

Addition effect of ruthenium on nickel steam reforming catalysts

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Abstract

Several Ni-based catalysts supported on a mixture of MgO, La₂O₃, and Al₂O₃ were prepared. The catalytic performance in the steam reforming of *m*-cresol was evaluated. In the investigation of the effect of Ru loading added to the Ni-catalyst, it was found that the presence of Ru strongly enhances the catalytic performance of the Ni-based catalyst when increasing Ru loading up to 2 wt%. Effect of Ni loading to the Ru-based catalyst system was also investigated. It was found that the addition of nickel to the Ru-based catalyst up to 15 wt% enhanced significantly the catalytic activity of the catalyst. The lifetime of the Ru–Ni catalysts in the reforming of *m*-cresol was further tested at 750 °C. In agreement with general observations of the use of Ni monometallic catalyst, deactivation of the catalyst due to the carbon deposition reaction already occurred in the reforming of the oxygenated compound. On the other hand, a reasonable high resistant on the carbon deposition in the reforming of *m*-cresol was given by the 2 wt% Ru–15 wt% Ni catalyst system. An effort in improving the strength of the catalyst support with this catalyst system was also conducted, and the catalyst showed significant increase in the stability of the reforming of oxygenated aromatic compound.

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1. Introduction

Hydrogen is an important raw material for the chemical industry and is a clean fuel that can be used in fuel cells and internal combustion engines [1]. The main process for hydrogen production is currently the catalytic steam reforming of methane, light hydrocarbons, and naphtha. Partial oxidation of heavy oil residues and coal gasification are also alternative processes to produce hydrogen. One of the promising approaches to the production of hydrogen from coal is catalytic steam reforming of a liquid product (also known as coal tar), which is generated from coal via carbonization. In this process, coal tar is produced in 3–5% yield. Although the yield is rather low, about 1,920,000 tons of coal tar was produced in Japan in 1995, due to the fact that a large amount of coal was used to produce blast furnace coke. It is very important to utilize coal tar effectively from the viewpoint of coal utilization. Generally, in treating coal tar, the recovered crude tar is distilled in

a distillation tower to give the five standard fractions in order of ascending boiling ranges: light oil, naphthalene oil, creosote and anthracene oil, and pitch [2]. The light oil fraction (boiling range: ca. <195 °C) contains benzene, tar acids and tar bases and resembles crude benzole. The naphthalene oil fraction (boiling range: ca. 195–230 °C) contains naphthalene and a range of tar acids and tar bases. The tar acids and bases are extracted by washing successively with alkali and acid. The neutral fraction usually contains about 30% naphthalene, which is removed either by crystallization and hot processing, continuous fractionation, or by crystallization and centrifugal washing. Pure naphthalene is used to make phthalic anhydride, an intermediate for plasticizer, polyesters and resins. Although petroleum-based phthalic anhydride obtained via *o*-xylene has largely replaced this source, naphthalene is an invaluable component in coal tar. The creosote fraction (boiling range: ca. 230–300 °C) contains substituted naphthalene, the higher boiling tar acids and base oils. The components are not usually separated, and creosotes are used in bulk for timber preservation and for bending with pitch to make road tar. The anthracene oil fraction (boiling range: ca. 300–350 °C) contains mainly polynuclear hydrocarbons, such as anthracene, phenanthrene and pyrene,

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and high boiling tar acids. These oils are used much like creosote and are predominantly a mixture of benzene from light oil, and phenol, cresol and naphthalene from middle and creosote oil. It is a promising one to transfer these fractions to hydrogen via the steam reforming process in the future.

Renewable lignocellulosic biomass can be used as another alternative feedstock for hydrogen production. Two possible technologies that have been explored in recent years are steam gasification [3–6] and catalytic steam reforming of pyrolysis oils [7,8]. Bio-oil derived from the pyrolysis of biomass is an appropriate feedstock for further catalytic steam reforming to give H_2 and CO_2 via a conversion strategy similar to that of catalytic steam reforming of alcohols and oxygenated aromatics.

However, the reforming of organics including aromatic ring, such as coal tar-derived or lignin-derived aromatic phenols, would bring about a problem, which is the carbon deposition taking place preferentially on the catalyst. Thus, the present study has concerned to investigate a series of catalysts having reasonably high activity and stability for production of hydrogen from coal tar-derived oils as well as biomass pyrolysis oils. Special attention has been given in the reforming of coal tar- or lignin-derived aromatic phenols.

Two strategies can be employed to decrease carbon deposits on the catalyst. The first one is based on enhancing steam adsorption on the catalyst with the objective of gasifying any carbon or carbon precursors formed on the catalyst surface. The second strategy aims at modifying the surface reactions via the addition of other metals.

