Precious metal-promoted Ni–Mg–Al–Fe–O catalyst for hydrogen production with fast startup via catalytic partial oxidation of butanol

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ARTICLE INFO

Article history:
Received 8 May 2014
Received in revised form 21 November 2014
Accepted 27 November 2014
Available online 17 December 2014

Keywords:
Catalytic partial oxidation of butanol for hydrogen production
Rhodium
Ni–Mg–Al–Fe–O catalyst
LDH-derived catalyst

ABSTRACT

The layered double hydroxides (LDH)-derived Ni–Mg–Al–Fe–O catalyst with/without precious metals of Rh, Ir, Ru and Pt was prepared by co-precipitation and impregnation, and tested in catalytic partial oxidation (CPOX) of butanol for fast and variable hydrogen production. The results of X-ray diffraction (XRD), X-ray photoelectron spectra (XPS) and temperature-programmed reduction (TPR) indicate that the Ni–Mg–Al–Fe–O catalyst without reduction has an induction period up to 8 h at 700 °C in the CPOX process because of the slow reduction of Ni species in solid solution of Mg(Ni)O during the CPOX process. With promotion of Rh in Ni–Mg–Al–Fe–O, there was high initial activity near 4.1 mol-H2/mol-butanol because the reducibility was improved and the Ni0 species emerged in the beginning and remained stable, suggesting that the Rh-NMAF catalysts can be a promising candidate with high initial activity and stability in CPOX of butanol for hydrogen production, especially for variable hydrogen supply for on-board applications. The Ni–Mg–Al–Fe–O catalyst promoted by Ir, Ru and Pt also showed potential in CPOX of butanol for hydrogen production.

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Introduction

Hydrogen has been viewed as a clean energy carrier, especially for on-board applications, e.g., vehicles powered by proton exchange membrane (PEM) fuel cells. Storing gaseous hydrogen at high pressure or storing liquid hydrogen near 20.3 K compromises the convenience of small-scale applications [1,2]. Producing hydrogen onsite via processing of energy-dense resource, e.g., liquid fuels, shows advantages for...
powering the aforementioned apparatuses with a longer endurance. Hydrogen can be produced via steam reforming (SR) of traditional fossil resources, e.g., natural gas and coal, which brings about emission of additional greenhouse gases. Liquid alcohols from fermentation of bio-mass are alternative renewable energy-dense resources, and can also be used as the feed of SR for hydrogen production. SR of light alcohols, e.g., bio-ethanol, has long been studied, and is proved an effective route for hydrogen production with high yield [3].

SR is an endothermic process, which needs heat to be sustained. Besides SR, there are exothermic options for hydrogen production: oxidative steam reforming (OSR) or auto-thermal reforming (ATR) and catalytic partial oxidation (CPOX) [4,5]. ATR/OSR and CPOX include the exothermic reaction of oxidation, and can adjust the reaction heat via adjusting the ratio of O2/fuel in the feed, while ATR/OSR includes water in the feed and a high H2 yield can be obtained [5–8]. ATR of ethanol (Eq. (1)) and CPOX of ethanol (Eq. (2)) have been studied over catalysts with nickel, cobalt and precious metals, and proved being an effective route for hydrogen production [9–11].

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} + \frac{3}{2} \text{O}_2 + \text{H}_2\text{O} &= 2\text{CO}_2 + \text{5H}_2 + 4.65 \text{kJ} \quad (1) \\
\text{C}_2\text{H}_5\text{OH} + \text{O}_2 &= \text{CO}_2 + \text{CO} + 3\text{H}_2 + 64.35 \text{kJ} \quad (2) \\
\text{C}_4\text{H}_9\text{OH} + \frac{3}{2} \text{O}_2 + \text{H}_2\text{O} &= 3\text{CO} + \text{CO}_2 + 6\text{H}_2 + 36.88 \text{kJ} \quad (3) \\
\text{C}_4\text{H}_9\text{OH} + 2\text{O}_2 &= 3\text{CO} + \text{CO}_2 + 5\text{H}_2 + 102.01 \text{kJ} \quad (4)
\end{align*}
\]

