

산화-환원 전처리에 따른 Ni/SiO₂ 촉매의 캐스터오일 수소화

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(2017년 3월 8일 접수, 2017년 3월 27일 심사, 2017년 4월 16일 채택)

Effect of Oxidation-reduction Pretreatment for the Hydrogenation of Caster Oil over Ni/SiO₂ Catalyst

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(Received March 8, 2017; Revised March 27, 2017; Accepted April 16, 2017)

초 록

캐스터오일은 수소화반응을 통해 계면활성제의 중간체 등 유용한 화학산업의 원료로 활용 가능하다. 본 연구에서는 캐스터오일의 수소화용 니켈촉매의 제조조건과 전처리 조건에 대한 영향을 연구하였다. 니켈촉매는 침전제와 pH를 다르게 하여 실리카 담체상에 침전법으로 담지되었고, 다시 산화와 환원의 반복된 전처리를 행하였다. 니켈촉매의 활성은 캐스터오일의 요오드 값을 측정하여 비교하였고, 니켈촉매의 분산도는 XRD, BET, TEM을 통하여 분석하였다. 니켈촉매의 활성을 CO산화반응실험을 통하여도 비교하였다. 산화와 환원 사이클의 반복에 의해 니켈의 재분산이 실리카 상에서 발생하였고, 이것이 캐스터오일 수소화반응 활성을 증진시키는데 기여하였다.

Abstract

Castor oil can be used as a useful raw material for chemical industries such as intermediates of surfactants through hydrogenation reaction. In this study, effects of the preparation method and pretreatment condition on the nickel catalyst for the hydrogenation of castor oil were investigated. The nickel catalyst was supported on the silica carrier by the precipitation method with different Ni contents, solution pH values, and precipitants. Repeated pretreatments of oxidation and reduction cycles were then carried out. The activity of the nickel catalyst was measured by comparing the iodine value of the castor oil. The dispersion of nickel on the catalyst was analyzed by X-ray diffraction (XRD), N₂ adsorption-desorption, and transmission electron microscopy (TEM). The activity of nickel catalyst was also compared by CO oxidation experiments. The redispersion of nickel occurred on the silica by repeated oxidation and reduction cycles, and this effect contributed to promoting the castor oil hydrogenation activity.

Keywords: hydrogenation, Ni catalyst, castor oil, oxidation-reduction treatment, dispersion

1. Introduction

Castor is a widely cultivated, inexpensive, environment-friendly, and industrial oil plant. Castor oil, as an important and special feed, has long been known as a medicinal oil and has been used as an ingredient in the oleochemical industry[1-4]. The broad and versatile use of castor oil is due to its main component, ricinoleic acid (12-hydroxy-9-cis-octadecenoic acid), which represents ~90% of the fatty acids in the vegetable triglycerides[5]. Oil hydrogenation is a very important operation in

the industrial process of producing starting components for the cosmetic and chemical industry (lubricants, emulsifiers, soaps, creams, pastes, and others)[2]. The field of catalytic hydrogenation of castor oil has seen a lot of advances in recent years, especially regarding efforts to lower the iodine value of castor oil[6]. Castor oil, like many other plant oils, is a valuable renewable resource for the chemical industry[3,4,7].

Nickel, copper, copper-chromite, platinum, and palladium are the most common metals used as active heterogeneous catalysts for partial hydrogenation. However, hydrogenation with Ni catalysts has been the choice of industry, largely due to its availability, low cost, and inert nature of the metal relative to the oil[1,8-15]. Ni supported on kieselguhr is the most widely used catalyst for industrial hydrogenation. This support is produced mainly from amorphous SiO₂, and has suitable textural, thermal, and chemical characteristics for the reaction under study[15,16].

