Effects of Steam on Toluene Hydrogenation over a Ni Catalyst

Ryosuke Atsumi, Keisuke Kobayashi, Cui Xieli, Tetsuya Nanba, Hideyuki Matsumoto, Keigo Matsuda, Taku Tsujimura



Please cite this article as: Atsumi R, Kobayashi K, Xieli C, Nanba T, Matsumoto H, Matsuda K, Tsujimura T, Effects of Steam on Toluene Hydrogenation over a Ni Catalyst, *Applied Catalysis A, General* (2019), doi: https://doi.org/10.1016/j.apcata.2019.117374

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2019 Published by Elsevier.



#### Effects of Steam on Toluene Hydrogenation over a Ni Catalyst

Ryosuke Atsumi<sup>1\*</sup>, Keisuke Kobayashi<sup>2</sup>, Cui Xieli<sup>1</sup>, Tetsuya Nanba<sup>1</sup>, Hideyuki Matsumoto<sup>1</sup>, Keigo Matsuda<sup>2</sup>, Taku

Tsujimura<sup>1</sup>

<sup>1</sup>National Institute of Advanced Industrial Science and Technology, 2-2-9 Machiikedai, Koriyama, Fukushima 963-

0298, Japan

<sup>2</sup>Department of Chemistry and Chemical Engineering, Graduate School of Science and Engineering, Yamagata

University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, JAPAN

\*Corresponding author

#### **Graphical abstract**



#### Highlights

- Toluene hydrogenation with steam-containing hydrogen (wet-H<sub>2</sub>) was conducted using an industrial Ni catalyst for H<sub>2</sub> storage.
- Methylcyclohexane selectivity increased with increasing steam partial pressure.
- Wet-H<sub>2</sub> produced in a water electrolysis system can be used directly in toluene hydrogenation.

#### Abstract

The catalytic toluene hydrogenation over Ni/SiO<sub>2</sub> was carried out using H<sub>2</sub> or a H<sub>2</sub>/H<sub>2</sub>O mixture. The toluene conversion and MCH selectivity were evaluated under partial steam pressures 0-10 kPa, at H<sub>2</sub>/toluene molar ratios 1-5, and at temperatures 393-453 K. In the absence of steam, toluene conversion increased with increasing H<sub>2</sub> partial pressure, and the MCH selectivity decreased with increasing temperature. In the presence of steam, the toluene conversion showed near-constant activities over the entire range of steam partial pressures, and the MCH selectivity increased with increasing steam partial pressure. This result indicated that the addition of steam inhibited byproduct formation. To clarify the effects of steam on the side-reaction, the byproducts composition was analyzed using a gas chromatograph. The results showed that the addition of steam inhibited demethylation, the ring-opening reaction of MCH, the disproportionation of toluene, and isomerization to convert six-membered ring compounds into five-membered ring compounds.

#### Keywords

Toluene hydrogenation: Nickel catalyst: Low-grade hydrogen: Methylcyclohexane: Hydrogen carrier

#### 1. Introduction

Hydrogen (H<sub>2</sub>) storage using liquid organic hydride is important to the utilization of renewable electricity generated from wind, solar, and hydropower [1-4]. Methylcyclohexane ( $C_7H_{14}$ , MCH) is one of the candidates for chemical H<sub>2</sub> storage materials [1-4]. MCH can store H<sub>2</sub> via toluene ( $C_7H_8$ ) hydrogenation:

$$C_7H_8 + 3H_2 \rightarrow C_7H_{14} - 205 \text{ kJ mol}^{-1}$$
 (1).

This reaction has been studied extensively in the petrochemical industry, and the infrastructure for MCH synthesis and transportation has been established [2]. MCH also has relatively high volumetric and gravimetric  $H_2$  densities (47 kg-H<sub>2</sub> m<sup>-3</sup> and 6.1 wt% respectively), good transportability, and relatively low toxicity [2,4]. The Fukushima Renewable Energy Institute, AIST (FREA) has demonstrated a pilot-scale toluene hydrogenation system in which a 150-kW-class alkaline water electrolysis (AWE) system has been installed to generate renewable H<sub>2</sub> [5]. The demonstration system can utilize a power input that fluctuates with time to generate H<sub>2</sub>, which simulates the surplus energy of renewable energy sources [5]. Kojima et al. [5] reported that the H<sub>2</sub> production rate was highly synchronized with power input fluctuations and relatively short time delay. Although it has been reported that AWE efficiency decreases with increased input current frequency [8,10,11], AWE shows second-order response fluctuation in input power [8,9]. To achieve steady operation of the hydrogenation reactor, the toluene hydrogenation system needs a buffer tank (and a  $H_2$  compressor) or batteries to absorb the fluctuation of  $H_2$  or surplus energy, yet this can increase the capital cost of the system. Therefore, we believe that directly providing fluctuating H<sub>2</sub> from AWE to the reactor is important to utilize renewable H<sub>2</sub> effectively.