Besides ethanol, n-butanol is an attractive renewable fuel and has a higher energy density than ethanol, increasing the economics for storage and transport associated with ethanol [12]. N-butanol can be obtained via fermentation of starch resources as well as bio-mass using yeasts and bacteria, such as Escherichia coli and Clostridia, which were reported effective to break down and ferment bio-mass, especially from the extra abundant cellulosic resources [12–14]. Meanwhile, compared with ethanol, the solubility of n-butanol in water is about 73 g/L or butanol/water = 0.08 (mass) at 25 °C, which is too low for OSR/ATR of butanol (Eq. (3)), because a ratio of butanol/water = 1 (molar) or 4.12 (mass) is needed for the OSR/ATR reaction. Therefore, considering the feeding system, CPOX of butanol without water, e.g., C4H9OH + 2O2 (Eq. (4)), can be more attractive for hydrogen production [15,16].

CPOX of butanol has been tested over precious metals-supported catalysts, e.g., Rh/x-Al2O3 with 1.0 wt% of Rh for auto-thermal partial oxidation of n-butanol from LD Schmidt’s group [17], in which a H2 selectivity of about 55% (or 2.75 mol-H2/mol-butanol). Another catalyst of Rh/γ-Al2O3 with 0.7353 g of Rh was prepared by Lee IC’s group [18], tested in CPOX of iso-butanol, and produced a selectivity to H2 at 62.92%, which is corresponding to about 3.15 mol-H2/mol-butanol.

In the previous work, LDH-derived Ni-based catalysts were prepared and tested in CPOX of n-butanol for hydrogen production, as reported by Huang et al. [16], in which the reduced Ni–Mg–Al–Fe–O catalyst produced a yield near 4.03 mol-H2/mol-butanol with feed of O2/butanol = 2.0. Characterizations indicate that about 27.0% of Ni0 in solid solution of Mg(Ni)O was obtained after reduction, and remained stable in the 31-h CPOX test.

For practical applications, hydrogen supply without delay during startup and re-startup is a vital factor, especially for on-board applications. Therefore, the reduction procedure, which may last hours in the previous CPOX test, was eliminated in the present work, and the Ni–Mg–Al–Fe–O catalyst without reduction produced a low initial activity with an induction time up to 8 h, which is still too long to be accepted for fast startup in on-board applications.

To narrow down or even eliminate the induction period, in the current work, higher startup temperatures were tested. Meanwhile, precious metals, which were widely used as promoters in Ni-based catalysts and Co-based catalysts because spillover of hydrogen atoms over precious metals is helpful to reduce Ni species and Co-clay catalysts [19,20], were introduced in the Ni–Mg–Al–Fe–O catalyst to improve the initial activity without delay of hydrogen supply. The crystal phases and valences of Ni species over surface of the Ni–Mg–Al–Fe–O catalyst were studied to target the variation of the catalyst during CPOX test and thus to improve the catalytic performance.

Experimental

Preparation

The Ni–Mg–Al–Fe–O catalyst was prepared by co-precipitation [16]. The aqueous solution of nitrate salts of nickel, magnesium, iron and aluminum (Alfa Aesar) was prepared at Ni/Mg/Al/Fe = 0.35/2.65/0.5/0.5 (molar), and precipitated with mixed solution of sodium carbonate and sodium hydroxide as precipitator at ratios of CO32−/OH− = 1/16 and (total of metal cation electron charge)/OH− = 1/8. The precipitation was conducted at pH 10 ± 0.5, aged at 78 °C for 24 h, filtered and washed with deionized water for 3 times, dried at 105 °C for 24 h, and calcined at 650 °C for 4 h. The obtained oxide was named as NMAF.

Precious metal-promoted catalysts were prepared by incipient wetness impregnation. The solutions of rhodium chloride, iridium chloride, ruthenium chloride and platinum chloride (Alfa Aesar) were prepared firstly, and were impregnated into the NMAF catalyst, respectively. After drying at 105 °C for 4 h, these catalysts were calcined at 650 °C for 4 h. The loading of precious metals was 0.25% (mass). The catalysts were named as Rh-NMAF, Ir-NMAF, Ru-NMAF and Pt-NMAF, respectively.

