Reforming of Biomass Raw Fuel Gas over Monolithic Catalyst

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Abstract: The performance of the Ni monolithic catalyst for dry reforming and partial oxidation reforming (POR) of biomass fuel gas were studied at 750 ℃ during 108 hours with naphthalene as tar model compound. The catalyst shows good performance in both dry reforming and POR. Tar was completely converted to permanent gases and lighter hydrocarbon compounds. The catalyst kept its activity during the lifetime test.

Key words: biomass fuel gas; monolithic catalyst; POR; tar elimination
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Biomass is a renewable and clean energy source. The main components of biomass fuel gas produced from biomass gasification are H_2, CO, CH_4, tar and other light hydrocarbons[1]. Converting the biomass fuel gas to low H_2/CO ratio (≈ 1) synthesis gas is an ideal way for synthesis of liquid fuels. We have prepared the high stable Ni based catalysts reported in previous paper[2]. In this paper we prepared monolithic catalysts by impregnation of Ni on cordierite surface. The reforming performance of catalyst in both dry reforming and POR was investigated.

1 EXPERIMENTS

1.1 Catalyst preparation and activity test

Monolithic catalysts were prepared by impregnate of Ni on cordierite support. Dry reforming and POR of biomass fuel gas were studied at 750 ℃. The flow rate of biomass fuel gas was 300 sccm and the O_2/N_2 (95/5) flow rate was 60 sccm. The composition of the biomass fuel gas is: H_2 16%, CO 12%, C_2H_4 2.5%, CO_2 22%, CH_4 15%, N_2 32%.

1.2 Gas Sampling and Analysis

The content of N_2, CO, CO_2, CH_4, H_2, C_2H_4 in outlet gas were analyzed with gas chromatograph equipped with TCD and FID. Tar cracked resultants were analyzed by GC/MS.

2 RESULTS AND DISCUSSION

2.1 Reforming reaction

Fig. 1 (A) shows the H_2/CO ratio of outlet gas. In dry reforming runs, average H_2/CO ratio increase from 0.95 to 1.15. The effect of O_2 on raising H_2/CO ratio is evident. In POR runs, the average ratio of H_2/CO increase from 1.09 to 1.35. O_2 reacted with CH_4 and H_2 to produce H_2O, which can raise the H_2/CO ratio by water gas shift reaction. C_2H_4 wasn't detected in both reforming runs. Fig. 1 (B) shows the conversion of CO_2 in different runs. In dry reforming runs, the average conversion of CO_2 is 80%.

No pressure change was found in the whole reactions. Fig. 1 (B) shows the CH_4 conversion in both runs. In dry reforming, the average conversion of CH_4 was 92% with the highest record of 93.8%. In POR, average conversion of CH_4 was 95.4% with the highest record of 98%. This may due to the reaction of partial oxidation of methane[3-4]. In both reforming processes, no drop of conversion of CH_4 was detected, which indicated that the catalysts have excellent activity and stability.

2.2 Biomass tar cracking

The content of naphthalene in biomass fuel gas was 4.26 g/m^3. The conversion of Fig. 1 components change vs time on stream tar is higher than 99%. Most of tar converted to permanent gases. Table 1 shows the lighter components remained in synthesis gas, the con-

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centration of which is very low. MC—3 catalyst shows good tar elimination ability.

Tab. 1 The content of tar species in the outlet fuel gas over MC—3 catalyst

Species	butylene	benzene	toluene	ethylbenzene	m-xylene	p-xylene	styrene
Concentration($\mu g/m^3$)	151.4	276.2	35.3	8.9	9.2	5.0	493.4

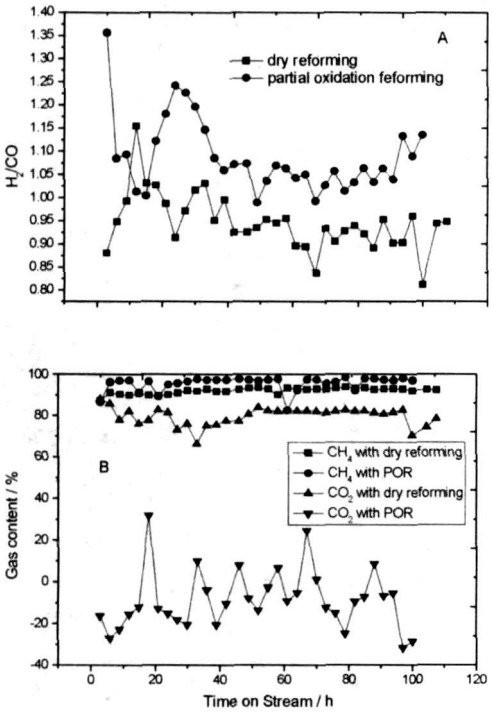

Fig. 1 Componeht change vs. time on stream

2.3 Mechanism

The mechanism maybe that the tar is absorbed on the Ni atom, formed media compounds. CO_2 also absorbed and cleaved to CO and O free radicals. CO desorbed then form the final products. O free radical attacked the media compounds to form the resultants. When O free radical attacks the naphthalene, the longer bonds such as II, IV bonds are easier to cleave and form resultants such as benzene and styrene. The inert species formed coke[5].

3 CONCLUSIONS

MC-3 monolithic catalyst shows excellent reforming activity in both two reactions. Tar was completely converted to permanent gases and lighter hydrocarbon compounds. No pressure drop was detected and the conversions of CH_4 and H_2/CO ratio of outlet gas kept stable during the 108 h.

References:

[1] CORELLA J, SANZ A. Modeling circulating fluidized bed biomass gasifiers. A pseudo-rigorous model for stationary state [J]. Fuel Proc Tech, 2005, 86 (9): 1021—1053.

[2] WANG T, CHANG J, CUI X. Reforming of raw fuel gas from biomass gasification to syngas over highly stable Ni-Mg solid solution catalysts [J]. Fuel Proc Tech, 2006, 87 (5): 421—428.

[3] BHARADWAJ S S, SCHMIDT L D. Catalytic partial oxidation of natural gas to syngas [J]. Fuel Proc. Tech, 1995, 42 (2/3): 109—127.

[4] LI C, FU Y. Effect on the carbon deposit in CO_2 reforming of CH_4 over Ni/Ce—Zr—AL—Ox catalyst by adding Steam [J]. Acta Phys-CHem Sin, 2004, 20: 906—910.

[5] CIMINO S, BENEDETTO A D, PIRONE R. Transient behaviour of perovskite-based monolithic reactors in the catalytic combustion of methane [J]. Catal Today, 2001, 69 (1—4): 95—103.

镍基整体式催化剂重整净化生物制粗燃气性能的研究

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摘 要: 以萘为焦油模型化合物, 考察了镍基整体式催化剂上生物质粗燃气干重整和临氧重整的性能。镍基重整催化剂表现出良好的催化重整活性, 焦油全部转化为 H_2、CO及微量轻质组分。在 750 ℃下连续反应 108 h 未检测到反应器压降变化和 CH_4与焦油转化率下降, 整体式催化剂表现出较好的活性和稳定性。

关键词: 生物质粗燃气; 整体式催化剂; 临氧重整; 焦油转化

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