Although the purity of H<sub>2</sub> produced by AWE is generally lower than that produced using polymer-

electrode electrolysis cells (PEECs) and solid-oxide electrolysis cells (SOECs) due to its diaphragm, AWE is costeffective and well-established compared to PEFCs and SOECs [6,7]. Hence it is important to evaluate the effects of trace impurities from AWE on toluene hydrogenation. Hydrogen generated on the cathode contains trace oxygen and is saturated with steam at the AWE operating temperature (generally 323 to 353 K) [6,7,34,35]. Hydrogen from AWE contains alkaline mist, e.g., KOH and NaOH, and a water scrubber removes the alkaline mist. If the water scrubber works at ambient temperature (298 K), the alkaline-free H<sub>2</sub> contains steam with a partial pressure of 3 kPa. The trace oxygen can be removed by a metal-loaded catalyst packed in a toluene hydrogenation reactor. Steam has been reported to cause the oxidative demethylation of toluene over a Ni catalyst [36,37], as described by the following equations:

$$C_6H_5-CH_3 + H_2O \rightarrow C_6H_6 + 2H_2 + CO$$
(3),

$$C_6H_5-CH_3 + 2H_2O \rightarrow C_6H_6 + 3H_2 + CO_2$$
(4).

Moreover, steam can also cause oxidation of the Ni surface, which leads to catalytic deactivation. However, there are only a few reports of toluene hydrogenation in the presence of trace steam and the effects of the partial pressure of steam on catalytic activity. Practical AWE systems include a pressure swing adsorption (PSA) or temperature swing adsorption (TSA) process to remove the trace steam from  $H_2$  [6,7]. However, when the energy input of the AWE fluctuates, the dew-point of the purified hydrogen can fluctuate due to the steam flow rate exceeding the PSA or TSA capacity. To generate pure  $H_2$  using a fluctuating power input, it is necessary to load a great deal of adsorbent, or extend the AWE cycle time (the period from adsorption to desorption). This overloading seems to

lead to higher capital expenditure for the AWE system. Therefore, it is important to estimate the effects of steam on the toluene hydrogenation process and determine an acceptable partial pressure of steam.

The toluene hydrogenation reaction can be catalyzed by using Pt [2,12-20,30], Ru [21], Ir [22], and Ni [23-31]. Pt-loaded catalysts exhibit the highest activity [2], while Ni catalysts are the most cost-effective. As reported by Lindfors et al. [23], Ni catalysts exhibit high activity for excess H<sub>2</sub> conditions with H<sub>2</sub>/toluene ratios greater than 3. In contrast, the activity drastically declines at H<sub>2</sub>/toluene ratios below 3. The result suggests that a H<sub>2</sub>/toluene ratio below 3 is not favorable for toluene hydrogenation. On the other hand, when the supply of surplus renewable energy fluctuates on a time scale of seconds, the toluene evaporator is not expected to exhibit an equivalent time-response. In other words, for the usage of renewable hydrogen, we should consider the situation in which the H<sub>2</sub>/toluene ratio will drop below 3. Therefore, it is important to estimate the catalytic activity of Ni catalysts against a wide range of H<sub>2</sub> partial pressures, including H<sub>2</sub>/toluene ratios below 3.

Nickel catalysts are active for C-C bond cleavage. Grenoble [32] reported the catalytic activities of group VIIB and VIII metals for toluene hydrodealkylation via the reaction shown in the following equation:

$$C_6H_5-CH_3 + H_2 \rightarrow C_6H_6 + CH_4$$
(2).

They reported that the catalytic activity of the evaluated metals follows the order Ni > Rh > Ir > Os > Ru > Pt > Pd> Re [32]. The side reactions in toluene hydrogenation using Ni-loaded catalysts have also been studied [25,30,33]. Cui et al. [33] investigated the iterative utilization of MCH (up to 10 cycles) with bench-scale toluene hydrogenation and MCH dehydrogenation reactors to demonstrate their practical use. The resulting data showed the byproduct formation and accumulation behavior for each processing cycle. To our knowledge, there is no

information on the effects of fluctuating H<sub>2</sub> input on toluene hydrogenation.