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Table 1. Procedure for the Preparation of Different Catalysts (Changing the Metal Weight Fraction, pH, and Precipitants. The Various Pretreatment Steps are Shown, Where Applicable)

Catalyst NO.	Catalyst code.	Ni (wt%)	pH	Precipitant
1	(40/4.5/S) Ni/SiO ₂	40	4.5	Sodium carbonate
2	(40/5.5/S) Ni/SiO ₂	40	5.5	Sodium carbonate
3	(20/4.5/S) Ni/SiO ₂	20	4.5	Sodium carbonate
4	(50/4.5/S) Ni/SiO ₂	50	4.5	Sodium carbonate
5	(40/4.5/A) Ni/SiO ₂	40	4.5	Ammonia water
1-1	(40/4.5/S) Ni/SiO ₂ ; C	40	4.5	Sodium carbonate
1-2	(40/4.5/S) Ni/SiO ₂ ; C-R	40	4.5	Sodium carbonate
1-3	(40/4.5/S) Ni/SiO ₂ ; C-R-O	40	4.5	Sodium carbonate
1-4	(40/4.5/S) Ni/SiO ₂ ; C-R-O-R	40	4.5	Sodium carbonate
1-5	(40/4.5/S) Ni/SiO ₂ ; C-R-O-R-O	40	4.5	Sodium carbonate
1-6	(40/4.5/S) Ni/SiO ₂ ; C-R-O-R-O-R	40	4.5	Sodium carbonate

The dispersion of metals on catalyst support is a very important factor for heterogeneous catalyst. Also, redispersion of metals on catalyst was observed in several catalysts, like Pt and Pt-Rh alloys. In these catalysts, oxidation-reduction pretreatment induced the metal redispersion. A high degree of dispersion can be acquired and a high catalytic activity is also achieved. In this study, we have applied this pretreatment to the Ni catalyst and studied Ni dispersion.

There are many studies about castor oil hydrogenation with Ni/SiO₂ catalyst. However, few studies have addressed the hydrogenation of castor oil over the Ni/SiO₂ catalyst that was pretreated by an oxidation-reduction cycle. The pretreatment effect of Ni catalyst for hydrogenation of castor oil, effect of precipitant, and content of Ni on hydrogenation catalytic activity were investigated. Particularly, the effect of repeated oxidation-reduction (OR) pretreatment of Ni catalyst was studied in terms of Ni particle size, state of Ni, dispersion, and catalytic activity. Pretreated Ni catalysts were also tested for their catalytic activity in the CO oxidation reaction. Physicochemical characteristics of these catalysts were measured by X-ray diffraction (XRD), N₂ adsorption-desorption, and transmission electron microscopy (TEM).

2. Experimental

2.1. Catalyst preparation

Ni/SiO₂ catalysts were prepared by the precipitation of nickel nitrate with either ammonium hydroxide or sodium carbonate in a solution where silica particles are suspended[8]. Solutions of nickel were prepared via the dissolution of Ni(NO₃)₂ · 6H₂O in distilled water. An aqueous solution of nickel (II) nitrate hexahydrate was added to the precipitants to adjust the pH. The precipitate was washed and filtered progressively. The precipitants, urea, sodium carbonate (Na₂CO₃), and aqueous ammonia, were prepared by dissolution in distilled water. After completion of the precipitation reaction, the precipitated solids were filtered, washed, and dried at 110 °C for 12 h. The dried solids were subsequently calcined at 500 °C for 4 h. The nomenclature of the catalysts includes the measured amount of metal supported on the SiO₂, the preparation method, and repetition of pretreatment method.

Those are summarized in Table 1.

2.2. Catalytic reactions

2.2.1. Hydrogenation of castor oil

Castor oil was used as the feedstock. Transfer hydrogenation was carried out in a 10-L reactor. In this study, 2.5 kg of the oil and 50 g of the catalyst were loaded into the batch reactor. The reactor was connected to a hydrogen source and during the process, H₂ pressure was maintained constant at 9 bar. The temperature of the reactor was controlled by a temperature controller at 140 °C, and the stirring speed was retained at 355 rpm for the duration of the reaction. The hydrogenation activity was determined through iodine value measured by the Wijs method.

2.2.2. Hydrogenation of propylene

Hydrogenation reactions were carried out in a conventional differential fixed-bed reactor whose inner diameter was 15 mm. The catalytic bed consisted of 0.15 g of catalyst powder. Typical feeding gas comprised propylene, hydrogen and nitrogen in the ratio 1 : 1 : 4. Flows were regulated by mass flow controllers (GMATE2000A). The reaction products were analyzed using a GC unit (HP 5890) containing a 30 m × 0.0320 mm AT-Q column, operating at 220 °C with helium as carrier gas.