The steam adsorption capability can be significantly improved by promoting the conventional Ni-alumina or Ni-silica/alumina formulations with Ca and/or K. An alternative is the use of magnesia as a magnesium–aluminum spinel which enhances steam adsorption and can be prepared as high-surface-area refractory ceramic pellets [8–10].

The major challenge in the reforming of organics involving aromatic ring is the loss of catalyst activity due to the deposition of coke or carbonaceous material on the catalyst surface. Thus, the present study concerns to investigate a series of catalysts having reasonably high activity and stability for production of hydrogen from these feedstocks such as coal tar, bio-oil, etc. Moreover, *m*-cresol was used as a representative model compound for the coal tar or lignin-derived oils; and its steam reforming test was carried out to evaluate the performance of the catalysts.

2. Experimental

2.1. Catalyst preparation

2.1.1. Catalyst preparation 1 (metal/ Al_2O_3 (M1))

The catalysts were prepared using a conventional impregnation method. γ - Al_2O_3 support exclude (\varnothing 3 × 5 mm length) obtained from Ketjen was used as a support

and was crushed and sieved to 20–30 mesh prior to use. Various nitrate salts (nickel nitrated hexahydrate, magnesium nitrate hexahydrate, and lanthanum nitrate hexahydrate) and ruthenium chloride solutions were used. The alumina was thoroughly mixed with an aqueous containing magnesium nitrate and lanthanum nitrate and then dried in an oven at 110 °C for 24 h (refer to Al_2O_3 (M1)). This modified support was then calcined at temperatures between 750 and 1000 °C for 6 h. Ni and Ru catalysts were prepared by impregnation of the modified Al_2O_3 support with aqueous solutions of the precursor ($Ni(NO_3)_2 \cdot 2H_2O$ or $RuCl_3 \cdot nH_2O$). The mixture was dried at 110 °C for 24 h and then calcined at 750 °C for 6 h or reduced under hydrogen stream with gas hourly space velocity (GHSV) of 1000 at 600 °C for 3 h. Ni–Ru bimetallic catalysts were prepared by impregnated successively with aqueous solution of $RuCl_3$ and $Ni(NO_3)_2$. The mixture was then treated by similar procedure above. The compositions of the Ni/ $MgO \cdot La_2O_3 \cdot Al_2O_3$ (Ni/ Al_2O_3 (M1)), Ru/ $MgO \cdot La_2O_3 \cdot Al_2O_3$ (Ru/ Al_2O_3 (M1)), and Ni–Ru/ $MgO \cdot La_2O_3 \cdot Al_2O_3$ (Ni–Ru/ Al_2O_3 (M1)) catalysts are listed in Table 1.

2.1.2. Catalyst preparation 2 (metal/ Al_2O_3 (M2))

In this catalyst system, the catalyst support was firstly prepared. This was accomplished by physical mixing alumina (boehmite), magnesium oxide, and lanthanum oxide. This mixture was pressed to form a disc, dried at 110 °C for 24 h, and then calcined at 750 °C for 6 h. The support calcined was crushed and sieved to 20–30 mesh. Subsequently, the impregnation with nickel nitrate and ruthenium chloride was carried out in a similar way as mentioned above. After that, the precursors was dried at 110 °C for 24 h and then calcined at 750 °C for 6 h. The composition of the Ni–Ru/ $MgO \cdot La_2O_3 \cdot Al_2O_3$ (Ni–Ru/ Al_2O_3 (M2)) catalyst is listed in Table 1.

2.2. Apparatus and procedure

Steam reforming runs were conducted in a laboratory bench scale tubular reactor. A schematic diagram of the experimental setup is shown in Fig. 1. *m*-Cresol and water were taken in separate burettes and pumped by reciprocating pumps to a preheater. Flow rates of water and *m*-cresol were kept at 0.1 and 0.4 cm^3/min , respectively (or $H_2O/C=3.7$, $WHSV=3\ h^{-1}$). In the preheater, water and *m*-cresol were

Table 1
Compositions of catalysts prepared

	Metal/ Al_2O_3 (M1) (mass%)	Metal/ Al_2O_3 (M2) (mass%)
Ni	0.0–20	15.0
Ru	0.0–3.0	2.0
MgO	10.0	10.0
La_2O_3	5.0	5.0
Al_2O_3	Balance	68.0