In the present study, we aimed to acquire the fundamental knowledge needed for the continued development of catalysts with applications to fluctuating H<sub>2</sub> feed systems. The toluene hydrogenation activity of a commercial Ni catalyst in a wide range of H<sub>2</sub>/toluene molar ratios was measured to understand the behavior of not only main product formation, but also byproduct formation under operation of the fluctuating H<sub>2</sub> supply. The formation of byproducts during hydrogenation was analyzed in detail. Furthermore, toluene hydrogenation was conducted using H<sub>2</sub>O-containing H<sub>2</sub> (hereafter referred to as wet-H<sub>2</sub>) to evaluate the effects of steam on the catalytic activity.

#### 2. Experimental

The toluene hydrogenation activity of a stabilized Ni catalyst (BASF SE, Ni5256) with or without the addition of H<sub>2</sub>O vapor was measured in a packed-bed reactor system at ambient pressure, and 3 g of catalyst was set in the reactor. Fig. 1 shows a schematic diagram of the packed-bed reactor. A 12.7 mm (1/8 inch) diameter cylinder-shaped industrial catalyst containing 57 wt% Ni was used. The specifications of the catalyst are summarized in Table 1. The catalyst pellets were packed in a 1/2-inch-diameter stainless steel tube. A K-type thermocouple was inserted into the bed to monitor the bed temperature. The reactor was heated by using an electric furnace. The flow rates of the reactants (H<sub>2</sub> and toluene) and the inert gas (N<sub>2</sub>) were controlled using pre-calibrated mass flow controllers. The flow rate of deionized water was controlled using a syringe pump. Liquid toluene and water were fed into an evaporator before the reactor to provide the feed of the toluene-steam mixture to the catalyst

bed. The evaporator consisted of a 1/2-inch-diameter stainless steel tube, in which ~1-mm-diameter stainless steel spheres were packed. The temperature of the stainless sphere bed was monitored using a K-type thermocouple and was maintained at 423 K using an electric heater. The exhaust gases from the catalyst bed were chilled at 293 K to recover liquid toluene, MCH, and byproducts. The samples were analyzed using a gas chromatograph (Agilent Technology Inc., GC system 7890A) equipped with a flame ionization detector (FID) and a DB-1 (dimethylpolysiloxane) column.

The catalyst packed in the reactor was pre-reduced in H<sub>2</sub> flow at 473 K for an hour [31]. A 0.15 g min<sup>-1</sup> flow of toluene (JUNSEI Chemical co. ltd., Guaranteed Reagent, 99.5%) was supplied to the catalyst bed. Hydrogen of grade 99.999995 vol% (Taiyo Nippon Sanso Corporation, G1-H<sub>2</sub>) was supplied at 40.4–201.8 mL min<sup>-1</sup>, which corresponded to a H<sub>2</sub>/toluene molar ratio from 1 to 5 (the stoichiometric ratio was 3, as described in Eq. 1). In order to evaluate the effects of steam on the catalytic activity, deionized water was supplied at a rate ranging from 0.4 to 18.6 mg min<sup>-1</sup>, corresponding to steam partial pressures of 1 to 10 kPa. The toluene conversion was calculated using the following equation:

$$(Toluene conversion \%) = (1 - X_{Toluene}) \times 100$$
(5)

where  $X_{Toluene}$  is the molar ratio of toluene in the recovered products. Equilibrium toluene conversion was also calculated by HSC chemistry 7 (Calculation of Equilibrium Composition ver. 7.10). The MCH selectivity was calculated using the following equation:

(MCH selectivity %) = 
$$[X_{MCH} / (1 - X_{Toluene})] \times 100$$
 (6)

The byproducts were categorized into five groups: demethylated compounds, ring-opened compounds, six-

membered ring compounds (excluding benzene and cyclohexane), five-membered ring compounds, and dimerized compounds. The respective selectivity for these byproducts was calculated using the following equation:

(Byproducts selectivity %) = 
$$X_{Byproducts} / [\xi(1 - X_{Toluene})] \times 100$$
 (7)

where  $\xi$  is the number of toluene molecules consumed to produce the product molecule. For the dimerized compounds,  $\xi = 2$ , while for the other compounds,  $\xi = 1$ . To ensure accuracy, byproduct selectivity was calculated for compounds with concentration of more than 0.01 mol%. Further, we distinguished these byproduct groups by the kind of hydrogen carrier: six-membered ring compounds, unusable byproducts; ring-opened compounds and five-membered ring compounds, toxic or inhibitor byproducts; demethylated and dimerized compounds.