2.2.3. Oxidation of carbon monoxide

The CO oxidation experiments with the Ni/SiO₂ catalyst were carried out in a continuous-flow quartz fixed-bed reactor (internal diameter = 5 mm) under atmospheric pressure. The Ni/SiO₂ catalyst (0.5 g) was loaded onto a ceramic holder which was located in the center of the quartz reactor. The reactants for CO oxidation were fed with a CO/O₂/N₂ volume ratio of 1/20/79 for a total flow rate of 275 cm³/min. The flow was controlled by an independent mass flow controller. The product gas stream was analyzed by residential combustion analyzer (Testo 310, Testo AG, Germany), which is a carbon monoxide measuring instrument to calculate the conversion of CO.

Table 2. Pretreatment Processes Applied to the Supported Ni Catalysts

Catalyst code	Pretreatment
C	Calcination
C-R	Calcination/Reduction
C-R-O	Calcination/Reduction/Oxidation
C-R-O-R	Calcination/Reduction/Oxidation/Reduction
C-R-O-R-O	Calcination/Reduction/Oxidation/Reduction/Oxidation
C-R-O-R-O-R	Calcination/Reduction/Oxidation/Reduction/Oxidation/Reduction

Table 3. Textural Properties of the Reduced Catalysts Measured by N₂-Sorption Analysis

Catalyst code	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
(40/4.5/S) Ni/SiO ₂	17	0.11	24.54
(40/5.5/S) Ni/SiO ₂	9	0.06	26.26
(20/4.5/S) Ni/SiO ₂	20	0.07	14.61
(50/4.5/S) Ni/SiO ₂	18	0.08	16.72
(40/4.5/A) Ni/SiO ₂	17	0.09	21.68
(40/4.5/S) Ni/SiO ₂ ; C	14	0.07	20.45
(40/4.5/S) Ni/SiO ₂ ; C-R	17	0.11	24.54
(40/4.5/S) Ni/SiO ₂ ; C-R-O	13	0.07	21.45
(40/4.5/S) Ni/SiO ₂ ; C-R-O-R	17	0.10	23.91

In this paper, the CO conversion was calculated from the change of the CO concentration :

$$\text{CO Conversion (\%)} = \frac{\text{Inlet CO Concentration} - \text{Outlet CO Concentration}}{\text{Inlet CO Concentration}} \times 100$$

2.3. Characterization

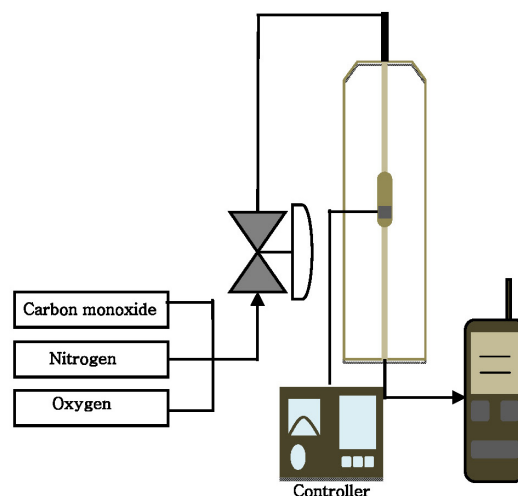
The X-ray Diffraction (XRD) patterns of the prepared Ni/SiO₂ catalysts were recorded on a diffractometer (D/MAX-2200 powder X-ray diffractometer, Rigaku, Japan) with Ni-filtered Cu K α ($\lambda = 0.15406$ nm). The operating voltage was 45 kV, and the current was 40 mA, with a 2θ scanning rate of 4° min^{-1} .

The BET surface areas and N₂ adsorption-desorption measurements were performed at -196°C using an automated gas sorption system (ASAP 2420, Micromeritics, USA).

The experiments for reduction-oxidation cycle (redox) performance were performed as below. The catalysts were pretreated with H₂ flow ($92 \text{ cm}^3/\text{g}_{\text{cat}}$) at 450°C for 4 h and then were cooled down to room temperature and reoxidized in air ($92 \text{ cm}^3/\text{g}_{\text{cat}}$) at 400°C for 4 h.

The textural properties of the samples as measured by N₂-adsorption and desorption are listed in Table 3. The BET analysis of the silica support showed a specific surface area of $30 \text{ m}^2/\text{g}$, while the prepared Ni/SiO₂ catalyst presented a surface area of 9 to $20 \text{ m}^2/\text{g}$.