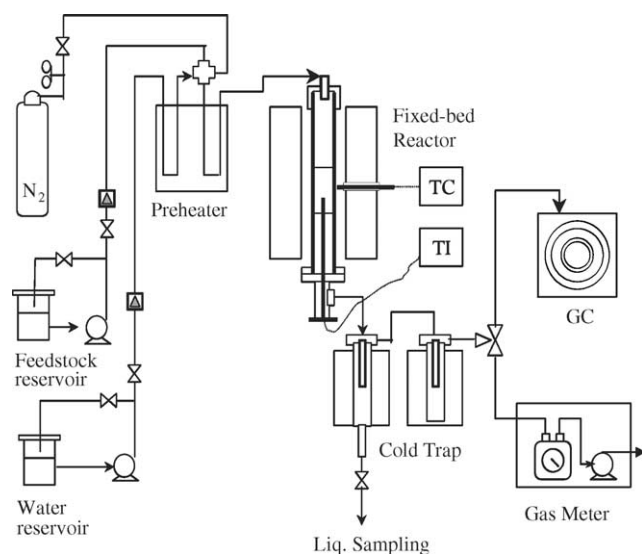


Fig. 1. Schematic diagram of the experimental apparatus.

mixed and preheated to approximately 400 °C. The preheated mixed stream then entered the reactor.

The tubular reactor was made of a 30 cm length of stainless steel pipe (SUS316, ID 0.8 cm). The catalyst bed placed at the center of the tubular reactor had a typical height of 5 cm. A metered flow of nitrogen was mixed with the reaction effluent at the reactor inlet. This was necessary because nitrogen was used as an internal standard in the subsequent gas chromatographic analysis. The reactor effluent together with the added nitrogen passed through two condensers connected in series. Most of the unconverted cresol, liquid products, and steam condensed in the first condenser. Methanol as the coolant in the condensers was cooled by a cooler at about −40 °C. The noncondensable gases passed through a sample valve to a gas flow meter and were then vented. During the course of a run, the total condensed liquid, together with the volume and composition of the product gases, was measured at regular intervals. Initially, the composition and product flow rates varied with the run time but achieved a steady state in approximately 30 min. The noncondensable gases were analyzed by GC-TCD. Determination of concentration of hydrogen in the gas was done on a Porapak Q column using nitrogen as the carrier gas, whereas that of CO, CO₂, CH₄, and N₂ was done on a Unibeads C column using helium as the carrier gas.

The conversion was calculated by dividing the total carbon in gaseous products with the carbon in the feed, as described in Eq. (1)

Conversion (%)

$$\begin{aligned}
 &= 100 \times [\text{C}] \text{ in gaseous product} / [\text{C}] \text{ in feed} \\
 &= 100 \times ([\text{C}] \text{ in CO} + [\text{C}] \text{ in CO}_2 \\
 &\quad + [\text{C}] \text{ in CH}_4) / [\text{C}] \text{ in cresol}
 \end{aligned} \quad (1)$$

where [C] represents the amount of carbon atom.

The total gas flow rate was calculated by the flow rate of nitrogen gas (F_{N_2} : a constant during the reaction, mL/min), as described in Eq. (2)

Flow rate of gaseous product (mL/min)

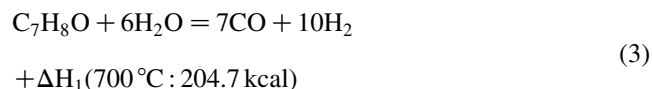
$$= F_{\text{N}_2}(1/X_{\text{N}_2} - 1) \quad (2)$$

X_{N_2} is the volume fraction of N₂ in the gaseous product.

3. Results and discussion

3.1. Initial experiment

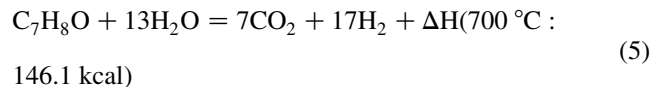
The activities of a series of catalysts in the steam reforming of *m*-cresol were tested. The steam reforming of *m*-cresol should proceed according to the following reaction:



This reaction is followed by the water–gas shift reaction

$$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 + \Delta H_2(700^\circ\text{C} : -8.3 \text{ kcal}) \quad (4)$$

Therefore, the overall process can be represented as follows:



