Effect of Alkali Vapor Exposure on Ni-MgO/γ-Al2O3/Cordierite Monolithic Catalyst for Biomass Fuel Gas Reforming


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Fly ash compounds, such as alkali salts, in the raw biomass fuel gas can contaminate and deposit on traditional granular Ni-based catalysts, which resulted in catalyst deactivation and pressure increase of the downstream reformer. The impact of alkali salt exposure (KCl, K2SO4, K2CO3, by evaporation at about 7.8 mg/L for 6 h) on dry CH4/CO2 reforming of model biomass fuel gas (H2/CO/C2H4/CH4/CO2/N2 = 15.8/12.1/2.5/1/15.0/22.1/32.6 vol %) over Ni-MgO/γ-Al2O3/cordierite monolithic catalyst (MC) was investigated and studied. The results showed that CH4 and CO2 conversions and CO and H2 yields increased at 700–850 °C for undeposited and deposited MC. Compared with undeposited MC, the deposited catalysts show lower CH4 conversion but higher CO2 conversion and CO yield at 750–830 °C. The stability tests also show that CH4 conversion and H2 content in the tail gas decreased dramatically from 87.2% to 32.0% and from 35.1% to 26.7%, respectively, after 17 h time on stream (TOS) for the deposited MC, while CH4 conversion kept steady of above 90% after 60 h TOS for undeposited MC at 750 °C. Characterization by N2-physisorption, XRD, ICP-AES, SEM-EDS, and XPS of MC indicate that alkali salt aerosol covering the catalyst surface or blocking mesopore channels was the main reason for the decreased reforming performance and MC deactivation, which occurred mainly at the top part of monolithic catalyst (K = 1.39 wt % by EDS), vicinal to the alkali source. The reforming of real biomass fuel gas (H2/CO/C2H4/CH4/CO2/N2 = 10.2/16.8/0.5/6.4/15.2/51.0 vol %) from air gasification of pine sawdust in the pilot plant (200–250 kg/h) by the reformer packed with MCP, larger in size than MC, exhibits pressure drop of less than 700 Pa, CH4 conversion of about 84%, and tar content from 4.8–5.3 g/m3 to 0.12–0.14 g/m3 during 60 h TOS at 600 °C. The porosity structure of MCP catalytic bed and relatively low alkali (K, Na = 0.03–0.07 wt %) deposition by fly ash from real biomass fuel gas were the main reasons for the excellent reformer performance.

1. Introduction

As one of the most promising technology to substitute fossil fuels, second-generation biofuel production has been studied widely,1 such as the Hynol project in the United States, Bio-Fuels projects in Sweden, Sun-diesel in Choren Company, Germany.2 Yet thermochemical gasification of biomass is inevitably accompanied by the formation of tar and inorganic impurities(Si, Ca, K, Na, S, Cl, Mg, Zn, Fe, Mn) and the obtained raw fuel gas is usually CO2-rich with low H2/CO ratio.3 To fulfill the stoichiometric requirement for syngas conversion to liquid fuels, reforming of CH4 and tar to increase H2/CO ratio has been focused on other catalysts, especially for monolithic catalysts,15 which have advantages as high catalytic performance per unit mass of active metal, high operating stability and low pressure drop of catalyst bed over fixed-bed reactor or slurry reactor.16 Few concrete experiments have been focused on other catalysts, especially for monolithic catalysts,15 which have advantages as high catalytic performance per unit mass of active metal, high operating stability and low pressure drop of catalyst bed over fixed-bed reactor or slurry reactor.16 Preliminary studies from our group have achieved remarkable CH4 and tar reforming performance from biomass fuel gas over monolithic Ni-based catalyst.17 In the present work, the effect of alkali salt vapor exposure (KCl, K2SO4, and K2CO3) on Ni-MgO/γ-Al2O3/cordierite monolithic catalyst (MC) for model biomass fuel gas reforming, as well as the stability of undeposited and deposited catalyst was investigated to evaluate the impact of inorganic salts (expected to be present in the biomass fuel gas) on a catalytic reformer unit. And the typical reforming results of real biomass fuel gas from fluidized bed gasification of pine sawdust (200–250 kg/h) in the pilot plant were also discussed.