The surface area and pore size of the catalysts were influenced by the solution pH used for precipitation, and Ni content. Precipitants had no effect on catalyst morphology, as shown in Table 3. Moreover, one reduction cycle increased the surface area, pore volume, and pore size of the catalysts. Furthermore, these properties were decreased upon increasing the number of pretreatment cycles.

**Figure 1. Schematic diagram of the apparatus used for the oxidation of carbon monoxide.**

(40/4.5/S) Ni/SiO₂ catalysts were obtained using transmission electron microscopy (JEM-2010, JEOL, Japan). The catalyst sample was pretreated using ethanol solution.

3. Results and Discussion

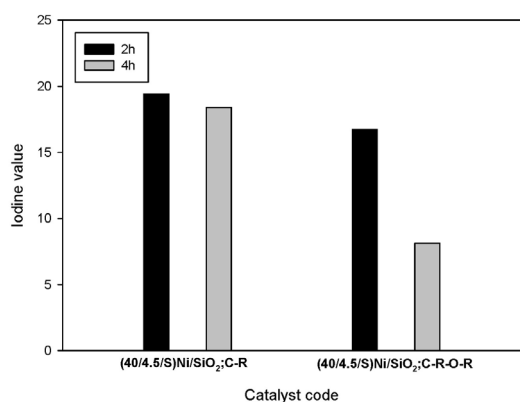
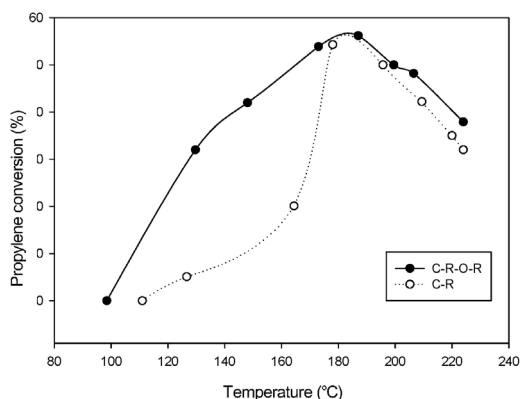
3.1. Catalytic activity

3.1.1. Hydrogenation of castor oil

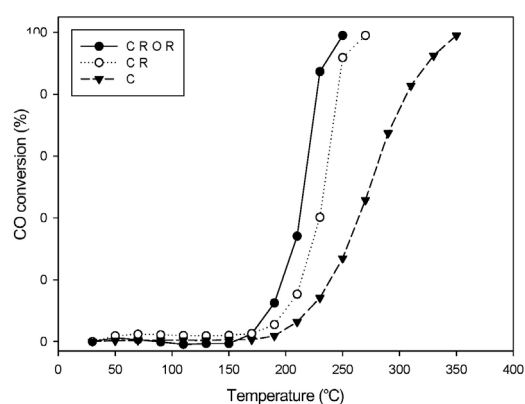
Figure 2 shows the iodine value of hydrogenated castor oil using the pretreated Ni catalysts. Iodine value represents the degree of

Table 4. Iodine Value and Extent of Hydrogenation of Castor Oil as a Function of Ni-Supported Catalysts on Stream at 140 °C

Catalyst code	Time (h)	Iodine index	Conversion (%)
(40/5.5/S) Ni/SiO ₂	2	19.92	77.1
	4	19.33	77.8
(20/4.5/S) Ni/SiO ₂	2	19.02	78.1
	4	18.96	78.2
(50/4.5/S) Ni/SiO ₂	2	18.72	78.5
	4	19.16	78.0
(40/4.5/A) Ni/SiO ₂	2	18.47	78.8
	4	17.08	80.4
(40/4.5/S) Ni/SiO ₂ ; C-R	2	19.42	77.7
	4	18.4	78.9
(40/4.5/S) Ni/SiO ₂ ; C-R-O-R	2	16.72	80.8
	4	8.13	90.7

**Figure 2. Efficiency of Ni-supported catalysts towards hydrogenation of castor oil as measured by iodine value on stream in.****Figure 3. Hydrogenation of propylene on pretreated and reduced (40/4.5/S) Ni/SiO₂ catalysts as a function of temperature.**

hydrogenation. A lower iodine value means a higher degree of hydrogenation. Catalytic activity does not have any special transition following as catalysts preparation methods. However, it was to be fit with castor oil hydrogenation after oxidation-reduction treatment. Table 4 shows hydrogenation activity as a function of oxidation-reduction cycles in the catalyst pre-treatment phase. There are a few differences in

**Figure 4. Conversion of carbon monoxide on pretreated Ni catalyst (40/4.5/S)Ni/SiO₂ as a function of temperature.**

the activity between the two methods.