According to the above equations, the theoretical molar ratio of steam/feed is 13 (or, steam (S) to carbon (C) mole ratio of 1.86). In the present study, a steam/feed molar ratio of 25.9 ($S/C = 3.7$) was used in the temperature range of 500–800 °C, and at a constant space velocity of 3 g-feed/g-catalyst h^{−1}. Preliminary runs were carried out to study the effect of nickel loading in the Ni/Al₂O₃(M1) catalyst system on the steam reforming of *m*-cresol because one of the most popular catalyst used in the steam reforming of hydrocarbon is nickel-based system. The metal loading of 15 and 20 wt% was chosen according to usual concentration used in the steam reforming. The conversion of *m*-cresol over two metal loading (15 and 20 wt% Ni) on the Ni/Al₂O₃(M1) catalyst system as a function of reaction temperature is shown in Fig. 2. The experimental result in the absence of active metal-nickel was also shown in the figure as a reference for comparison with the researched catalysts. The thermal decomposition of *m*-cresol, i.e. the reaction in the absence of nickel, hardly occurred at the temperature range studied. For instance, the conversion of *m*-cresol was only about 12% even at the highest temperature of 800 °C. Nickel seems to be an active species in the reforming of oxygenated aromatic compounds. The reforming of *m*-cresol proceed at a perceptible extent even at the lowest temperature studied (500 °C) and a complete conversion is achieved at temperature of 750 °C over both 15 and 20 wt%

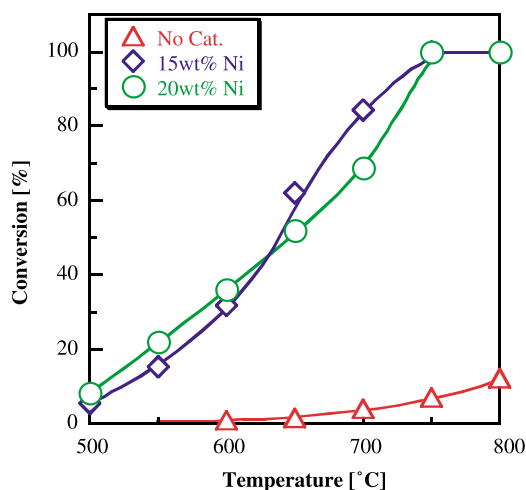


Fig. 2. Conversion of *m*-cresol over two Ni/Al₂O₃(M1) catalysts.

Ni/Al₂O₃(M1) catalysts. The two catalysts of different Ni-loadings showed similar catalytic activity at lower temperatures (500–600 °C), but the activity is lowered by increasing the Ni-loading at the higher temperatures. This observation also agreed with the reported result by Bangala et al. who investigated the effect of the nickel loading on alumina support on the steam reforming of naphthalene [9,10]. They reported that the conversion and gas yield increased with metal loading up to 15 wt% and declined at higher loading. These results should be attributed to the maximum loadings of the Al₂O₃ support which may be reached at close to 15 wt% of nickel loading. Once the maximum loadings was reached at 15 wt% Ni, then further increase in the metal loading to 20 wt% should result in decreasing the metal dispersion; consequently, this would decrease the catalyst activity.

The compositions of produced gas as a function of reaction temperature for 15 and 20 wt% Ni/Al₂O₃(M1) is shown in Fig. 3a and b, respectively. The product consists mainly of H₂, CO, and CO₂ along with minor amount of CH₄. In the case with 15 wt% Ni/Al₂O₃(M1) catalyst (Fig. 3a), as the temperature is raised from 500 to 750 °C, the concentration of H₂ and CO₂ in the gaseous products somewhat decreases (from 71 to 65% and from 22 to 18%

for H₂ and CO₂, respectively), while that of CO increases significantly from 2 to 20%. The significant increase in the CO concentration should be expected as a result of the thermodynamic equilibrium of the water–gas shift reaction as Eq. (4), which is exothermic reaction and raising temperature should cause the formation of much CO. On the other hand, the observed methane concentration is very low between the temperature ranges, i.e. not more than 0.2%. This observation leads to the overview of a reaction mechanism that an adsorbed organic molecule reacts with water on the catalyst surface until all carbon atoms are converted to CO or CO₂. Thus, methane may not be a reaction intermediate or primary product, but may be formed from CO through the methanation reaction (as shown in the following reaction), which may not be efficiently catalyzed under the reaction conditions used



The greatest obstacle to the successful industrial application is the relevant formation of coke which deactivates the catalysts, notably in the case of nickel-based catalyst [11]. Conventional nickel catalysts, which have been essentially designed for paraffinic hydrocarbon reforming, are not necessarily well suited to the molecular structure present in the coal tar, especially oxygenated aromatic compounds such as phenols. In fact, the catalyst lifetime of 15 wt% Ni/Al₂O₃(M1) in the reforming of *m*-cresol was only a several minutes after the condition of steady state was reached, as shown in Fig. 4. It is necessary to improve formulations and preparation methods of catalysts. The conceptual strategy is based on modifying the surface reactions via the addition of other active metals.