Catalytic performance test

The catalytic performance in CPOX of butanol was tested in a continuous flow fixed-bed reactor with an inner diameter of 4 mm. 100 mg of catalyst (20–40 mesh) was loaded in the reactor, heated to 700 °C in nitrogen, and reduced in hydrogen at 700 °C for 2 h for reduction treatment. The feed of butanol was pumped by a plunger pump (LC-20AD, Shimadzu), evaporated in an evaporator at 160 °C, mixed with air at a ratio of O2/butanol = 2.0, and introduced into the fixed-bed reactor.
Type-K thermocouples were used to detect the temperatures of furnace and backface of catalyst bed. The tail gas was connected via a heated line and analyzed on-line by a gas chromatography (GC2014, Shimadzu) with TCD and FID. Nitrogen in air was used as internal standard. The following parameters were defined to measure the catalytic performance.

\[
X_{\text{butanol}} = \frac{F_{\text{butanol in}} - F_{\text{butanol out}}}{F_{\text{butanol in}}}
\]

\[
S_i \text{ carbon-containing product} = \frac{n_i (F_{\text{butanol in}} - F_{\text{butanol out}})}{F_{\text{butanol in}}}
\]

\[
Y_{H_2} = \frac{F_{H_2 \text{ product}}}{F_{\text{butanol in}}}
\]

In the above equations, \(F_i\) in or out is the molar flow rate of \(i\) species at the inlet or outlet of the reactor. \(X_{\text{butanol}}\) is the conversion of butanol, \(S_i\) is the selectivity to the \(i\) species, \(n_i\) is the stoichiometric factor between butanol and carbon-containing products, and \(Y_{H_2}\) is the yield of \(H_2\) based on the input butanol. The mass balance on carbon and hydrogen typically has a margin of error of ±3%.

**Characterizations**

To screen the crystal phases of Ni-based catalysts, X-ray diffraction (XRD) was conducted by an X-ray diffractometer (D5000, Siemens) with a graphite monochromator for Cu Kα radiation at 40 kV and 30 mA.

To find the electronic properties of surface nickel species, X-ray photoelectron spectra (XPS) were recorded to screen catalysts by a spectrometer (Axis Ultra DLD, Kratos) using Al Kα radiation (1486.6 eV). The binding energies were calibrated relative to the C1s peak at 284.6 eV from the carbon contamination of the samples.

To check the reducibility of catalysts, temperature-programmed reduction (TPR) was carried out in a downstream fixed-bed reactor at atmospheric pressure. Calcined samples were stabilized to a gas with 5.0% \(H_2\) in a \(H_2/N_2\) mixture, and then the temperature was increased from room temperature to 800 °C at 10 °C/min. The uptake of hydrogen was recorded by a thermal conductivity detector (TCD).

**Results and discussion**

**CPOX test of NMAF**

In the previous work [16], the NiMgAlFe (Ni0.35Mg2.65Al0.5Fe0.5O4.5) catalyst was reduced with hydrogen at 700 °C, tested in catalytic partial oxidation (CPOX) of butanol with high-purified oxygen, and produced a \(H_2\) yield near 4.03 mol-\(H_2\)/mol-butanol in a 31-h test. For practical application, air, instead of high-purified oxygen, was fed with butanol in a longer CPOX test for 130 h in the current work, and there was still a stable activity for hydrogen production: as shown in Fig. 1, the hydrogen yield remained stable near 4.1 mol-\(H_2\)/mol-butanol, and \(CO_2\) and \(CO\) were the main products with selectivity near 17.4% and 74.5%, respectively.

7.3% of carbon existed as \(CH_4\). Only trace of by-products, e.g., \(C_3H_6\), \(C_2H_4\) and \(C_2H_6\), with selectivity of less than 0.8% was found in the product gas. During the CPOX test, the backface temperature of catalyst bed was monitored, and remained relatively stable within a range of 708–715 °C, which is slightly higher than the temperature of the tubing furnace at 700 °C.