2. Experimental Section

2.1. Catalyst Preparation. Two types of ceramic cordierite monolithic substrates (Yixing Nonmetallic Chemical Factory, Jiangsu Province, China) with the density, porosity, BET, cell density, specification of 1.71 g/cm3, 60%, 10.9 m2/g, 60 cell

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s/cm², q=4.0*5.0 cm and 1.03 g/cm³, 90%, 10.4 m²/g, 1.5 cells/cm², q=9.0*10.0 cm were used to prepare catalysts for reforming model biomass fuel gas and real biomass fuel gas respectively. At first, the bare monoliths were immersed into 30 wt % oxalic acid solution for 0.5 h, and then dipped into the ethanol solution of Ultrafine γ-Al₂O₃ powder under vacuum condition to increase pore volume and surface area. Then γ-Al₂O₃-coated monoliths were impregnated by 1N aqueous nickel nitrate (Ni(NO₃)₂.6H₂O) solution, dried overnight at 110 °C, and calcined at 900 °C. After that, MgO-loaded monolith was impregnated again by 1 N aqueous nickel nitrate (Ni(NO₃)₂.6H₂O) solution, dried overnight at 110 °C, and calcined at 850 °C. The two types of well-prepared catalysts were denoted as MC and MCP, respectively.

2.2. Alkali Salt Vapor Deposition on MC and Model Biomass Fuel Gas Reforming Procedure. The deposition of alkali salt vapor on MC was carried out in a horizontal reactor with two thermocouples, one was for alkali salt vaporization at 750 °C and the other was for reforming temperature controlling in Figure 1. In each run, MC was reduced in situ in 300 mL/min of 5% H₂/N₂ (vol%) flow at 750 °C and calcined at 900 °C. After that, MgO-loaded monolith was impregnated again by 1 N aqueous magnesium nitrate (Mg(NO₃)₂.6H₂O) solution, dried overnight at 110 °C, and calcined at 850 °C. The two types of well-prepared catalysts were denoted as MC and MCP, respectively.

2.3. Biomass gasification-reforming procedure. As shown in Figure 2, the system was made up by biomass feeder, gasifier, downer reactor, reformer, water bath, gas tank. Pine sawdust of 200–250 kg/h was air-gasified. The raw fuel gas passed through a purification unit to separate most fly ash particles and then through a multitupe (49 columns) reformer (cube-shaped, 1 m³ 1 m³ 1 m) heated with a burner to supply reforming heat from diesel combustion. The 49 tubes (ID: 93 mm, Length: 1.2 m) was arranged to be 7 columns and 7 lines in the reformer. Ten pieces of MCP were packed in one tubular tube and each piece of MCP was separated by 1 cm of inert Rashig rings. After that, the gas was washed by water to further eliminate particles and other impurities and pumped by roots blower to gas tank for dimethyl ether synthesis.

2.4. Catalyst Characterization. The elemental compositions of the catalysts were determined by inductively coupled plasmatom emission spectroscopy (ICP-AES) on a PEPLASMA-2000 instrument. The textural properties of undeposited and deposited MC were measured by N₂ physisorption at −196 °C on Micromeritics SORBFLOW-3210 apparatus and pore distribution was described by BJH model. X-ray diffraction (XRD) patterns were obtained on a BDX3300 using CuKα radiation at 40 kV and 30 mA. Ni Metal crystallite size was determined from the peak at 2θ = 44.3°, which is assigned to the diffraction of Ni (1 1 1) plane in XRD patterns [30], using Scherrer equation. The morphology of MC was obtained by scanning electron microscopy (SEM) on a JSM-6330F equipment with energy diffusive spectroscopy detector (EDS). The elemental compositions of the catalyst surface were identified by NP-1 X-ray Photoelectron Spectrometer (XPS) equipped with Mg-Kα radiation. The binding energies were referenced to the C1s band at 284.6 eV.