3.1.2. Hydrogenation of propylene

Figure 3 shows the catalytic performance of (40/4.5/S)Ni/SiO₂ and the pretreated catalyst for the hydrogenation of propylene at 100~220 °C. In our catalytic reaction, propane was mainly produced. It can be seen from Figure 3 that the maximum conversion of propylene occurred at 180 °C. However, hydrogenation activity with the pretreated catalyst was consistently higher than the reduced catalyst. Therefore, the catalyst was used for propylene hydrogenation after oxidation-reduction treatment.

3.1.3. Oxidation of carbon monoxide

Differences in activity were observed depending on the type of pre-treatment applied to the catalyst. Figure 4 shows that pretreatment lowers the temperature of the CO oxidation reaction. The catalyst and reduced catalyst attained complete oxidation of CO at 350 °C and 260 °C, respectively, whereas the pretreated catalyst oxidized CO completely at 230 °C. The catalyst was more suitable after reduction-oxidation-reduction treatment.

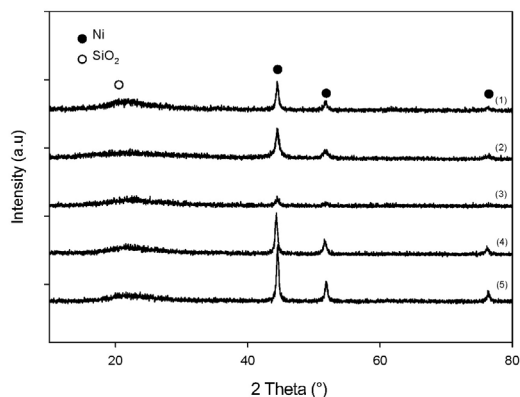


Figure 5. X-ray diffraction pattern of various prepared Ni catalysts : (40/4.5/S) Ni/SiO₂ (1), (40/5.5/S) Ni/SiO₂ (2), (20/4.5/S) Ni/SiO₂ (3), (50/4.5/S) Ni/SiO₂ (4) and (40/4.5/A) Ni/SiO₂ (5).

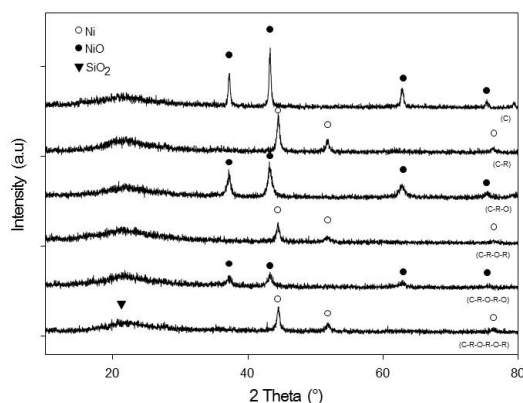


Figure 6. X-ray diffraction patterns of (40/4.5/S)Ni/SiO₂ Ni catalysts with different pretreatments.

3.2. Characterization

The XRD patterns of the prepared catalysts are shown in Figure 5. Since the crystalline peaks appear in the 2θ range of $40\text{--}80^\circ$, only this section of the diffractogram is shown. This indicates the presence of segregated large and small Ni particles on the catalyst surface.

Table 3 shows that the surface area tends to decrease with increasing pH, while the specific surface area does not show a difference depending on Ni content and precipitant. This shows that pH affects the specific surface area.

Figure 6 shows the XRD pattern of pretreated Ni/SiO₂ catalysts. Ni oxide peaks were present before reduction of the catalyst. The reflections of nickel oxide disappeared after reduction, and the typical X-ray pattern of metallic Ni was detected. After oxidation-reduction treatment, Ni particles were evenly dispersed which could explain the results. Metal particle was enlarged after one treatment. This means just one treatment improves the catalytic activity.

Figure 7 shows TEM image of (40/4.5/S) Ni/SiO₂ catalysts following different pretreatment.

