

The effect of basic promoters on the catalytic performance of Ni/ γ -Al₂O₃ in steam reforming of acetic acid

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ABSTRACT

The catalytic steam reforming of acetic acid (ASR) for H₂ production was conducted over Ni/ γ -Al₂O₃ modified by basic promoters in order to transform the acidic γ -Al₂O₃. Generally, the ability of acidic support on C-O bond cleavage induces unexpected reactions (decomposition, coke formation, etc.), rather than steam reforming. The catalytic activity was estimated by the conversion of acetic acid and H₂ selectivity. In the APR, Ni/ γ -Al₂O₃ and Ni/Mg/ γ -Al₂O₃ at 500 and 550°C showed higher conversion than the others. Especially, the latter showed exceeding 95% of H₂ selectivity at all temperatures (steam / carbon ratio = 5.3). Also, deposited carbon could contribute to H₂ production by carbon-steam reaction in ASR over the catalysts modified by Mg and La.

1. INTRODUCTION

Due to the exhaustion of fossil resource and the concern on global warming, hydrogen has been regarded as a promising source for future energy in diverse fields such as fuel cell (Mohanty 2012). In order to obtain hydrogen, the catalytic steam reforming (CSR) of natural gas or petroleum-based source and the gasification of coal have been utilizing in present commercial industries (Pena 1996). However, the processes emit simultaneously the green-house gases like CO₂ (Basagiannis 2007). As the other option to produce H₂ without additional CO₂ emission, CSR of bio-oil has been receiving significant attention recently. Bio-oil, which is derived from fast pyrolysis of lignocellulosic biomasses, is composed of various compounds including acids, esters, ketones, sugars, phenols, etc. Especially, acetic acid (AA) is one of the main compounds (up to 14 wt.%) in bio-oil (Mohanty 2012).

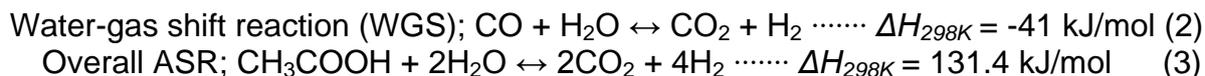
CSR of acetic acid (ASR) for H₂ production is summarized as following Eq. (1-3):



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According to above reactions, 1 mole of AA can be produced stoichiometrically to 4 moles of H₂. However, due to the undesired reactions (coke formation, reverse water-gas shift (RWGS), methanation, decomposition, etc.), theoretical H₂ yield cannot be obtained (Basagiannis 2007). So, the various literatures improving the selectivity toward ASR have been reported. An (2011) performed ASR over Ni/ γ -Al₂O₃ at 600°C (steam/carbon ration (S/C) = 2) and examined the effect of Ni loading amount on the H₂ selectivity and coking. When 12% Ni supported on γ -Al₂O₃ was employed at ASR, the conversion and H₂ selectivity were 50% and 90%, respectively. The amounts of total deposited coke were similar with all catalysts, while the amount of crystalline coke increased with Ni loading amount. Crystalline carbon might be generated from the accumulation of residual carbidic carbon with ungasified, because of Ni-C strong interaction (Li 2000). Wang (2013) tested the activity of Pd/HZSM-5 for ASR. This catalyst showed exceeding 90% of conversion at 600°C (S/C = 9.2), while its H₂ selectivity was 67%, which might be induced from acidic HZSM-5 leading cracking or decomposition of AA. Lemonidou (2013) addressed C-C bond cleavage would lead ASR and produce hydrogen, whereas, C-O bond cleavage would cause coke formation, methanation, and the other unexpected reactions during ASR using Rh/La₂O₃/CeO₂-ZrO₂. Davda (2005) described that lower acidic or more basic catalysts produced H₂ than acidic one, because acidic catalyst would lead C-O bond scission in aqueous-phase reforming. Accordingly, the effort to promote C-C bond scission by preparing the basic catalyst has been tried. Basagiannis and Verykios (2007) performed the ASR over the metal of group VIII supported on γ -Al₂O₃ modified with basic promoters. When AA was reformed by Ru or Ni catalyst modified Mg or La at 700°C (S/C = 5), the conversion was 100% and H₂ selectivity was exceeding 95%. In case of the ASR with Ni or Ru/Mg/ γ -Al₂O₃, the amount of coke was less than the other ASR. Additionally, the use of basic metal, especially La, induced ketonization reaction producing acetone.