It was suggested by Suzuki et al. [12] that ruthenium-based catalyst is very effective in preventing the carbon deposition during steam reforming. Furthermore, ruthenium metal itself is low in price than the other noble metals. Thus, in the following experiments the effect of addition of ruthenium to Ni/Al₂O₃(M1) on the catalytic performance towards the reforming of *m*-cresol was investigated, and the results will be discussed below.

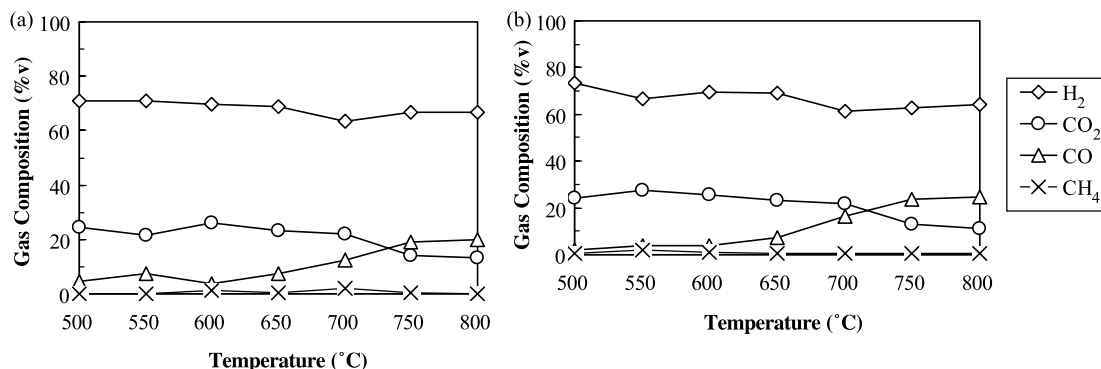


Fig. 3. Compositions of gas from catalytic steam reforming of *m*-cresol over 15% Ni (a) and 20% Ni (b) catalysts.

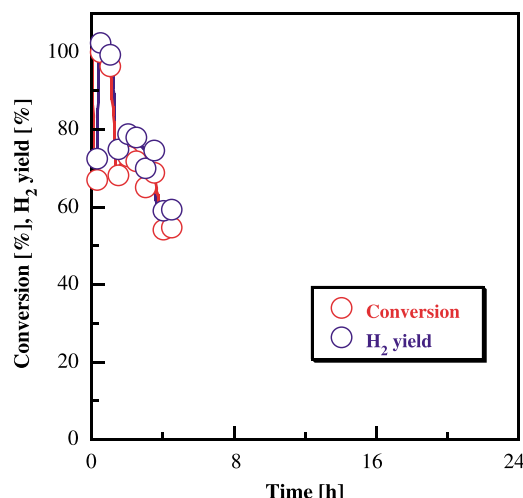


Fig. 4. Catalytic lifetime test of 15 wt% Ni/Al₂O₃(M1) in the steam reforming of *m*-cresol.

3.2. Effect of Ru loading in Ni–Ru/Al₂O₃(M1) system on catalytic performance

The effect of Ru loading in the Ni/Al₂O₃(M1) catalyst was investigated under the same condition as mentioned above. Fig. 5 presents effects of temperature and Ru-loading on the conversion of *m*-cresol. As expected, the conversion increased with raising temperature for all catalysts; complete conversion of cresol was observed at temperature of 650–750 °C depending on the amount of Ru-loading. As can be seen from Fig. 5, the catalytic performances of the Al₂O₃(M1)-supported bimetallic Ni–Ru catalysts are strongly dependent on the Ru content. The data show that the addition of Ru up to 2 wt% improves the activity of the monometallic Ni-catalyst at all reaction temperatures. Addition of Ru content to 3 wt%, however, decreased the catalytic performance towards *m*-cresol conversion as compared to the corresponding results with 2 wt% Ru.

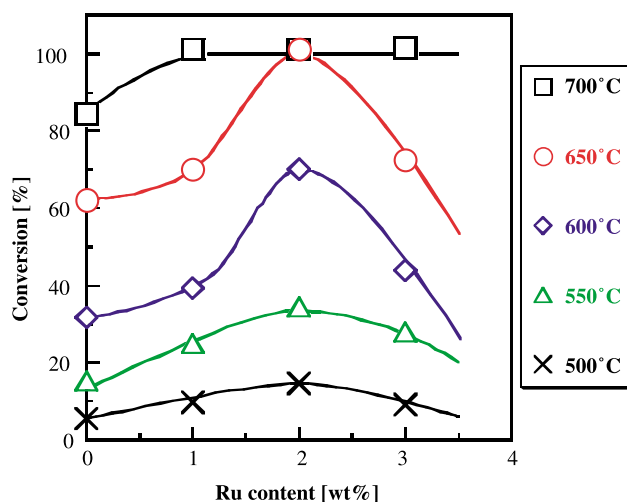


Fig. 5. Plots of *m*-cresol conversion versus amount of Ru-loading to 15 wt% Ni/Al₂O₃(M1) catalyst at various temperatures.