3. Results and Discussion

3.1. Textural Properties of MC. The textural properties of cordierite substrate and MC were summarized in Table 1. It was commonly accepted that alkali metal elements could be converted from organic form into inorganic form as sulphates and chlorides after gasification or combustion and the principal alkali metal was K, followed by Na, in this paper, KCl was used as model alkali salt in fly ash deposited on MC. The K vapor content in the carrier gas was 7.8 mg/L and K content in MC was 0.85 wt % after 6 h exposure by ICP-AES, which was higher than that from fly ash deposition during practical biomass gasification. It confirmed that the alkali salt vaporization reaction was applicable for simulating alkali salt deposition in a catalytic reforming bed. While K content after reforming reaction decreased to 0.57 wt %, which mainly resulted from metal loss during high temperature reforming reaction. It is clear that BET and BJH surface area increase remarkably from 10.9 m²/g to 40.0 m²/g and from 7.75–9.52 m²/g to 47.0–48.1 m²/g, respectively, after oxalic acid immersion and

\[ X_{\text{CO}_2} = \frac{(F_{\text{in}}X_{\text{in,CO}_2} - F_{\text{out}}X_{\text{out,CO}_2})/(F_{\text{in}}X_{\text{in,CO}_2})}{Y_{\text{H}_2} = \frac{(F_{\text{out}}X_{\text{out,H}_2} - F_{\text{in}}X_{\text{in,H}_2})/(2F_{\text{in}}X_{\text{in,C}_4,H_4}) + 2F_{\text{in}}X_{\text{in,CH}_4}}{Y_{\text{CO}} = \frac{(F_{\text{out}}X_{\text{out,CO}} - F_{\text{in}}X_{\text{in,CO}})/(2F_{\text{in}}X_{\text{in,C}_4,H_4} + F_{\text{in}}X_{\text{in,CO}_2} + F_{\text{in}}X_{\text{in,CH}_4})}{X_{\text{in}}}
\]

where \( X_{\text{in}} \) is inlet gas composition (vol%), \( X_{\text{out}} \) is outlet gas composition (%), \( F_{\text{in}} \) is total inlet gas flow rate (mL/min), \( F_{\text{out}} \) is total outlet gas flow rate (mL/min), \( X \) is conversion (%), and \( Y \) is yield(%)
superfine γ-Al2O3 deposition (BET surface area = 350 m²/g) in Table 1. The pore volume and the average pore diameter also increased to 0.094 cm³/g and 8.14 nm, respectively, which attributed to mesopore amount increase by pore expansion treatment on cordierite substrate. Reduction in H2/N2 flow did not change textural properties of the catalyst, because relatively low Ni and Mg impregnation amounts of 5.5 wt % and 3.3 wt % in Table 1. While BET area of KCl deposited MC decreased evidently to 15.1 m²/g, similarly with 10.9 m²/g of the original cordierite substrate. Pore volume decreased nearly by half to 0.05 cm³/g, but pore diameter kept constant of about 10 nm.11

The decrease of mesopore volume, BET might be caused by blockage of some mesopore channels and coverage of surface area by alkali salt aerosol deposition, discussed in section 3.3.

After reforming reaction, BET area and pore volume of KCl deposited MC decrease further to 11.2 m²/g and 0.03 cm³/g, respectively. According to BJH pore distribution results, mesopore fraction of the used deposited MC decreased with increased macropore fraction and increased pore diameter of 12.2 nm.

### 3.2. Structure Properties of MC

Figure 3 illustrates the XRD patterns of undeposited, reduced, and KCl deposited MC.

No obvious nickel diffraction peaks were detected for undeposited MC, but it exhibited obvious presence of NiO (JCPDS 34-0396, 37.1°, 43.3°, 62.8°). According to the literature,22 three major peaks at 44.3°, 51.8°, 76.5° and at 36.8°, 44.9°, 65.3° of the reduced MC were identified as NiO and NiAl2O4 (or NiMgO2), respectively. Because of the overlapping of main diffraction peaks of NiAl2O4 and NiMgO2 phase, it was difficult to identify the two compositions by XRD solely. The weak diffraction intensity corresponding to Ni0 for the reduced MC and KCl deposited MC indicates small Ni crystallite size and high dispersion of Ni particles on the catalyst surface. It might also be attributed to the formation of NiAl2O4 (or NiMgO2) spinel and the interaction between active Ni metal and high surface area of γ-Al2O3 support, which is difficult to be reduced. And the existence of NiO diffraction lines for the reduced MC and KCl deposited MC was the result of the reoxidation of metal Ni under atmosphere condition during XRD analysis. The similar XRD patterns also indicated that no new phase was formed during KCl deposition on MC or K content was too low to be identified by XRD or K existed as a noncrystal form.23