For practical applications of CPOX, especially for on-board applications, e.g., fuel cell-powered vehicles, a fast startup and high initial activity without delay of hydrogen supply are vital factors [2]. Reduction procedure, which lasts hours before reaction, is a drawback and was then eliminated in the following tests. As shown in Fig. 2(A), for the NMAF catalyst without reduction, there was a startup time up to 8 h for CPOX at 700 °C: the conversion of butanol remained near 100%, but the \(H_2\) yield merely started near 1.68 mol-\(H_2\)/mol-butanol in the beginning, and then increased gradually to 4.07 mol-\(H_2\)/mol-butanol near 8-h. The reason can be found in the carbon-containing products: In the beginning, there was high selectivity to \(C_2H_4\) (near 21.8%), to \(C_3H_6\) (near 4.05%) and to other by-products (mainly as \(C_3H_8\) and \(C_2H_6\)), which resulted in the low \(H_2\) yield. According to thermodynamic analysis [16], in the thermal equilibrium compositions of output gas in CPOX, the main by-product is \(CH_4\) (about 3.74%) and no other by-products of \(C_2H_4\) and \(C_2H_6\) remain in the output gas; the difference between experimental results and thermodynamics suggests that the process was mainly kinetically controlled in the beginning over the unreduced NMAF catalyst. Also as shown in Fig. 2(A), overtime, the selectivity to these by-products of \(C_2H_4\) and \(C_2H_6\) decreased with increase in \(CO\) and \(H_2\), and became stable after 8-h.

In order to shorten the startup time, higher initial temperatures were then tested. As shown Fig. 2(B), when the initial temperature was 750 °C, the induction time was narrowed down to about 3 h with \(H_2\) yield reaching 3.95 mol-\(H_2\)/mol-butanol, which remained stable when the temperature decreased to 700 °C. A shorter time of 0.75 h was obtained when the startup temperature was 800 °C, as indicated by Fig. 2(C).

**Fig. 1 – The catalytic performance of reduced NMAF in CPOX of butanol at 700 °C, 11,000 h⁻¹ and 1 atm with air and butanol.**
Although the startup time over the unreduced NMAF catalyst was narrowed down to less than 1 h with initial temperature at 800 °C, it is still too long and unacceptable for practical applications without obvious delay of hydrogen supply. To further shorten or even eliminate the induction time and restart time, the NMAF catalyst was promoted by precious metals and tested in CPOX.

Precious metals, e.g., rhodium, iridium, ruthenium and platinum, are reported to be helpful to reduce transition metals because of spillover effect of hydrogen atoms, and maybe also help to activate the Ni-based catalyst without reduction procedure [19,20]. As shown in Fig. 3, CPOX was firstly tested over Rh-NMAF without reduction treatment, and the activity of Rh-NMAF reached the normal values in the beginning of CPOX: the conversion of butanol remained stable near 100%, and CO₂ and CO were the main carbon-containing products with trace of CH₄ (about 6.5% in selectivity), while the H₂ yield remained stable near 4.1 mol-H₂/mol-butanol, which is higher than those of Rh/α-Al₂O₃ with 1.0 wt% of Rh (about 2.75 mol-H₂/mol-butanol) [17] or Rh/γ-Al₂O₃ with 0.7353 g of Rh (3.15 mol-H₂/mol-butanol) [18]. To further simulate intermittency in the practical applications, the feed of butanol was shut off at 46-h with the air flow remained on to re-oxidize the catalyst, and then resumed at 68-h with both butanol and air flows turned on. As shown in Fig. 3, the catalytic performance resumed immediately. Another standby operation was conducted at 100-h and then the CPOX process resumed at 118-h, while the catalytic performance still remained stable, suggesting Rh effectively improved the initial activity and stability of the unreduced NMAF catalyst.

To check the reactivity of Rh, an Rh/γ-Al₂O₃ catalyst was prepared with mass loading of 0.25%, and tested in CPOX at 700 °C with O₂/butanol = 2.0. Over the Rh/γ-Al₂O₃, there was an unstable performance observed: the H₂ yield started near 3.8 mol-H₂/mol-butanol, but then dropped to 2.1 mol-H₂/mol-butanol at 5-h because of high selectivity to by-products of C₂H₄ and C₃H₆ (about 8.6% and 4.3%, respectively). The result suggests that Rh mainly acted as a promoter in the NMAF catalyst for hydrogen production via CPOX of butanol.