In order to estimate the surface acidic properties of the Ni catalyst with and without steam, temperatureprogrammed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD) was performed. A total of 0.1 g of the as-prepared catalyst was packed in a quartz tube with an inner diameter of 6 mm and pre-reduced using 50 mL min<sup>-1</sup> of pure H<sub>2</sub> at 473 K for an hour. Then, 200 mL min<sup>-1</sup> of dry or humidified argon (Ar, 99.9999% purity, Taiyo Nippon Sanso Corporation, G1-Ar) gas was flowed into the quartz tube at 298 K, followed by 100 mL min<sup>-1</sup> of an Ar/NH<sub>3</sub> mixture (argon-balanced NH<sub>3</sub> standard gas). The partial pressures of H<sub>2</sub>O and NH<sub>3</sub> in Ar were 1 vol%, and the Ar was humidified with deionized water using a bubbler. After the quartz tube was purged with 100 mL min<sup>-1</sup> of Ar for 10 min, the sample with adsorbed NH<sub>3</sub> and H<sub>2</sub>O was heated from 298 to 873 K using an electric heater with an Ar flow rate of 100 mL min<sup>-1</sup> and a heating rate of 3 K min<sup>-1</sup>. The effluent gas was analyzed by using a Fourier Transform Infrared Spectrometer (FT-IR) equipped with a multi-reflection gas cell.

#### 3. Results and Discussion

#### 3.1 Toluene hydrogenation at various H<sub>2</sub>/toluene ratios

To determine the activity of the catalyst under a fluctuating supply of  $H_2$ , the toluene conversion and MCH selectivity at different  $H_2$ /toluene ratios were evaluated at temperatures from 393 to 453 K. Fig. 2 shows the observed and equilibrium toluene conversion at  $H_2$ /toluene ratios of 1–5. The catalyst exhibited higher activity at lower temperatures and higher  $H_2$ /toluene ratios. Equilibrium toluene conversion also decrease as temperature increased. At 393 K and  $H_2$ /toluene ratios > 3.5, ~100% toluene conversion was achieved. The MCH selectivity calculated using Eq. 6 is shown as a function of the  $H_2$ /toluene ratio and temperature in Fig. 3. MCH selectivity at 393 K seems to decrease.

The composition of the byproducts is summarized in Fig. 4, in which the vertical axis represents the selectivity for each byproduct group, as calculated using Eq. 7. Table 2 lists the compounds detected by GC-FID. Although the MCH selectivity was relatively stable at different H<sub>2</sub>/toluene ratios (see Fig. 3), the selectivity for five-membered ring compounds increased with increasing H<sub>2</sub>/toluene ratio; in contrast, the selectivity for the six-membered ring compounds decreased with increasing H<sub>2</sub>/toluene ratio (see Fig. 4). The ratio of ring-opened and dimerized products remained nearly constant.

From Fig. 4(a) and (b), it can be seen that the demethylation of toluene and ring-opening selectivities were almost independent of the H<sub>2</sub>/toluene ratio; however, these reactions increased probably due to an increase in the C-C bond cleavage rate over the Ni surface with increasing temperature [32]. This result agrees with the data reported by Masalska [25]. On the other hand, as shown in Fig. 4(c), the selectivity toward the six-membered ring

compounds decreased with increasing  $H_2$ /toluene ratio. Possible pathways to six-membered ring compounds, such as xylenes, are the disproportionation reaction (Eq. 8) and the methylation of toluene, in which the methyl group is derived from the cracking of aromatic compounds [25].

$$2C_7H_8 \rightarrow C_6H_6 + C_8H_{10} \tag{8}.$$

If disproportionation is dominant, the trend in the graph of six-membered ring compounds will be similar to that of the demethylated compounds. Since their trend lines were different (Fig 4 (a) and (c)), this means the disproportionation reaction to form benzene and six membered ring compounds was only a minor pathway. For the formation of five-membered ring compounds, Upare et al. [38] reported the mechanism of MCH isomerization over the Ni/SiO<sub>2</sub> catalyst, and suggested that MCH was converted to dimethyl cyclopentane and ethyl cyclopentane at the acid sites on SiO<sub>2</sub>, followed by the ring-opening of these products to form methylhexane or heptane. In this study, dimethyl cyclopentane (a C7 compound) was detected; thus, MCH was likely a precursor of dimethyl cyclopentane. As listed in Table 2, methyl cyclopentane (a C6 compound) and ethyl methylcyclopentane (a C8 compound) were also detected. These byproducts might be formed from a similar reaction mechanism as for dimethyl cyclopentane formation [25].