The present work deals with basic promoter's effect on the catalytic activity (conversion and H₂ selectivity) in ASR. Ni/ γ -Al₂O₃ was modified by Mg, La, Cu, and K, as the basic promoters.

2. Experimental

2.1 Catalyst preparation

γ -Al₂O₃ as a support was purchased from Alfa Aesar and nickel precursor was used Ni(NO₃)₂·6H₂O (≥97%, Junsei Chemical Co., Ltd.). As basic promoters, Mg(NO₃)₂·6H₂O (≥98%), La(NO₃)₃·6H₂O (≥98%), and KNO₃ (≥99%) were employed from Junsei Chemical Co., Ltd., and Cu(NO₃)₂·2.5H₂O (≥98%) was obtained from Aldrich Chemistry. The catalysts were prepared by wetness impregnation method. Each basic metals (M) were loaded on γ -Al₂O₃ by 15 wt.%. Prepared M/ γ -Al₂O₃ were calcined at 700°C for 4h in air. After the calcination, 17% of Ni (metal base) was impregnated on calcined M/ γ -Al₂O₃. Then, the samples were calcined at the same

condition with above one. Prepared catalysts were reduced 700°C for 1h with 25% H₂/N₂ before use for ASR. Each Ni/γ-Al₂O₃, Ni/Mg/γ-Al₂O₃, Ni/La/γ-Al₂O₃, Ni/Cu/γ-Al₂O₃ and Ni/K/γ-Al₂O₃ catalyst were marked as NA, NMA, NLA, NCA and NKA.

2.2 Steam reforming of acetic acid (ASR) and product analysis

Steam reforming of acetic acid was performed by continuous tubular reaction system (T-Eng. Inc.). Quartz tube (4mm I.D x 800mm L) was used as the tubular reactor. The volume of catalyst bed was 0.044 mL. The reaction system was briefly described at Fig. 1.

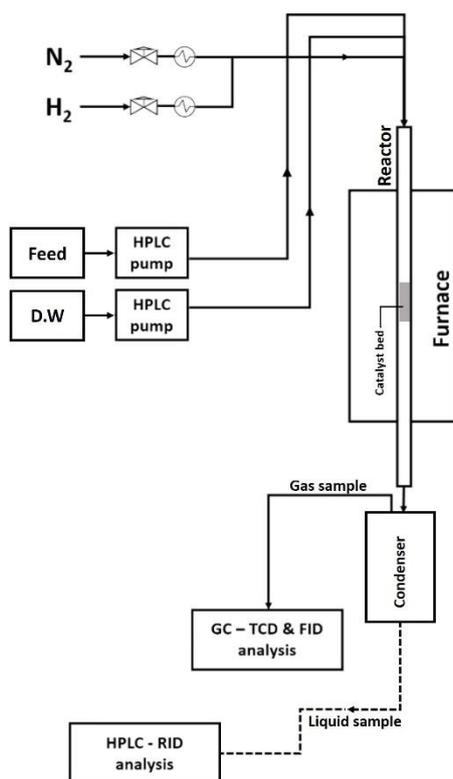


Fig. 1. Schematic diagram.