**CPOX test of Rh-NMAF**

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**Fig. 2** – Fast startup test of NMAF without reduction in the CPOX of butanol at 11,000 h⁻¹ and 1 atm with air and butanol at startup temperatures of (A) 700 °C, (B) 750 °C, and (C) 800 °C.

**Fig. 3** – The catalytic performance of Rh-NMAF without reduction in the CPOX of butanol at 700 °C, 11,000 h⁻¹ and 1 atm with air and butanol.
Characterizations of NMAF and Rh-NMAF

The CPOX test indicates that there was an induction time for hydrogen supply over NMAF without reduction, while Rh-NMAF showed high initial activity. To investigate the effect of Rh on the NMAF catalyst, a series of NMAF and Rh-NMAF catalysts were tested in CPOX at 700 °C, stopped feed of butanol/air and switched into nitrogen at different time, cooled down to room temperature in nitrogen, and then screened with XRD and XPS to find the variation in crystal phases and valences of metals during CPOX.

As shown in Fig. 4(A), over the spent NMAF catalyst at 10 min of CPOX, there are peaks of the face-centered cubic (FCC) phase of periclase (MgO, PDF #: 45-0946). Because NiO can form a similar FCC structure (PDF #:47-1049), there is probably solid solution of Mg(Ni)O, or Mg0.4Ni0.6O (PDF #: 34-0410), in a Fm-3m space group [21]. No obvious peaks of Fe-containing species were found, suggesting that Fe may have also been inserted into the solid solution of Mg(Ni)O [21,22]. Neither peaks of Ni0 nor peaks of Fe0 were found.

For the catalysts with longer time in the CPOX process, peaks of nickel or nickel/iron alloy emerged near 43.9°, 51.3°, and 76.3° and became stronger over these spent catalysts, especially the catalyst after 16 h in CPOX, suggesting that more nickel species were reduced to Ni0 overtime. The emergence of nickel or nickel/iron species, which is active to CPOX for hydrogen production [16], is consistent with the increase of H2 yield in the CPOX test, as suggested by Fig. 2.
For the Rh-NMAF catalyst with 0.25% of Rh, the periclase of MgO is still the main phase and no Rh-containing species were found. As shown in Fig. 4(B), the peaks of nickel or nickel/iron were found in the beginning of CPOX and became stronger overtime. The result may explain the high initial activity with a H₂ yield near 4.0 mol-H₂/mol-butanol in the beginning of CPOX and the stable activity overtime.

To confirm the existence of Ni⁰ species which is active to CPOX for hydrogen production [16], the catalysts were screened with XPS as well. As shown in Fig. 5, the spectra of Ni 2p₃/₂ can be deconvoluted into three peaks near 852.5 eV, 855.4 eV and 861.8 eV, which can be attributed to the species of Ni⁰, Ni²⁺ and shake-up peak of Ni³⁺, respectively [23]. Over the NMAF catalyst after 10-min test, there is a weak peak of Ni⁰ near 852.5 eV with about 5.9% of nickel species existing as Ni⁰, according to quantitative analysis on peak areas. For the NMAF catalyst after 70-min and 8-h test, the peak of Ni⁰ becomes stronger with up to 26.8% of nickel existing as Ni⁰ at 8-h. The increasing content of Ni⁰ is consistent with the stronger peaks of nickel in XRD as well as the increasing activity with higher H₂ yield in CPOX test.

For the Rh-NMAF catalyst after 10-min CPOX test, there is a strong peak of Ni⁰ species with about 25.9% of nickel species existing as Ni⁰, indicating the nickel species can be more reducible with Rh in CPOX and also explaining the high initial activity and stability with two standby operations in CPOX.

TPR was also conducted to test the reducibility of these catalysts. For the NMAF catalyst in Fig. 6, there are two reduction peaks near 790 °C and 484 °C, which can be attributed to the reduction of solid solution of Mg(Ni)O and Fe-containing species of MgFe₂O₄, Fe₃O₄ and/or NiFe₂O₄, respectively [9,24]. With Rh in Rh-NMAF, there are two more peaks emerging near 219 °C and 398 °C, indicating there were Ni/Fe species reduced with promotion of Rh via hydrogen spillover effect [19,20].