To find appropriate operation conditions regarding the temperature and the H<sub>2</sub>/toluene ratio, the results of the activity tests were compared again. In the range 393 to 453 K, a favorable temperature was 393 K, because the highest toluene conversion and MCH selectivity and lowest byproducts formation were obtained. For discussion of the appropriate H<sub>2</sub>/toluene ratio, we compared conversion and selectivity at 393 K. When the H<sub>2</sub>/toluene ratio was lower than 3, a higher MCH selectivity was obtained. Also, there were fewer unusable and toxic byproducts, and

more hydrogen carrier byproducts, than for a H<sub>2</sub>/toluene ratio above 3. On the other hand, these conditions can lead to the remainder of unreacted toluene. Therefore, the favorable H<sub>2</sub>/toluene ratios were stoichiometric or below stoichiometry.

#### 3.2 Effect of steam on the catalytic activity

Toluene hydrogenation was carried out using wet-hydrogen to determine the effect of steam on the catalytic activity of Ni. Figs. 5 and 6 show the toluene conversion and MCH selectivity as a function of the steam partial pressure for  $H_2$ /toluene ratios of 1–5 at temperatures from 393 to 453 K. The conversion was relatively constant at the different steam partial pressures at all of the  $H_2$ /toluene ratios and temperature conditions (Fig. 5). On the other hand, as shown in Fig. 6, the MCH selectivity increased with increasing steam partial pressure. This positive effect of steam was observed most clearly at higher temperatures and lower  $H_2$ /toluene ratios. Even in the presence of  $H_2O$ , toluene conversion and MCH selectivity at 393 K were higher than those at other temperatures.

To clarify the details of the side-reaction inhibition effect of steam, the selectivity for each byproduct group under different steam partial pressures was evaluated using a H<sub>2</sub>/toluene ratio of 3 (Fig. 7). The decrease in the selectivity for demethylated compounds was a major cause of the increase in MCH selectivity. Although steam addition can potentially lead to oxidative demethylation, as described in Eq. 3 and 4 [36, 37], this reaction was not dominant in this work. It was believed that this was due to the relatively low temperature and steam partial pressure used in this study. Masalska [25] reported the effect of the metal/Brønsted-acid site ratio on MCH selectivity in toluene hydrogenation over Ni-loaded ZSM-5 catalysts, and Brønsted acid sites and higher temperature were suggested to enhance activity for side-reactions such as dehydrogenation, cracking, and disproportionation of

toluene. Upare et al. [38] also reported the reaction pathway of the MCH ring-opening reaction and isomerization over Ni, as well as on the acid sites of SiO<sub>2</sub>, which were suggested to be involved in the isomerization of MCH and ring-opening of the isomers.

To confirm the suppression effect of steam addition on byproducts formation, NH<sub>3</sub>-TPD measurements were conducted to assess the contribution of the acid sites. Fig. 8 shows the NH<sub>3</sub>-TPD profile with or without steam during pretreatment. Both profiles exhibited a peak at around 350 K. The desorption amounts of NH<sub>3</sub> with and without wet-Ar pretreatment were 4.9 and 5.4 mol g<sub>cat</sub><sup>-1</sup>, respectively. From these results, steam addition appears to have little influence on the acidic property of the surface of Ni/SiO<sub>2</sub>. Considering these results, in the presence of water vapor, the competitive adsorption of H<sub>2</sub>O and toluene might decrease toluene coverage, resulting in a decrease in the surface residence time of toluene. If toluene molecules reside on the catalyst surface for a shorter time, a greater number of molecules desorb before the side-reactions are initiated. According to past research on the photocatalytic decomposition of volatile organic compounds (VOCs), aromatic compounds and water vapor are competitively adsorbed on the solid surface, thereby decreasing the VOCs adsorption amount at higher steam partial pressures.

The present study clarified the robustness of the Ni catalyst against  $H_2O$  at temperatures below 453 K and the positive effect of steam addition on MCH selectivity. Although current AWE systems utilize  $H_2$  purification, such as PSA and TSA to remove trace  $H_2O$  [6,7], our data suggests that wet- $H_2$  can be positive for toluene hydrogenation, which would decrease the exergy loss during the gas-liquid separation process. When MCH is synthesized using a  $H_2/H_2O$  mixture, the  $H_2O$  must be collected in an MCH recovery tank. The water phase is

expected to form under an oil (MCH) phase, which would allow the water phase to be removed from the tank by an extraction operation.