After the reactor was mounted at the furnace, the reactor was heated by 450°C with the flow of 50mL/min of N₂. ASR was conducted at 450°C, 500°C, and 550°C for 2h with each temperature. AA as a model compound for bio-oil was employed from Samchen Chemical Co., Ltd., and was diluted by distilled water (D.W) for 35.7 wt.%. Then, AA solution was pumped into the heated reactor by using solvent delivery pump (Eldex Laboratories Inc.). In order to make S/C for 5.3, D.W was inserted additionally by using Minichemi pump manufactured by NS. The gas, which was passed through the catalyst bed, was collected by cold-trap to analyze liquid product and unconverted AA. Condensed liquid sample was analyzed by high performance liquid chromatography system (HPLC, Shimadzu) equipped with refractive index detector (RID). In order to determine exact amount of the components in liquid sample, the

standard reagents (AA ($\geq 99.5\%$, Samchen Chemical Co., Ltd.), acetone ($\geq 99.9\%$, Sigma-Aldrich)) was utilized. Uncondensed gas was directly analyzed by on-line gas chromatography (GC, GC-7890A, Agilent instruments Inc.) equipped with thermal conductive detector (TCD) and flame ionization detector (FID) to quantify H_2 , CO, CO_2 , CH_4 , and other hydrocarbons. Standard gases for quantitative analysis were purchased from Special Gas Co., Ltd. The conversion of AA and H_2 selectivity were calculated by following equations:

$$\text{Conversion (\%)} = \frac{\text{the moles of converted AA}}{\text{the moles of AA (input)}} \times 100 \quad (4)$$

$$\text{H}_2 \text{ selectivity (\%)} = \frac{\text{the moles of produced H}_2}{\text{the moles of converted AA} \times 4} \times 100 \quad (5)$$

3. Results and discussion

The ASR over each catalysts modified by basic metals were conducted. The conversion and H_2 selectivity as a function of temperature were depicted at Fig 2(a) and (b), respectively.

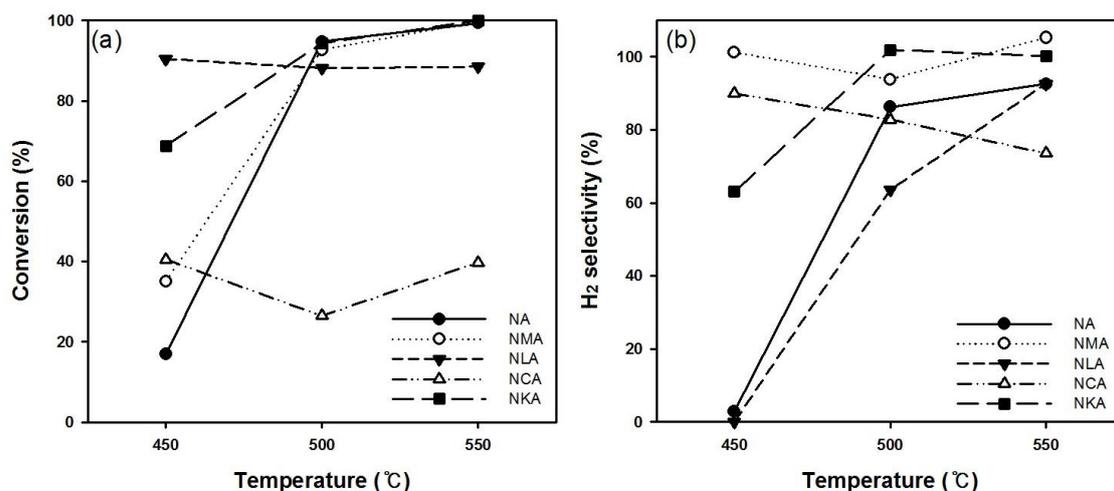


Fig. 2. The conversion and H_2 selectivity of the ASR over each catalysts by temperature; S/C = 5.3, 1 atm, 50 mL/min of N_2 flow.

In Fig. 2(a), the conversion of ASR over NA was 16.9% at 450 °C, while those of the other catalysts were 35.0% (NMA), 90.4% (NLA), 40.5% (NCA), and 68.8% (NKA), which might be due to impregnation of alkali promoters. When the temperature increased above 450 °C, the conversion of AA over NA, NMA, and NKA were exceeded 90%, on the other hands, that of NLA decreased slightly. Based on the result of HPLC analysis, acetone was detected from the liquid sample of ASR over NLA (not shown here), addressing that AA was ketonized. Pant (2013) was reported that ketonization reaction occurs at the temperature below 800 °C with basic oxides like lanthania (Eq. (6)).