According to the pretreatment, Ni particles size of (40/4.5/S) Ni/SiO₂ : C-R-O-R catalysts were decreased than (40/4.5/S) Ni/SiO₂ : C catalysts. Through the ROR (Reduction/Oxidation/Reduction), it can be confirmed that the dispersion of Ni is increased and thus the hydro-

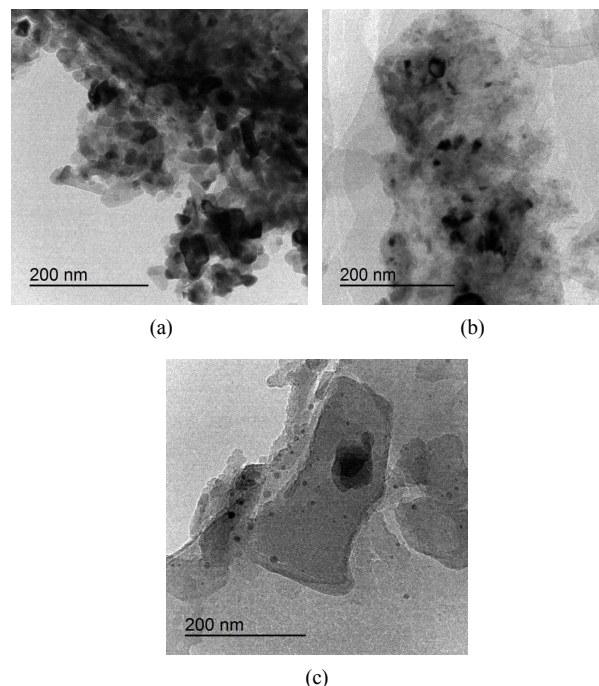


Figure 7. TEM images of (40/4.5/S) Ni/SiO₂ following different pretreatment protocols : (a) C (b) C-R (c) C-R-O-R.

genation and the oxidation reaction are more effective.

4. Conclusions

The hydrogenation and oxidation experiments were crucial for studying the activity of the Ni catalysts. Based on our experiments, the main findings of this study can be summarized as below :

Differences in the material characterization of the catalyst are influenced by the solution pH, Ni content, and choice of precipitant during the process of manufacture. Particle size and dispersion are not correlated with pH, but surface area is influenced. As Ni content is varied, particle size and size dispersion can be strongly affected by the precipitant.

Oxidation-reduction (OR) treatment was performed to study the effect of surface modification of the catalysts for Hydrogenation of castor oil. OR treated catalysts were determined suitable for castor oil hydrogenation. Characterization was performed by BET, XRD and TEM; The dispersion is increased after OR treatment, so that hydrogenation activity of castor oil is better than before. It means increase of dispersion and catalyst surface was made more favorable for catalyzing the hydrogenation of castor oil.

Propylene hydrogenation was performed to confirm the activity improvement of the pretreatment protocols on the catalyst surface, as a possible template for catalyzing hydrogenation reactions in general. Both the pretreated and untreated catalyst exhibited maximum catalytic activity at about 180°C . The hydrogenation activity of the pretreated catalyst was higher than others at several temperatures. Thus, this catalyst is expected to be useful for hydrogenation in addition to castor oil

hydrogenation.

OR-treated Ni catalyst was tested for catalyzing the oxidation of CO. The pretreated catalyst approaches 100% conversion of carbon monoxide at a lower temperature than the untreated catalyst. This suggests that the catalyst may be activated at a lower temperature than previously expected. Furthermore, this shows that Ni/SiO₂ can be suitable as a catalyst for many kinds of industrial processes.

Acknowledgments

This work was supported by a research grant from Hankyong National University in the year of 2015.