#### 4. Conclusion

Toluene hydrogenation was carried out using dry- and wet-H<sub>2</sub> in a packed reactor with an industrial Ni/SiO<sub>2</sub> catalyst. When MCH was synthesized from toluene using dry-H<sub>2</sub>, a higher H<sub>2</sub>/toluene ratio inhibited the disproportionation of toluene, while higher temperatures accelerated the demethylation reaction, disproportionation reaction, isomerization reaction, and ring-opening reaction (or cracking) of MCH. The dimerization selectivity showed only weak correlation with the H<sub>2</sub>/toluene ratio and temperature under the conditions tested. The toluene conversion remained near-constant at steam partial pressures ranging from 0 to 10 kPa in the temperature range from 393 to 453 K, while the MCH selectivity increased with increasing steam partial pressure. The selectivity for demethylated compounds notably decreased with increasing steam partial pressure. It was hypothesized that Brønsted acid sites on the surface of the support were occupied by H<sub>2</sub>O or hydroxyl groups generated from dissociative H<sub>2</sub>O adsorption. NH<sub>3</sub>-TPD measurements were conducted to investigate the acid sites on the Ni/SiO<sub>2</sub>; prior to TPD, the catalyst was exposed to wet- or dry-Ar at 298 K. The NH<sub>3</sub>-TPD profiles indicated that the wet-gas treatment decreased the number of acid sites, while the acid strength was not affected. These results might suggest that the occupation of the acid sites on Ni/SiO<sub>2</sub> by steam resulted in lesser number of reaction sites available for catalyzing side-reactions.

#### Author contribution

Acquisition of data:

Ryosuke Atsumi, Keisuke Kobayashi, Cui Xieli

Analysis and interpretation of data: Ryosuke Atsumi, Keisuke Kobayashi, Tetsuya Nanba

**Drafting of manuscript:** Ryosuke Atsumi, Tetsuya, Nanba

**Critical revision:** Tetsuya Nanba, Hideyuki Matsumoto, Keigo Matsuda, Taku Tsujimura

#### References

- [1] Bourane, M. Elanany, T. V. Pham, S.P. Katikaneni, Int. J. Hydrogen Energy 41 (2016) 23075–23091.
- [2] F. Alhumaidan, D. Cresswell, A. Garforth, Energy & amp; Fuels 25 (2011) 4217–4234.
- [3] P. Preuster, C. Papp, P. Wasserscheid, Acc. Chem. Res. 50 (2016) 74-85.
- [4] R.B. Biniwale, S. Rayalu, S. Devotta, M. Ichikawa, Int. J. Hydrogen Energy 33 (2008) 360-365.
- [5] H. Kojima, H. Matsumoto, T. Tsujimura, Int. J. Hydrogen Energy 42 (2017) 13444–13453.
- [6] K. Zeng, D. Zhang, Prog. Energy Combust. Sci. 36 (2010) 307-326.
- [7] O. Schmidt, A. Gambhir, I. Staffell, A. Hawkes, J. Nelson, S. Few, Int. J. Hydrogen Energy 42 (2017)30470–30492.
- [8] H. Saleet, S. Abdallah, E. Yousef, Int. J. Appl. Eng. 12 (2017) 3730-3739
- [9] K. Mazloomi, N. Sulaiman, S.A. Ahmad, N.A. Md. Yunus, Int. J. Electrochem. Sci. 8 (2013) 3731-3739 (2013)
- [10] Z. Dobó, Á.B. Palotás, Int. J. Hydrogen Energy 42 (2017) 5649–5656.
- [11] Z. Dobó, Á.B. Palotás, Int. J. Hydrogen Energy 41 (2016) 11849–11856.
- [12] S.D. Lin, M.A. Vannice, Stud. Surf. Sci. Catal. 75 (1993) 861-874.
- [13] S.D. Lin, M.A. Vannice, J. Catal. 143 (1993) 554–562.
- [14] S.D. Lin, M.A. Vannice, J. Catal. 143 (1993) 563–572.
- [15] J.W. Thybaut, M. Saeys, G.B. Marin, Chem. Eng. J. 90 (2002) 117–129.