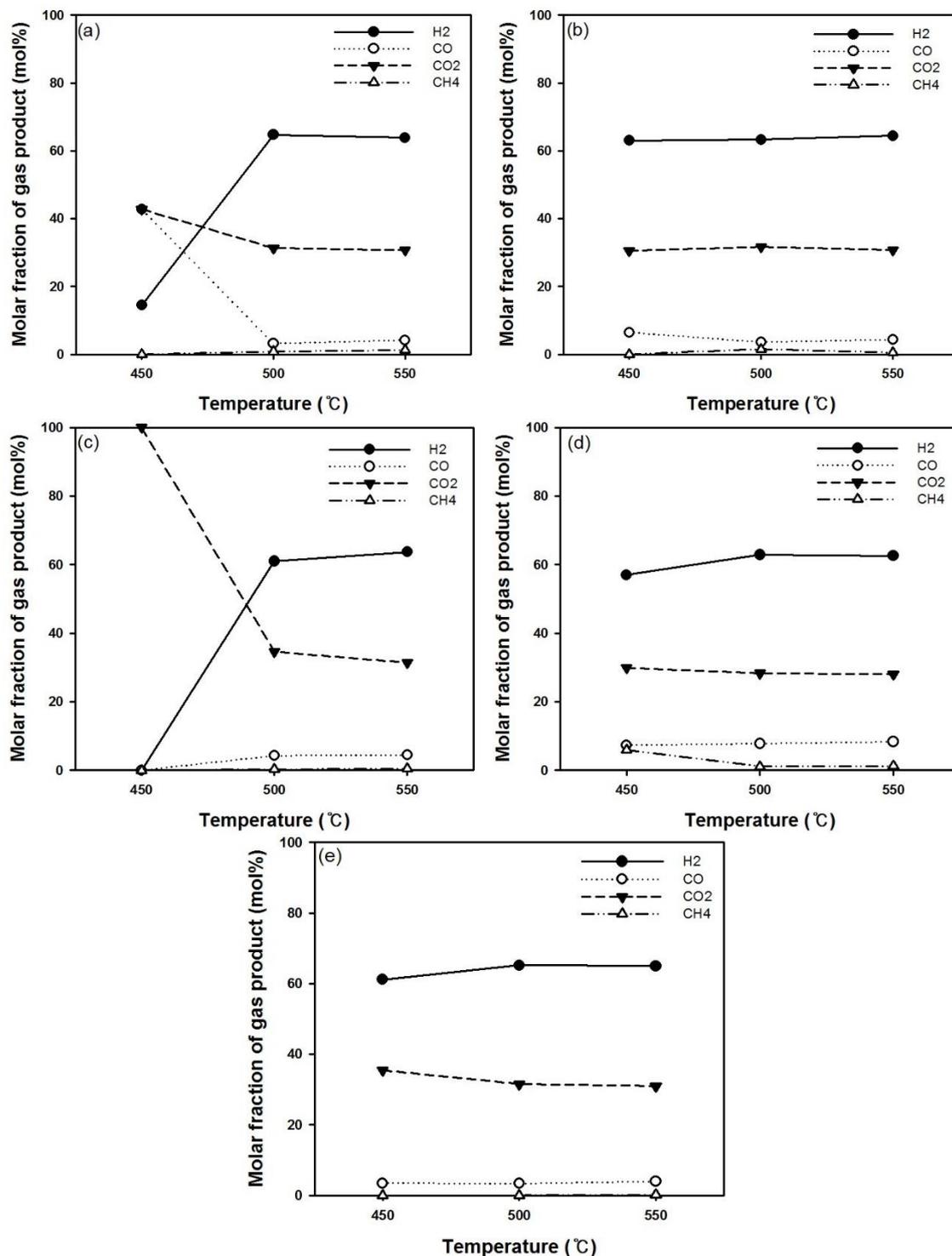
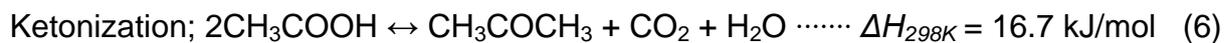
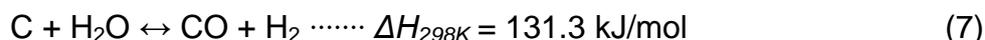


Fig. 3. The molar fraction of gas products in ASR over (a) NA, (b) NMA, (c) NLA, (d) NCA, and (e) NKA by temperature; S/C = 5.3, 1atm, 50 mL/min of N₂ flow.

