Renewable Energy from Nature— Hydrogen Production from Bio-ethanol Steam Reforming

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Abstract: Ethanol and ethanol-water mixture were converted directly into H_2 with ~60% selectivity and ~100% conversion by a catalytic reforming on nickle lanthanide oxide catalysts. The catalysts were optimized and the reforming reaction were performed at temperatures sufficiently low that the water gas shift (WGS) reaction can be combined to decrease CO. This process has great potential for low-cost H_2 generation in fuel cells for small portable applications while where liquid fuel storage is essential and where systems must be small, simple, and robust.

Key words: hydrogen production; ethanol steam reforming; catalyst system
CLC number: O646 Document code: A Article ID: 0529-6579 (2007) S1-0037-03

In order for hydrogen fuel cells to have a large impact on reducing greenhouse gas emissions, the hydrogen needs to be derived from sunlight, either directly or indirectly from biomass through photosynthesis. The use of hydrogen fuel cells in vehicles or in portable power plants will require light weight H_2 storage or "on-board" reforming of hydrogen-containing compounds into H_2[1]. Promoting the use of bio-fuels is an important Chinese objective. Bio-ethanol, derived from biomass, may be the best alternative to achieve the integration of renewable sources in the energy mix. Introduction of bio-ethanol as a renewable fuel, in association with hydrogen and fuel cells, also will ease the demand of fossil fuels since this fuel is already produced in Europe, America and China and can be produced at much higher rates. Currently, large quantities of ethanol are produced in Brazil and the U. S. from grains such as corn, wheat and sugar cane. The cost of production of aqueous ethanol, as required in the hydrogen production process, is significantly lower than the cost of anhydrous ethanol which is required in internal combustion engines. In the reformation of ethanol for hydrogen production, a large fraction of the hydrogen fuel originates from water, thus water is functioning as a hydrogen source.

1 Experimental results and discussions

Perfect reaction of ethanol steam reforming shoud be:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2, \quad \Delta H_R \cong +180\ kJ/mol \tag{1}$$

which could be seen to be combined by steam reforming reaction:

$$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2, \quad \Delta H_R \cong +260\ kJ/mol \tag{2}$$

and water gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2, \quad \Delta H_R \cong -40\ kJ/mol \tag{3}$$

We have used Ni and other transition metals with additives of Y_2O_3, Al_2O_3, La_2O_3, CeO_2 as catalysts for these reactions[2-3]. We show here only results from Ni/Y_2O_3 because it was more stable and gave greater WGS activity.

The catalysts activity and selectivity of steam reforming of ethanol was conducted with a fixed-bed reactor fitted in a programmable oven with three heat sections, with an operating range up to 300℃, 700℃ and 1000℃, respectively. The flow rate of ethanol-water solution was controlled by a pump. The components of the effluent were through a condenser, then were introduced to a gas chromatograph (GC).

Typical results of ethanol steam reforming on $Ni-Y_2O_3$ are shown in Fig. 1 and Table 1. Fig. 1 shows that for catalyst Ni/Y_2O_3, in the temperature range of 250 ~ 350℃, The selectivities curves indicat that the WGS reaction of CO has occurred in the range of 250 ~ 280℃. When temperature increased to 300℃, the de-

①收稿日期: 2007-01-10
基金项目: 中-希国际科技合作资助项目; 国家自然科学基金资助项目 (9041002; 50606020)
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composition of ethanol at low temperature

$$C_2H_5OH \rightarrow CO + CH_4 + H_2, \quad \Delta H_R \cong +49\ kJ/mol \quad (4)$$

occurred so as to make the increasing of the selectivity of H_2 and CO[4]. When temperature increased to 320℃, the relative fraction[5] of WGS reaction increased so as to decrease the selectivity of CO and keep the increasing the selectivity of H_2. The conversion of ethanol has reached to 95.3% at 320℃. This high result means very good activity of the Ni/Y_2O_3 catalyst. So, according to the distribution of selectivities in this reaction system the predominant reactions are the reforming reaction of ethanol and water. As the temperature increases, however, the WGS reaction and the decomposition of ethanol become the dominant reactions.

Thermodynamics claimed when $T > 200$℃, the decomposition of ethanol (reaction (4)), will be favored. However, when $T > 530$℃, the methanation will be avoided. If the methanation could be avoided the lose of 3 mol H_2 to form one CH_4 would be prevented. But the high temperature will cause the sinter of catalysts and coke formation. There is one couple contradiction. The WGS reaction can decrease CO and increase H_2, it was favored at temperature range 200 ~ 400℃. So, we hope to combined the WGS reaction and the reforming reaction at an appropriate temperature. In the process of heat treatment, the surface area change of active particles (such as metal) mostly due to the change of crystal grain and type, but generally it was the change of grain size that lead to the change of surface area. Through heat treatment we get more active and stable sample.