- [16] S. Chytil, W.R. Glomm, E. Vollebekk, H. Bergem, J. Walmsley, J. Sjöblom, E.A. Blekkan,
- Microporous Mesoporous Mater. 86 (2005) 198-206.
- [17] Z. Liu, J. Mi, Y. Yang, Y. Song, L. Deng, Mater. Lett. 65 (2011) 3548-3551.
- [18] V.V. Pushkarev, K. An, S. Alayoglu, S.K. Beaumont, G.A. Somorjai, J. Catal. 292 (2012) 64–72.
- [19] J. Chupin, N.S. Gnep, S. Lacombe, M. Guisnet, Appl. Catal. A Gen. 206 (2001) 43-56.
- [20] J. Rousset, L. Stievano, F.J.C.S. Aires, C. Geantet, A. Renouprez, M. Pellarin, J. Catal. 197 (2001)
- 335–343.
- [21] P. Kluson, J. Had, Z. Belohlav, L. Cerveny, Appl. Catal. A Gen. 149 (1997) 331-339.
- [22] M. Zieliński, M. Wojciechowska, Catal. Commun. 18 (2012) 1-4.
- [23] L.P. Lindfors, T. Salmi, S. Smeds, Chem. Eng. Sci. 48 (1993) 3813–3828.
- [24] S. Smeds, D. Murzin, T. Salmi, Appl. Catal. A Gen. 125 (1995) 271–291.
- [25] A. Masalska, Appl. Catal. A Gen. 294 (2005) 260-272.
- [26] Á. Szegedi, M. Popova, V. Mavrodinova, M. Urbán, I. Kiricsi, C. Minchev, Microporous Mesoporous Mater. 99 (2007) 149–158.
- [27] G.M.S. ElShafei1, T. Zaki, Gh. Eshaq, M. Riad, Adsorpt. Sci. Technol. 24 (2006) 833-849
- [28] H. Littman, H. Bliss, Ind. Eng. Chem. 51 (2002) 659–662.
- [29] L.P. Lindfors, T. Salmi, S. Smeds, Chem. Eng. Sci. 48 (1993) 3813–3828.
- [30] O.V. Masloboishchikova, E.G. Khelkovskaya-Sergeeva, V.I. Bogdan, T.V. Vasina, L.M. Kustov, Russ.
- J. Phys. Chem. 80 (2006) 551-556.

- [31] J. Choi, S. Zhang, J.M. Hill, Catal. Sci. Technol. 2 (2012) 179–186.
- [32] D.C. Grenoble, J. Catal. 56 (1979) 32–39.
- [33] X. Cui, M. Ishii, T. Tsujimura, T. Ttaniguchi, Y. Hashimoto, T. Nanba, J. Japan Pet. Inst. 62 (2019)67–73.
- [34] R.L. LeRoy, C. T. Bowen, J. Electrochem. Soc. 127 (1980) 1954–1962.
- [35] P. Haug, B. Kreitz, M. Koj, T. Turek, Int. J. Hydrogen Energy 42 (2017) 15689–15707.
- [36] G.N. Maslyanskii, G.L. Rabinovich, Pet. Chem. U.S.S.R. 1 (1962) 104-109.
- [37] G.L. Rabinovich, G.N. Maslyanskii, V.S. Vorob'ev, L.M. Biryukova, I.I. Ioffe, Pet. Chem. U.S.S.R. 13

(1973) 155–160.

- [38] D.P. Upare, S. Yoon, C.W. Lee, J Porous Mater 20 (2013) 1129–1136.
- [39] S. Suganuma, K. Nakamura, A. Okuda, N. Katada, Mol. Catal. 435 (2017) 110–117.
- [40] L. Zhang, W.A. Anderson, S. Sawell, C. Moralejo, 68 (2007) 546–553.
- [41] S. Wang, H.M. Ang, M.O. Tade, 33 (2007) 694–705.
- [42] J. Zhao, X. Yang, 38 (2003) 645-654.
- [43] R.K. Nath, M.F.M. Zain, M. Jamil, 62 (2016) 1184–1194.
- [44] M. Zhu, Z. Tong, Z. Zhao, Y. Jiang, Z. Zhao, (2016).
- [45] T. Areerob, N. Grisdanurak, S. Chiarakorn, (2016) 5538–5548.
- [46] J. Mo, Y. Zhang, Q. Xu, J. Joaquin, R. Zhao, Atmos. Environ. 43 (2009) 2229–2246.
- [47] A. Veksha, E. Sasaoka, A. Uddin, Carbon N. Y. 47 (2009) 2371–2378.
- [48] H. Liu, B. Yang, N. Xue, J. Hazard. Mater. 318 (2016) 425-432.

[49] L. Zhong, C. Lee, F. Haghighat, J. Hazard. Mater. 243 (2012) 340-349

Journal Pre-proof

#### Table & Figures List

- Table 1Specifications of the commercial Ni/SiO2 catalyst.
- Table 2 Major byproducts derived from toluene hydrogenation over Ni/SiO<sub>2</sub> catalyst.

Notably, o-xylene and 1,2-dimethyl cyclohexane were not detected herein, and that all the five-membered

ring compounds detected were saturated.