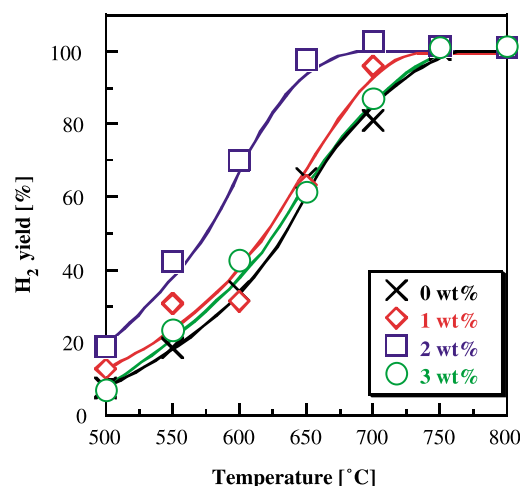


Fig. 6. Effects of temperature and amount of Ru-loading to 15 wt% Ni/Al₂O₃(M1) catalyst on hydrogen yield.

This may be due to that the hydrothermal atmosphere at high temperature resulted in sintering of Ru cluster dispersed on the catalyst which has higher Ru loading, reducing the dispersion of Ru and the catalytic activity.

The hydrogen yield over all combination of Ru–Ni catalysts as a function of temperature is presented in Fig. 6. The yield was expressed on the basis of possible amount of hydrogen yielded from stoichiometric conversion according to Eq. (5). An excellent hydrogen yield was obtained with adding Ru of 2 wt% to the Ni-catalysts. Furthermore, the increase in the hydrogen yield with this catalyst combination than the other at 750 °C even giving the same level of conversion is due to the enhancement of the water–gas shift reaction.

Catalytic activity results discussed above have shown that in the case of alumina material supported samples, the presence of Ru strongly enhances the catalytic activity of the Ni-based catalyst with increase in Ru-loading up to 2 wt%. Recently, Crisafulli et al. [13] reported that, in the study on the effect of addition of Ru onto supported Ni-catalyst towards the reforming of methane, addition of Ru strongly enhances the catalytic performance of the Ni/SiO₂ sample, both in term of activity and stability. On the basis of FT-IR spectra of adsorbed CO, H₂ and O₂ chemisorptions and temperature programmed reduction measurements, they suggested that the strong improvement in the activity and stability of silica supported Ni–Ru bimetallic samples was due to an increase in the metallic dispersion of Ni as a consequence of the formation of Ni–Ru clusters with the surface mainly covered by Ni. An enrichment of the catalyst surface in Ni has also been reported by Rinkowski et al. [15] in the case of Ni–Pt bimetallic systems. A similar effect of coverage of the Ru atoms has also been described on Ru–Cu systems supported on silica [14]. According to the study reported by Rinkowski et al. [15], it is probable that the formation of bimetallic clusters of ruthenium and nickel occurs as they are reduced. From the above considerations,

it should be concluded that the main effect of the presence of Ru in the Ni–Ru/Al₂O₃ catalyst favors the formation of small Ni particles on the surface; consequently, this enhances the catalytic activity of the catalyst.

3.3. Effect of Ni loading to Ni/Ru/Al₂O₃(M1) catalyst system on catalytic performance

Effect of Ni-loading to the Ni/Ru/Al₂O₃(M1) catalyst system was further investigated to provide the composition of Ni–Ru on the support that has an excellent catalytic performance in the steam reforming of oxygenated compounds. In the following experiments, the Ru-content of 2 wt% was selected since at this concentration it has given the excellent performance as described in the above results. On the other hand, the Ni-content was varied in the range of 0–20 wt%. Experiments were also conducted under similar conditions as mentioned above.