Calculated by Scherrer equation, Ni(111) crystal size for reduced MC and KCl deposited MC were 42.2 and 42.3 nm, respectively, in Table 1, which illustrated that no obvious sintering happened during KCl deposition process. It could also be concluded preliminarily that the decreased catalyst surface area should be attributed to KCl exposure. Such results are in disagreement with the results from Moradi,24 who found BET area slightly increased over KCl deposited Pt-based catalyst at 300°C, but are correspondent with the work of Einvall,21 which also showed the BET decrease over Ni-based catalyst. The difference may be resulted from the various deposition process and distinctly different deactivation mechanism of these catalysts.

### 3.3. SEM and XPS Analysis

To evaluate the change of surface morphology after KCl exposure, MC samples, perpendicular to biomass fuel gas flow were obtained from different positions of MC bed. The photos of sampling positions were shown in Figure 4 and the corresponding SEM images were shown in Figure 5.
The surface micrograph of the reduced MC revealed that the monolithic surface was covered by amorphous massive materials, mainly NiAl₂O₄ spinel structures, which are adhered by polydispersed spherical particles of Ni phase according to the EDS analysis. This is in good accordance to XRD characterization in Figure 3, where there are existences of NiAl₂O₄ and Ni phase. The particle size measured by SEM dates was larger than that by XRD patterns because the particle observed by SEM was the agglomeration result of numerous supported Ni crystalline by XRD.

As shown in Figure 5B, some catalyst surface of the top part of KCl deposited MC (position 1 in Figure 4B) is covered by irregularly shaped sheet microstructure with round edges, mainly K aerosol with the content of 1.39 wt % by EDS. The particle size measured by SEM dates was larger than that by XRD patterns because the particle observed by SEM was the agglomeration result of numerous supported Ni crystalline by XRD.

As shown in Figure 5B, some catalyst surface of the top part of KCl deposited MC (position 1 in Figure 4B) is covered by irregularly shaped sheet microstructure with round edges, mainly K aerosol with the content of 1.39 wt % by EDS. The particle size measured by SEM dates was larger than that by XRD patterns because the particle observed by SEM was the agglomeration result of numerous supported Ni crystalline by XRD.

The K/Ni atom ratio difference by EDS and XPS for the top part of KCl deposited MC in Table 2 was due to the variation of layer thickness analyzed by EDS and XPS, about 5 µm by EDS and 5 nm by XPS which means that XPS analyses only few layer of the samples. About 52-fold of K/Ni atom ratio by EDS and XPS, which was 5.74 and 0.11 respectively, indicated that K not only deposited on the MC surface, but permeated in the mesopores of MC and decreased active metal surface in section 3.1.

According to the literature, binding energy at 294.7 and 292.7 eV was assigned to K₂p and K₂p⁺, respectively. The XPS results of binding energy at 293.0 eV for KCl deposited MC might be K²⁻ with σ varying from 0.5 to 0, which means an indirect electrostatic interaction of K with the active Ni metal. For the top part of reduced MC, XPS pattern shows two peaks at ~855.8 and 862.0 eV, respectively, indicated that Ni was in two different conditions and corresponded to NiAl₂O₄ and NiO respectively with relative intensities of 70.6% and 29.4%. These results also suggest the strong interaction between Ni and γ-Al₂O₃. And the oxidation state of Ni for the reduced MC by XPS was due to the reoxidation of Ni by O₂ in air condition before analysis, similar with the oxide phase of NiO by XRD in Figure 3.

As shown in Figure 5D, the filamentous carbon was found on the surface of KCl deposited MC after dry CH₄/CO₂ reforming reaction. Closer inspection from inset of Figure 5D shows that these filaments were entangled with catalyst particles. EDS spectra of the filamentous domain also shows peaks corresponding to catalytic Ni element, cordierite elements and carbon. The spent KCl deposited MC was also examined for the amount of carbon formed by combustion with air flow over the sample at 800 °C for 2 h in a furnace. The weight change of 1.94 wt % was primarily caused by carbon deposition on the sample since the weight change due to Ni phase was relatively low.