The activity results indicate that the unreduced NMAF has a low initial activity because of most of nickel existing as Ni²⁺ instead of Ni⁰ in the beginning of CPOX, and thus an induction period up to 8 h was observed. With promotion of Rh in Rh-NMAF, as shown by the results of TPR, the reducibility was improved, a higher content of Ni⁰ (about 25.9% as indicated by XPS results) was observed in the beginning of CPOX, and the initial activity of Rh-NMAF reached about 4.1 mol-H₂/mol-butanol, suggesting that Rh-NMAF is a promising candidate for hydrogen production without delay of hydrogen supply during startup.

**Effect of feed and temperature in CPOX over Rh-NMAF**

To find optimal conditions of CPOX for hydrogen production over Rh-NMAF, the ratios of O₂/butanol and temperatures were studied. As shown in Fig. 7, when ratio of O₂/butanol was set at 1.5, the conversion of butanol was near 100% at 700 °C, and the yield of H₂ reached 3.84 mol-H₂/mol-butanol; meanwhile, about 76.9% of hydrogen from butanol was transformed into H₂, and about 9.0% of hydrogen was transformed into H₂O, while the remaining hydrogen (about 10.7%) existed in hydrocarbons (mostly as methane). For the carbon in butanol, the selectivity to CO is near 71.9%, the selectivity to CO₂ is near 16.9%, and the selectivity to CH₄ reaches 10.7%. The results suggest that to obtain a higher H₂ yield, more hydrogen need to be extracted from methane and water.

With higher ratio of O₂/butanol in the feed of CPOX, the H₂ yield increased and reached 4.13 mol-H₂/mol-butanol at O₂/butanol = 2.0, because the selectivity to CH₄ decreased to 6.5% and more hydrogen atoms were transformed into H₂O with the H₂O yield increasing slightly to 0.66 mol-H₂O/mol-butanol.

When the ratio of O₂/butanol increased further to 2.5, 3.0 and 3.5, the H₂ yield gradually decreased and dropped to 2.51 mol-H₂/mol-butanol eventually, because more hydrogen atoms in butanol were oxidized into H₂O with the H₂O yield reaching slightly to 0.66 mol-H₂O/mol-butanol. Meanwhile, more oxygen in feed resulted in sharp increase in CO₂ and decrease in CH₄ and CO. The results indicated that the optimal ratio of O₂/butanol is near 2.0.

To find the effect of temperature, the catalytic performance of Rh-NMAF was tested at different temperatures. As shown in Fig. 8, a low initial activity near 3.22 mol-H₂/mol-
butanol was obtained at 600 °C because there was a high selectivity to CH₄ near 19.3% (the carbon selectivity is not presented in the figure). The H₂ yield increased slightly but then decreased to about 3.3 mol-H₂/mol-butanol at 20-h because of increase in by-products of C₂H₄, C₂H₆, C₃H₆, etc., which resulted in coking and deactivation overtime, as observed over the spent catalyst.

With higher temperatures, the selectivity to CH₄ decreased to about 12.8% at 650 °C, to about 7.1% at 700 °C, and to about 3.9% at 750 °C; meanwhile, no other by-products of C₂H₄, C₂H₆, C₃H₆, etc., were detected. As a result, the H₂ yield increased with increasing temperatures, reaching 3.71 mol-H₂/mol-butanol at 650 °C, 4.04 mol-H₂/mol-butanol at 700 °C and 4.61 mol-H₂/mol-butanol at 750 °C. The results suggest that higher temperature is helpful to constrain by-products of C₂H₄, C₂H₆, C₃H₆, etc., and to obtain high conversion of CH₄ and H₂ yield.

**CPOX test of Ir-NMAF, Ru-NMAF and Pt-NMAF**

Rh-promoted NMAF showed high initial activity and stability in CPOX, and other precious metals-promoted NMAF catalysts were also tested in CPOX to find alternative candidates. For the Ir-NMAF, as shown in Fig. 9(A), high catalytic performance was observed: without reduction, the initial activity with 4.0 mol-H₂/mol-butanol was obtained and remained stable in the 120-h CPOX with two standby operations.