Figs. 7 and 8 present effects of temperature and amount of Ni-loading to 2 wt% Ru/Al₂O₃(M1) catalyst on the *m*-cresol conversion and H₂ yields, respectively. As described in the previous results, the addition of a small amount of Ru to Ni-catalyst enhanced substantially the catalytic activity of the Ni-catalyst. However, the Ru monometallic sample did not show to be an active species in the reforming of *m*-cresol; the conversion over this catalyst only reached a level of 12% even at higher temperature of 750 °C. Loading 10 wt% Ni to the Ru-catalyst enhanced dramatically the catalyst activity, where the complete conversion of *m*-cresol was achieved at 700 °C. The significant addition effect of Ru to the Ni-catalyst was continuously observed as increasing the Ni-loading up to 15 wt%, which should be the maximal loading of Ni for a monolayer dispersion of Ni on the M1 support as mentioned above. On the other hand, only a slight addition effect of Ru was observed in the case of 20 wt% Ni-catalyst (comparing Figs. 2 and 7). As mentioned above, the dispersion of Ni on the 20% Ni-catalyst should be lower

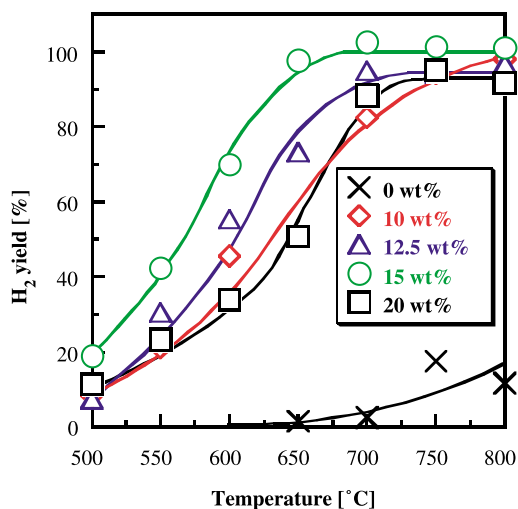


Fig. 8. Effects of temperature and amount of Ni-loading to 2 wt% Ru/Al₂O₃(M1) catalyst on hydrogen yield.

than other lower Ni loadings catalysts. Therefore, the addition effect of Ru on the dispersion of Ni on 20% Ni-catalyst was not significant comparing with other lower Ni loading catalysts.

The above results clearly indicate that the catalytic activity in the steam reforming of *m*-cresol is not given by the presence of Ru species (at concentration up to 2 wt%), but is given by the presence of Ni species. Thus, the enhancement of the catalytic activity of Ni–Ru bimetallic catalysts as compared to the Ni monometallic catalyst should be attributed to that the presence of small amount of Ru improves the metal dispersion of Ni covering the catalyst surface via the formation of a Ni–Ru cluster.

3.4. Stability test of catalysts

The following experiments were conducted to test the lifetime of several research catalysts in the reforming of

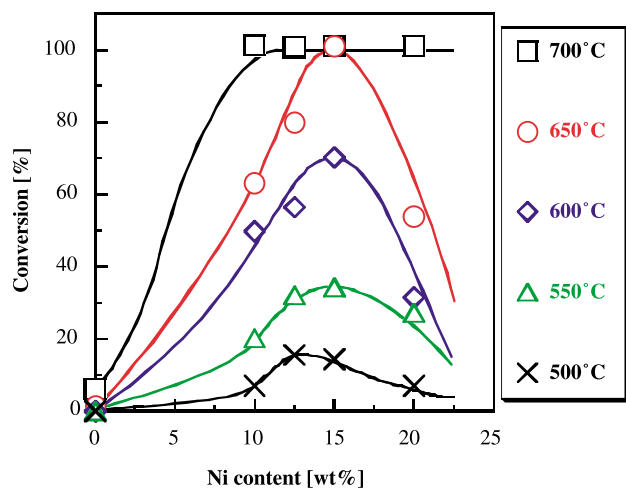


Fig. 7. Plots of *m*-cresol conversion versus amount of Ni-loading to 2 wt% Ru/Al₂O₃(M1) catalyst at various temperatures.

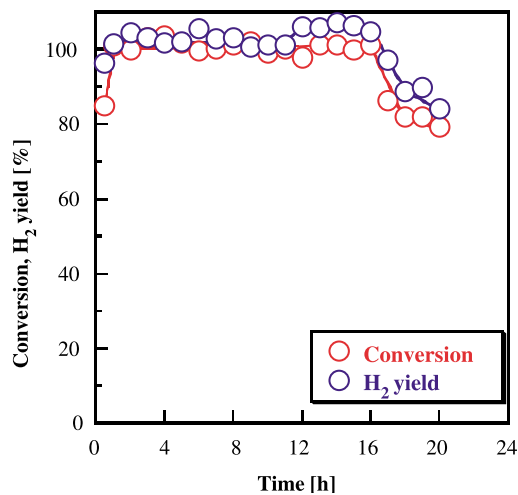


Fig. 9. Catalytic lifetime test of calcined 15% Ni–2% Ru/Al₂O₃(M1) for reforming of *m*-cresol (the support was calcined at 750 °C).