Nevertheless Ni-based catalysts are more prone to carbon deposition than precious metal catalysts during reforming reaction, particularly due to the formation of filamentous carbon, which was found by many other researchers. While the carbon deposition degree in this paper was relatively low, there still exists small domains of spherical particles of active phase on MC surface. This would be the reason why the catalyst could maintain its activity after few hours’ reaction in section 3.5.

### 3.4. CH₄/CO₂ Reforming Activities for Model Biomass Fuel Gas over MC

Both reduced MC and KCl, K₂SO₄, and K₂CO₃ deposited MC were evaluated for dry CH₄/CO₂ reforming of model biomass fuel gas mentioned in section 2.2 at 700–850 °C. The results are listed in Table 3. C₂H₄ in the feed gas was converted completely. For undeposited MC and...
H2 and produced CO. So CO yield increase is higher than that endothermic reverse water gas shift reaction, which consumed CO yields. While high reaction temperature also promoted the CO2 conversion and CO yield under same reaction condition at as the alkali aerosol coverage increase by XPS results in this existing in the form of alkali silicate or nitrate, and mainly amount. Praliaud described that alkali metal acted as a promoter, of H2, which resulted in decreased H2/CO ratio in tail gas, CO2 conversions, which also resulted in the increased H2 and

<table>
<thead>
<tr>
<th>Table 2. SEM-EDS and XPS Analysis Results of MC</th>
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<tr>
<td>catalyst</td>
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<tr>
<td>reduced catalyst</td>
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<tr>
<td>deposited catalyst</td>
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Table 3. Effect of Potassium Salt Vapor Deposition on MC Reforming Activities

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>Fad/Fin</th>
<th>CH4</th>
<th>CO2</th>
<th>CH4</th>
<th>CO2</th>
<th>CH4</th>
<th>CO2</th>
<th>CH4</th>
<th>CO2</th>
<th>nH2/nCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>780</td>
<td>0.11</td>
<td>88.26</td>
<td>75.43</td>
<td>78.54</td>
<td>90.07</td>
<td>60.53</td>
<td>77.47</td>
<td>2.67</td>
<td>1.83</td>
<td>0.87</td>
</tr>
<tr>
<td>750</td>
<td>0.12</td>
<td>89.29</td>
<td>67.62</td>
<td>60.25</td>
<td>45.22</td>
<td>1.46</td>
<td>6.52</td>
<td>33.93</td>
<td>28.25</td>
<td>0.91</td>
</tr>
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<td>780</td>
<td>0.12</td>
<td>89.29</td>
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<tr>
<td>800</td>
<td>0.13</td>
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<td>60.25</td>
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<td>33.93</td>
<td>28.25</td>
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<tr>
<td>830</td>
<td>0.14</td>
<td>89.29</td>
<td>67.62</td>
<td>75.43</td>
<td>60.25</td>
<td>1.46</td>
<td>6.52</td>
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<tr>
<td>850</td>
<td>0.15</td>
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<td>6.52</td>
<td>33.93</td>
<td>28.25</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Note: nH2 is outlet H2 content (%), vol, and nCO is outlet CO content (%), vol.

deposited MC, both CH4 and CO2 conversion increased with the increased temperature. This can be explained by the following chemical equations, mainly occurring in the catalytic bed:27,28

\[
\begin{align*}
\text{CH}_4 + \text{CO}_2 &= 2\text{CO} + 2\text{H}_2 \\
\text{C}_2\text{H}_4 + 2\text{CO}_2 &= 4\text{CO} + 2\text{H}_2 \\
\text{CO}_2 + \text{H}_2 &= \text{CO} + \text{H}_2\text{O} \\
2\text{CO} &= \text{C} + \text{CO}_2 \\
\text{CH}_4 &= \text{C} + 2\text{H}_2
\end{align*}
\]

The endothermic dry reforming reaction between CH4 and CO2 was enhanced by temperature increase to favor CH4 and CO2 conversions, which also resulted in the increased H2 and CO yields. While high reaction temperature also promoted the endothermic reverse water gas shift reaction, which consumed H2 and produced CO. So CO yield increase is higher than that of H2, which resulted in decreased H2/CO ratio in tail gas, accordingly from 700 to 850 °C for undeposited and deposited MC in Table 3.