- Fig. 1 Schematic of the experimental setup.
- Fig. 2 Toluene conversion over the Ni/SiO<sub>2</sub> catalyst vs. the H<sub>2</sub>/toluene ratio with dry-H<sub>2</sub>.
- Fig. 3 MCH selectivity over the Ni/SiO<sub>2</sub> catalyst vs. the H<sub>2</sub>/toluene ratio with dry-H<sub>2</sub>.
- Fig. 4 Byproduct selectivity as a function of the H<sub>2</sub>/toluene ratio over the Ni/SiO<sub>2</sub> catalyst.
- Fig. 5 Toluene conversion over the Ni/SiO<sub>2</sub> catalyst as a function of steam partial pressure (0–10 kPa) at a H<sub>2</sub>/toluene ratio of 1:5.
- Fig. 6 MCH selectivity over the Ni/SiO<sub>2</sub> catalyst as a function of steam partial pressure (0–10 kPa) at a H<sub>2</sub>/toluene ratio of 1:5.
- Fig. 7 Byproduct selectivity over the Ni/SiO<sub>2</sub> catalyst as a function of steam partial pressure (0-10 kPa) at H<sub>2</sub>/toluene ratio = 1:5 and temperatures ranging from 393 to 453 K.
- Fig. 8 Desorbed NH<sub>3</sub> in the exhaust gas during the TPD measurement of Ni/SiO<sub>2</sub> catalysts with and without wet-Ar treatment (1 vol% H<sub>2</sub>O) at 298 K.

Table 1	Specifications	of the commercial	Ni/SiO <sub>2</sub> catalyst.
---------	----------------	-------------------	-------------------------------

Shape	Cylinder
Diameter [mm]	12.7
Height [mm]	2-5
BET surface area [m <sup>2</sup> g <sup>-1</sup> ]	270
Ni content [wt%]	57

ound

#### Table 2 Major byproducts derived from toluene hydrogenation over Ni/SiO<sub>2</sub> catalyst.

Notably, o-xylene and 1,2-dimethyl cyclohexane were not detected herein, and that all the five-membered ring

compounds detected were saturated.

Byproduct group	Carbon number	Compound			
Demethylated compounds	6	Benzene			
	6	Cyclohexane			
Ring-opened products	5	Methylbutane			
	5	Isoprene			
	8	Methylheptane			
	8	Dimethylhexane			
	8	Trimethylpentane			
Six-membered ring compounds	8	m-Xylene			
	8	p-Xylene			
	8	Ethylbenzene			
	8	1,3- and 1,4-Dimethylcyclohexane			
	8	Ethylcyclohexane			
	9	1,3,5-Trimethylbenzene			
	9	1.3.5-Trimethylcyclohexane			
Five-membered ring	6	Methylcyclopentane			
compounds	7	dimethylcyclopentane			
	8	Ethyl methylcyclopentane			
Dimerized compounds	12	Biphenyl			
	13	Methylbiphenyl			



Fig. 1 Schematic of the experimental setup.



Fig. 2 Toluene conversion over the Ni/SiO<sub>2</sub> catalyst vs. the H<sub>2</sub>/toluene ratio with dry-H<sub>2</sub>.



Fig. 3 MCH selectivity over the Ni/SiO<sub>2</sub> catalyst vs. the H<sub>2</sub>/toluene ratio with dry-H<sub>2</sub>.



Fig. 4 Byproduct selectivity as a function of the H<sub>2</sub>/toluene ratio over the Ni/SiO<sub>2</sub> catalyst.

(a) Demethylated compounds, (b) ring-opened compounds, (c) six-membered ring compounds, (d) five-membered

ring compounds, and (e) dimerized compounds.



Fig. 5 Toluene conversion over the Ni/SiO<sub>2</sub> catalyst as a function of steam partial pressure (0–10 kPa) at

H<sub>2</sub>/toluene ratio of 1:5.



Fig. 6 MCH selectivity over the Ni/SiO<sub>2</sub> catalyst as a function of steam partial pressure (0–10 kPa) at

H<sub>2</sub>/toluene ratio of 1:5.



Fig. 7 Byproduct selectivity over the Ni/SiO<sub>2</sub> catalyst as a function of steam partial pressure (0–10 kPa) at H<sub>2</sub>/toluene ratio = 1:5 and temperatures ranging from 393 to 453 K.



Fig. 8 Desorbed NH<sub>3</sub> in the exhaust gas during the TPD measurement of Ni/SiO<sub>2</sub> catalysts with and

without wet-Ar treatment (1 vol% H<sub>2</sub>O) at 298 K.

Partial pressures of H<sub>2</sub>O and NH<sub>3</sub> in Ar were 1 vol%, and the Ar was humidified with deionized water using a

bubbler.