NCA showed below 40% of conversion, which was the worst in the others. Bimbela (2012) addressed that the present of Cu in the catalyst made the activity of the catalyst for ASR lower, even though Cu would lead unstable adsorption between copper and coke, which could retard coke formation on the catalyst. In case of H₂ selectivity (Fig. 2(b)), NMA performed exceeding 95% at all temperatures, while that of NCA decreased with increasing the temperature. The H₂ selectivity of NA, NLA and NKA grew with rising the temperature. H₂ selectivity of NMA and NLA exceeded 100%, meaning that hydrogen could be produced from the other reaction, not only ASR. Goicoechea (2015) showed that the pathway to gain hydrogen from the reaction between carbon and steam as Eq. (7):



Produced CO by Eq. (7) can be converted by reverse-WGS (Eq. (2)) to produce hydrogen and carbon dioxide, leading 1 mole of carbon generate 2 moles of hydrogen finally. Thus, more H₂ might be obtained from the carbon-steam reaction of deposited carbon in the ASR.

In order to examine detailed gas product, the molar fractions of the gas products from the ASR using each catalysts were described at Fig. 3. Stoichiometrically, when AA is fully converted by ASR (Eq. (3)), the molar fractions of H₂ and CO₂ were 66.7% and 33.3%, respectively. When AA was converted by NA (Fig. 3(a)), 42.8 mol% of both CO and CO₂ and 14.4 mol% of H₂ at 450°C, addressing AA would be decomposed by Eq. (8) with insufficient ASR.



At 500, 550°C, the molar fraction of H₂, CO₂ and CO were 64, 31 and 3.5 mol%, approximately, meaning that AA would be converted through ASR pathway mainly (Eq. (3)). Negligible amount of methane was traced. In case of the ASR employing NMA which shows excellent H₂ selectivity, the gas product was composed of 63.5 mol% of H₂, 31 mol% of CO₂ and 5% of CO, approximately, even 450°C unlike NA, noting that NMA might have the outstanding ability toward ASR even lower temperature. In the ASR over NLA (Fig. 3(c)), only CO₂ was identified at 450°C, which means AA might be converted by ketonization reaction. According to rising temperature, the molar fractions of gas components were converged to stoichiometric distribution by ASR (63.6 mol% of H₂ and 31.4 mol% of CO₂ at 550°C). When NCA was used in ASR, the molar fractions of both CH₄ and CO₂ was relatively higher than the others at 450°C, indicating that AA might be decarboxylated by NCA at the temperature (Eq. (9)).



Similar with the gas product for ASR over NLA, the fraction of CO₂ at NKA at 450°C was a little higher than those of the other temperatures, and any CH₄ gas was not detected by GC (Fig. 3(e)). Also, acetone was detected in liquid sample by HPLC, which means that ketonization reaction might be performed by NKA at 450°C. At above

450°C, the distribution of gas product by NKA followed the tendency of the others.

4. CONCLUSIONS

ASR was conducted to produce hydrogen by using NA modified basic promoters. NMA showed higher activity for APR than the others. In the ASR over NMA, the conversion at 550°C was \approx 100% and H₂ selectivity was exceeding 95% at all temperatures (S/C = 5.3). When the catalysts with La and K were used, ketonization reaction producing acetone might be involved at lower temperature. NCA showed the worst performance for ASR in modified catalysts. Additionally, H₂ could be obtained from steam-carbon reaction, not only ASR, by using NA promoted by Mg or La.

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