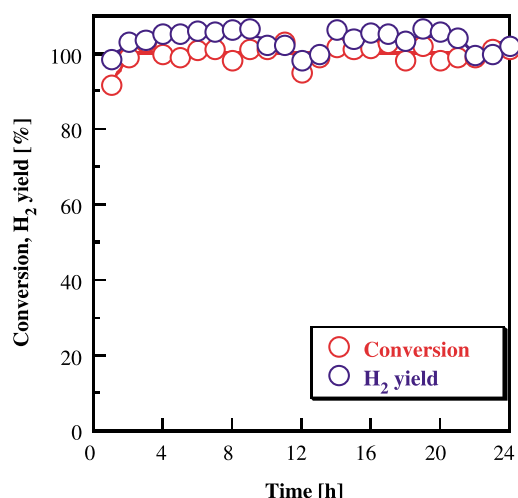


Fig. 10. Catalytic lifetime test of calcined 15% Ni-2% Ru/Al₂O₃(M2) for reforming of *m*-cresol (the support was calcined at 750 °C).

m-cresol. The steam reforming experiments were carried out at 750 °C, S/C ratio of 3.7, and at space velocity of 3.0 g-feed/g-catalyst h⁻¹.

As shown in Fig. 4, in the case of 15 wt% Ni/Al₂O₃(M1) catalyst, a complete conversion of carbon in *m*-cresol to CO, CO₂ and CH₄ is reached during the initial reaction times (30–60 min), and then the conversion decreases rapidly to a level of about 50% after testing for 4 h. The reforming reaction could not be performed continuously since the pressure in the reactor increased drastically due to the carbon blocking. In similar tendency, the overall gas and H₂ yields decrease after 1 h of feeding *m*-cresol. The deactivation of the conventional Ni/Al₂O₃ due to the carbon deposition is generally observed in the steam reforming of organic compounds, especially reforming of higher molecular weight compounds and aromatic compounds. It was reported that the deactivation of this kind catalyst due to the carbon deposition in the steam reforming of kerosene occurred for 24 h on stream [12]. As observed in the present study, it seems that the carbon deposition in the catalytic reforming of oxygenated aromatic compounds, such as cresol, occurs more quickly.

The catalytic lifetime test of bimetallic 15 wt% Ni-2 wt% Ru/Al₂O₃(M1) was carried out as shown in Fig. 9. Different from the monometallic Ni/Al₂O₃(M1) catalyst system, the carbon conversion of *m*-cresol is maintained constant at about 98–100% for 17 h in the case of 15 wt% Ni-2 wt% Ru/Al₂O₃(M1) catalyst. Since these catalysts were prepared by similar ways, as mentioned previously, thus it clearly indicates that the addition of Ru species to the Ni/Al₂O₃ catalyst system can effectively improve the stability of the Ni-catalyst in a hydrothermal atmosphere at high temperature and extend catalyst lifetime during the steam reforming of oxygenated aromatic compounds. Further, no significant deactivation was observed in all the run time (24 h) in the case of 15 wt% Ni-2 wt%

Ru/Al₂O₃(M2) catalysts as shown in Fig. 10. This indicates that the support also plays an important role to inhibit the formation of coke. As shown in Figs. 9 and 10, the Ni-Ru bimetallic catalyst system gives an excellent hydrogen yield, i.e. over 98% of the potential hydrogen production from the stoichiometry. As comparison, the monometallic Ni-catalyst gives the maximum hydrogen yield of about 82%, which was about 15% lower than that in the case of the bimetallic Ni-Ru catalyst. These results therefore confirm that the bimetallic Ni-Ru catalyst system can efficiently convert oxygenated hydrocarbon to hydrogen, which may be through the enhancement for the water-gas shift reaction.

4. Conclusions

The steam reforming reaction of *m*-cresol as a model compound of a low reactivity present in the coal tar fractional oil was carried out by using several the Ni-based catalysts prepared with different supports. It was found that the hydrogen rich gas was effectively able to be generated in the steam reforming of *m*-cresol. Compared with Ni-catalysts, Ru-Ni catalysts show excellent performance in the reforming reaction. This means that the addition of Ru onto Ni-catalysts improved remarkably the catalytic activity and stability of Ni-catalysts. It was found that the support also plays an important role to inhibit the formation of coke, i.e. to improve the stability of the catalyst on stream. The combination of 15 wt% Ni-2 wt% Ru/MgO-La₂O₃-Al₂O₃ catalyst gave the best catalytic activity and longer lifetime.

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