Compared with undeposited MC, most potassium salt vapor deposited MC exhibited lower CH4 conversion, but a little higher CO2 conversion and CO yield under same reaction condition at 750–830 °C. It could be attributed to the presence of alkali aerosol deposition on MC surface, which caused the decrease of BET area, pore volume, Ni metal surface, and CH4 adsorption amount. Praliaud described that alkali metal acted as a promoter, existing in the form of alkali silicate or nitrate, and mainly associated with an anion.26 However, K vapor deposited on Ni(111) were in the form of K0.5 with σ varying from 0.5 to 0 as the alkali aerosol coverage increase by XPS results in this paper. It could be assumed that an indirect electrostatic interaction occurred between the deposited alkali metal and the active Ni metal. Alkali metal would migrate from the top part of the monolithic catalyst (vicinal to the alkali source) to the whole reforming bed.24 Besides, the deposition of alkali salt vapor may decrease catalyst surface acidity and change the adsorption characteristics of MC, which promoted the carbon elimination reaction, shown in eq 4. And the electron enrichment of metallic phase by alkali metal might increase the back-donation of metal electron to the 2π* antibonding of CO2,29 so CO2 molecules were adsorbed preferentially on MC surface. That promoted the reverse reaction of eq 4, which increased CO2 conversion and CO yield, but decreased the H2/CO ratio in the tail gas.

Although K2SO4 has the highest melt temperature of 1067 °C, K2SO4 deposited MC showed most serious decrease of CH4 conversion among three potassium salts of KCl, K2SO4 and K2CO3. And the deactivation results in Table 3 were similar to that of powdered Pt/Rh catalysts, where BET order after salt deposition was: NiKCl > NiZnCl2 > NiK2SO4 and BET decrease degree was in linear relationship with molecular weight of the deposited salt.11 Besides, KCl was in the melting state, while K2SO4 and K2CO3 still kept in solid state under reforming reaction of 750 °C in this paper, so it might result in different catalytic reforming mechanism on these three potassium salt vapor deposited MC. In the same time, the deactivation of K2SO4 deposited MC may also be caused by sulfide poisoning besides the active Ni phase decrease mentioned above.14 It also should be pointed that the irregular CO2 conversion results at high temperature of 850 °C and H2 yield might also result from the different reforming mechanism and interactions of the complex reforming system,30 where the main reactions were accelerated at different temperature respectively according to their thermodynamic properties.
3.5. Stability of KCl Deposited MC. It is known that Ni-based catalyst deactivation due to carbon deposition via Boudouard and methane decomposition reactions was serious during CH₄ or liquid fuel reforming. In this paper, it was mainly focused on the effect of alkali impurities on biomass fuel gas reforming system, which also contributed to catalyst. The stability tests were carried out at 750 °C.

For undeposited MC, CH₄ conversion maintained about 90% after 60 h time on stream (TOS) and tail gas compositions changed slightly in Figure 6: CH₄ content increased from 1.03 to 1.38 vol % and H₂ content was almost the same of 32.0%. While after KCl vapor deposition, CH₄ conversion decreased from 87.2% to 32.0% and H₂ content in tail gas decreased from 35.1 to 26.7 vol % after 17 h TOS. According to SEM-EDS results, it could be conferred that the deactivation by KCl deposition was probably caused by a weak interaction between alkali and Ni and MgO, resulting in rapid migration of alkali metal through the whole catalyst bed in 3.3. In the beginning, the alkali was primarily retained at the top part of MC bed (position 1 in Figure 5B). Subsequently, extra alkali salt vapor spread the bed and poisoned the whole catalyst, which might be the main reason for the decreased CH₄ conversion due to the coverage of Ni phases by alkali vapor deposition.

