/kieselguhr, and the reaction performed under the optimal operation conditions (130 °C, 400 psi, WHSV = 3 h^{-1}) for 120 h, and the change in the catalyst activity monitored. Fig. 10 shows the result of the long-term test. With respect to the conversion, no significant change was observed over the 120 h of the experiment. However, the quantity of high-boiling-point by-products generated from C_9-aldehyde hydrogenation slightly increased, which decreased the alcohol selectivity and, as a consequence, the selectivity for C_9-alcohol was decreased by 2.1% over the 120 h ration time. Consequently, the yield of C_9-alcohol at the beginning of the reaction was 91.5%, but this was decreased to 89.4% after 120 h. On the other hand, compared with the result of a long-term experiment using $Cu/ZnO/Al_2O_3$, the activity of the Ni–MgO/kieselguhr catalyst lasted longer.

4. Conclusions

When a promoter, either CaO, Ce_2O_3 or MgO, was added to the Ni/kieselguhr catalyst, the BET surface area increased, as did that of the Ni. In the reaction for the manufacture of C_9-alcohol, using C_9-aldehyde and hydrogen in a batch reactor, the Ni–MgO/kieselguhr catalyst showed the highest activity. Moreover, the Ni–MgO/kieselguhr catalysts, using Na_2CO_3 as the precipitant showed the highest activity.

According to the result of an experiment for optimizing the reaction conditions for the manufacture of C_9-alcohol, using C_9-aldehyde and hydrogen in a trickle bed reactor loaded with Ni–MgO/kieselguhr catalyst, the C_9-alcohol yield was 91.5 wt% at 130 °C and 400 psi, with WHSV = 3 h^{-1}. The C_9-aldehyde hydrogenation performance of the Ni–MgO/kieselguhr catalyst was similar to that of $Cu/ZnO/Al_2O_3$, but superior to that of $Cu–Ni–Cr–Na/Al_2O_3$ and $Ni–Mo/Al_2O_3$. When the stability of

the catalyst was tested through a long-term catalysis experiment, the C_9-alcohol yield was slightly decreased after 120 h, due to the increase in the quantity of high-boiling-point by-products, but was higher than that in the long-term experiment with $Cu/ZnO/Al_2O_3$.

Acknowledgement

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