References

1. S. Liu, Q. Zhu, Q. Guan, L. He, and W. Li, Bio-aviation fuel production from hydroprocessing castor oil promoted by the nickel-based bifunctional catalysts, *Bioresour. Technol.*, **183**, 93-100 (2015).
2. R. C. S. Schneider, V. Z. Baldissarelli, M. Martinelli, M. L. A. von Holleben, and E. B. Caramão, Determination of the disproportionation products of limonene used for the catalytic hydrogenation of castor oil, *J. Chromatogr. A*, **985**, 313-319 (2003).
3. D. S. Ogunniyi, Castor oil: A vital industrial raw material, *Bioresour. Technol.*, **97**, 1086-1091 (2006).
4. H. Y. Shirame, N. L. Panwar, and B. R. Bamniya, Bio diesel from castor oil-A green energy option, *Low Carbon Econ.*, **2**, 1-6 (2011).
5. R. C. S. Schneider, V. Z. Baldissarelli, F. Trombetta, M. Martinelli, and E. B. Caramão, Optimization of gas chromatographic-mass spectrometric analysis for fatty acids in hydrogenated castor oil obtained by catalytic transfer hydrogenation, *Anal. Chim. Acta*, **505**, 223-226 (2004).
6. S. McArdle, J. J. Leahy, T. Curtin, and D. Tanner, Hydrogenation of sunflower oil over Pt-Ni bimetallic supported catalysts: Preparation, characterization and catalytic activity, *Appl. Catal. A*, **474**, 78-86 (2014).
7. M. I. P. da Silva, M. P. Nery, and C. A. T. Soto, Castor oil catalytic hydrogenation reaction monitored by Raman spectroscopy, *Mater. Lett.*, **45**, 197-202 (2000).
8. S. K. Saraswat and K. K. Pant, Synthesis of hydrogen and carbon nanotubes over copper promoted Ni/SiO₂ catalyst by thermocatalytic decomposition of methane, *J. Nat. Gas Sci. Eng.*, **13**, 52-59 (2013).
9. R. Atsumi, R. Noda, H. Takagi, L. Vecchione, A. Di Carlo, Z. Del Prete, and K. Kuramoto, Ammonia decomposition activity over Ni/SiO₂ catalysts with different pore diameters, *Int. J. Hydrogen Energy*, **39**, 13954-13961 (2014).
10. J. Vicente, J. Ereña, C. Montero, M. J. Azkoiti, J. Bilbao, and A. G. Gayubo, Reaction pathway for ethanol steam reforming on a Ni/SiO₂ catalyst including coke formation, *Int. J. Hydrogen Energy*, **39**, 18820-18834 (2014).
11. L. Dong, Y. Du, J. Li, H. Wang, Y. Yang, S. Li, and Z. Tan, The effect of CH₄ decomposition temperature on the property of deposited carbon over Ni/SiO₂ catalyst, *Int. J. Hydrogen Energy*, **40**, 9670-9676 (2015).
12. Z. Jia, B. Zhen, M. Han, and C. Wang, Liquid phase hydrogenation of adiponitrile over directly reduced Ni/SiO₂ catalyst, *Catal. Commun.*, **73**, 80-83 (2016).
13. E. Ruckenstein and S. H. Lee, Redispersion and migration of Ni supported on alumina, *J. Catal.*, **86**, 457-464 (1984).
14. K. Mette, S. Kühn, A. Tarasov, H. Döder, K. Kähler, M. Muhler, R. Schlögl, and M. Behrens, Redox dynamics of Ni catalysts in CO₂ reforming of methane, *Catal. Today*, **242**, 101-110 (2015).
15. M. Gabrovska, J. Krstić, R. Edreva-Kardjieva, M. Stanković, and D. Jovanović, The influence of the support on the properties of nickel catalysts for edible oil hydrogenation, *Appl. Catal. A*, **299**, 73-83 (2006).
16. D. J. Suh, J. S. Chung, T. Lim, and S. H. Moon, Effect of nickel-silicate formation on catalytic properties of Ni/SiO₂ prepared by precipitation method, *Korean Chem. Eng. Res.*, **27**, 620-628 (1989).
17. D. Potoczna-Petru, J. M. Jabłoński, J. Okal, and L. Krajczyk, Influence of oxidation-reduction treatment on the microstructure of Co/SiO₂ catalyst, *Appl. Catal. A*, **175**, 113-120 (1998).
18. L. Tang, D. Yamaguchi, B. Leita, V. Sage, N. Burke, and K. Chiang, The effects of oxidation-reduction treatment on the structure and activity of cobalt-based catalysts, *Catal. Commun.*, **59**, 166-169 (2015).
19. J. Okal and H. Kubicka, Influence of oxidation-reduction treatment on activity and selectivity of Re supported on γ -alumina, *Appl. Catal. A*, **171**, 351-359 (1998).