3.6. Reforming of Real Practical Biomass Fuel Gas over MCP. The quick deactivation of KCl deposited MC for dry CH₄/CO₂ reforming of model biomass fuel gas in section 3.5 was due to the low Ni loading amount (5.5 wt %, NiO) and high KCl deposition amount (7.8 mg/L KCl in carrier gas for 6 h, K content of 0.85 wt % and 1.39 wt % at the top part of deposited MC by ICP-AES and EDS respectively), which is far higher than K amount by emission of atomized alkali salt solution for 2 h (37 mg/m³)¹¹ and real K content in fly ash during biomass gasification. To investigate the real performance of cordierite monolithic catalyst of MCP, larger in size than MC, the reforming procedure of our pilot-scale integrated dimethyl ether synthesis system from air gasification of pine sawdust (200—250 kg/h) was carried out and the results are shown in Figure 7 and Table 4.

It can be seen that the pressure drop of the reformer fluctuated over the first 2 h TOS, and the highest pressure drop was up to 1200 Pa (Figure 7A) because of the unstable gasification process. But after about 2 h TOS, the pressure drop kept stable of about 700 Pa and that would decrease the power requirement for roots blower, which ventilated biomass fuel gas to the gas tank. The reforming effect of real raw biomass fuel gas over MCP was obvious: CH₄ conversion of raw biomass fuel gas (initial compositions, H₂/CO/C₂H₄/CH₄/CO₂/N₂ = 10.2/16.8/0.5/6.4/15.2/51.0 vol % in Figure 7C) was above 84% during 60 h TOS at 600 °C in Figure 7B. CO₂ conversion was relatively low to below 40% because of the low reforming temperature in the reformer, resulting from inadequate external heat transfer of the burner by combusting diesel. And tar content decreased from 4.8—5.3 to 0.12—0.14 g/m³ after catalytic reforming, which resulted in more than 40 vol % content of H₂ and CO with H₂/CO ratio of around 1, higher than the original content of 27 vol %.

The particle size of fly ash was 0.15—0.85 mm in this gasification process, confirmed by SEM. After 60 h operation, the K and Na content in MCP at different positions of reformer (as shown in Figure 2) was similar of 0.03—0.07 wt % except at the reformer inlet (0.26 and 0.11 wt %, respectively, in the intermediate tube) in Table 4. It was because of the relatively slow fuel gas flow in the up-draft reformer and vicinity to the alkali source, where K and Na in the fly ash were inclined to deposit. And this was accordance with high K content at the top part of MC during model experiments in section 3.3, which approved the application possibility of model alkali salt evaporation method to investigate fly ash impurities on reforming.
ing performance. Because of the low alkali content in practical reforming process, CH₄ conversion, H₂, and CO yields kept high after 60 h operation in Figure 7, which is different from the quick deactivation of deposited MC by high K amount in Figure 6.

Conclusion

The deposition of alkali salt vapor (KCl, K₂SO₄, and K₂CO₃) on the Ni-MgO/γ-Al₂O₃/cordierite monolithic catalyst showed that the high content of alkali was mainly existence at the top part of monolithic catalyst (vicinal to alkali source), which caused quick catalyst deactivation for dry CH₄/CO₂ reforming performance of model biomass fuel gas (H₂/CO/C₂H₄/CH₄/CO₂/N₂=15.8/12.1/2.51/15.0/22.1/32.6 vol %). The extent of catalyst deactivation increased with alkali salt agglomeration on the catalyst surface and the potassium compound, in the form of K⁺ (Na⁺) with ᵃ varying from 0.5 to 0, which resulted in an indirect electrostatic interaction between the oxygen atom of adsorbed CO₂ and the active Ni metal.

Compared with the high conversion of CH₄ (above 80%) and tar (above 90%) and high H₂, CO content (>40 vol %) in tail gas after 60 h real biomass fuel gas reforming operation in the pilot-scale integrated gasification/reforming system, it could be concluded that far lower K and Na content in monolithic catalyst in the reformer, caused by real fly ash, was the main reason. And the reforming process in the pilot-scale plant was tested to be feasible for produce biomass synthesis gas for the following liquid fuel synthesis and direct dimethyl ether synthesis process are ongoing by our group. The synthesis reaction heat and tail gas combustion will be applied to generate heat for the reformer as much as possible.

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