Similar activity was observed over Ru-NMAF (Fig. 9(B)): the H₂ yield started near 3.8 mol-H₂/mol-butanol and remained stable with two standby operations in a 120-h CPOX test.

For the Pt-NMAF catalyst (Fig. 9(C)), the H₂ yield reached 3.8 mol-H₂/mol-butanol in the beginning, remained stable with two standby operations, but decreased slightly to about 3.3 mol-H₂/mol-butanol because of increase of by-products of C₂H₄, C₂H₆ and C₃H₆.

These catalysts were screened with TPR and XRD as well. As shown in Fig. 6, over these catalysts with promotion of precious metals, reduction peaks below 400 °C were found, indicating these precious metals also helped to reduce the nickel/iron species in solid solution of Mg(Ni)O [20].

The crystal phases in these unreduced catalysts were shown in Fig. 10(A) of XRD, and there are similar peaks of periclase of Mg(Ni)O. No peaks of precious metals were found.
because of their low loading at 0.25%. The spent catalysts after a 120-h CPOX test were screened with XRD as well, as shown in Fig. 10(B), in which peaks of Ni$^0$ were observed in Ir-NMAF, Ru-NMAF and Pt-NMAF. For the Pt-NMAF catalyst, the peaks of Ni were obscure, indicating there were less Ni$^0$ species in Pt-NMAF, as compared with Ir-NMAF and Ru-NMAF, which may explain the slight decrease in H$_2$ yield in the 120-h CPOX test.

To check the reactivity of these precious metals, $\gamma$-Al$_2$O$_3$-supported precious metals with mass loading of 0.25% were also tested in CPOX at 700°C with O$_2$/butanol = 2.0. Over the catalysts with precious metals of Ru, Ir and Pt, there is still unstable performance with H$_2$ yield dropping to a range of 0.5–1.5 mol-H$_2$/mol-butanol within 5 h (The sures of these Al$_2$O$_3$-supported precious metals catalysts are not shown here). The results indicate that these precious metals mainly acted as promoters in the NMAF catalyst for hydrogen production via CPOX of butanol.

In light of the aforementioned results, the unreduced NMAF catalyst produced a low initial H$_2$ yield near 1.68 mol-H$_2$/mol-butanol in CPOX, because there were only 5.9% of Ni species had been reduced in the periclase structure of Mg(Ni)O in the beginning of CPOX. Overtime, the Ni$^0$ species increased, as suggested by the XRD and XPS, and the H$_2$ yield increased in the mean time and reached 4.1 mol-H$_2$/mol-butanol at 8 h. For the precious metal of Rh promoted NMAF without reduction, because there was high content of Ni$^0$ (about 25.9%) in the beginning of CPOX, the initial activity near 4.1 mol-H$_2$/mol-butanol was recorded, and remained stable in the 130-h CPOX test with two standby operations.

Conclusions

The precious metals-promoted NMAF catalysts were tested in CPOX of butanol for hydrogen production. The un-promoted NMAF catalyst produced a low initial activity near 1.68 mol-H$_2$/mol-butanol, which was increased and reached 4.1 mol-H$_2$/mol-butanol at 8 h. The characterization results suggest that there was trace of Ni$^0$ (about 5.9%) in the unreduced NMAF in the beginning of CPOX, and then the content of Ni$^0$ species increased over time, explaining the increase in H$_2$ yield. For the Rh-NMAF without reduction, there was high Ni$^0$ content at 10-min in CPOX, which explains the high initial activity and stability with standby operations in CPOX. The results suggest that the Rh-NMAF catalysts can be a promising candidate with high initial activity and stability in CPOX process for hydrogen production, especially for variable hydrogen supply for on-board applications. The NMAF catalyst promoted by Ir, Ru and Pt also showed potential in CPOX of butanol for hydrogen production.

Acknowledgments

The research work is partly supported by the fund (Grant No. PLC201205) of State Key Laboratory of Oil and Gas Reservoir Geology and Exploration (Chengdu University of Technology), NSFC (Grant No. 21276031), the Sichuan Provincial Education Department (Grant Nos. 12ZA011, 13CZ0010), and the International Cooperation Program by Science and Technology Department of Sichuan Province (Appl. No. 15GH0046).

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