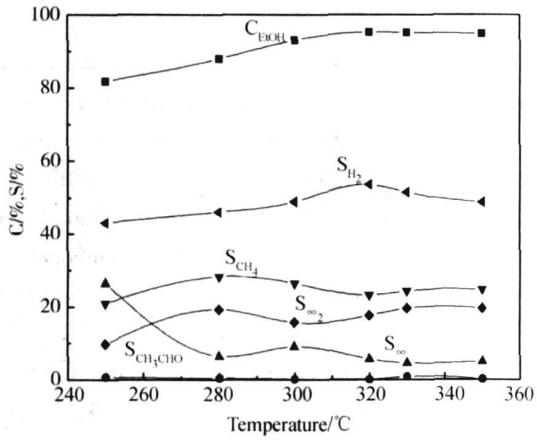

Fig. 1 Effect of reaction temperature (250 ~ 350℃) on conversion of ethanol (C_{EtOH}) and on selectivity of hydrogen (S_{H_2}), carbon monoxide (S_{CO}), carbon dioxide (S_{CO_2}), methane (S_{CH_4}) and acetaldehyde (S_{CH_3CHO}), obtained over the Ni/Y_2O_3 catalyst sample reduced by hydrogen for 2 h at 450℃. Experimental conditions: mass of catalyst 4 g, particle size 0.5 ~ 1 mm, $H_2O/EtOH$ mol ratio 3 : 1, liquid flow rate 0.05 $cm^3 \cdot min^{-1}$, $P = 1$ atm.

The test results in table 1 show that the modified sample treated at 500℃ with NiO grain size of 13.3 nm and Y_2O_3 of 76 nm is more greater for ethanol reforming. During the 79 h test at 350℃, the sample is stable, and no CO detective measured in the first 49 h. The mean selectivity of H_2 is about 65.0%, the output gas flow rate is stable.

2 Conclusion

These simple experiments demonstrate that ethanol can be converted into H_2 simply and with high efficiency. Fast and efficient renewable fuel reforming is one of the critical steps in producing H_2 for fuel cells and the "hydrogen economy"[1] and ethanol is now the most available and economical renewable fuel. This process just realizes the ideal of "Energy from nature, make the usage of energy more harmonious with nature".

Tab. 1 Ethanol steam reforming over modified sample Ni/Y_2O_3 at 350℃

T (h)	Selecivity (mol%) H_2	CO	CH_4	CO_2	C_2	Conversion (mol%) Ethanol	H_2O	Flow rate Liquid income ml·min-1	Gas outcome/ml·S-1
3	56.6		10.7	15.7	17.0				
4	58.6		12.8	19.1	9.5				
7.3	64.6		12.7	16.9	6.8				
8	64.5		12.6	16.4	6.5				0.04
14.3	50.3		7.0	10.8	31.8				0.09
15	68.7		12.1	20.2					
16	68.6		12.9	20.1				0.05	
20	68.7		12.9	21.1					0.05
22	66.2		12.6	21.2					
26	62.9		11.3	19.2	6.6				
38	66.8		10.0	16.1					0.06
41	65.2		12.3	22.5					0.04
50	65.0	0.5	12.3	22.2					0.04
61	60.1		10.8	17.2	11.8				0.06
65	61.1		12.5	24.3				0.2	0.23
70	62.3	0.4	12.1	22.8	2.8			0.3	0.38
75	64.0		12.8	23.4				0.4	0.42
79	64.9	0.4	12.7	22.0		98.6	87.9	0.5	0.38

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(下转 43页)

stabilization were discussed in the paper. Heavy metal absorption added with bentonite is influenced by the surface properties of this adsorptive material, while sulfide has chemical reactions with heavy metal ions to form insoluble substances.

(2) Bentonite has excellent adsorptive properties on heavy metals like Cd and Ni in neutral circumstance. This method is restricted in lower pH circumstance.

(3) Heavy metal stabilization with sulfide is a kind of effective method by decreasing the leaching concentration of heavy metals to meet the standard of sludge utilization in agriculture. When 10～15 gram of reagent was used, leaching concentration of Zn was 3～4 mg/L only, the ratio of the unsteady speciation of heavy metals in sludge reduces greatly while that of stable speciation increases after stabilization.

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利用膨润土及硫化物对污泥中重金属的稳定化研究

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摘　要：分别采用膨润土及硫化物对污泥中重金属进行了稳定化研究，通过重金属形态分析及浸出毒性实验，研究了两种物质吸附及稳定化污泥中重金属的作用，从而为污泥农用中重金属的处理提供一个有效的方法。结果表明，经过处理后，污泥中重金属的浸出毒性减少，可以满足污泥农用标准，重金属不稳定形态含量显著减少。其中，膨润土对重金属 Cd、Ni具有较好的吸附效果，pH值是影响吸附的重要因素；而硫化物对重金属 Zn、Cu和 Cd具有较好的稳定化效果，当加入 10%的药剂时，Zn的浸出浓度仅为 4.96 mg/L，同时污泥中重金属不稳定形态的比例减少了约 50%～60%。

关键词：污泥，重金属，膨润土，硫化物

中图分类号：X131

(上接第 38页)

来自自然界的可再生能源 — 生物质乙醇重整制氢

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摘　要：在镧系金属氧化物载镍催化剂上通过催化重整乙醇和乙醇水溶液可以直接转化为 H_2，H_2 的选择性达到 60%，乙醇的转化率达到 100%。优化催化剂及降低重整反应的温度以使水汽转化反应同时发生来降低产物气中 CO的含量。该过程对于生产小型燃料电池的低成本燃料 H_2，以及便携燃料电池系统需要液态燃料存储的应用具有巨大的潜在价值。

关键词：制氢；生物质乙醇；水蒸汽重整；催化剂；系统

中图分类号：O646