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Hydrogen production for SOFCs application via autothermal reforming of volatile organic compounds on Ru-pyrochlore catalysts

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Abstract

Volatile Organic Compounds (VOCs) from industrial coating operations could be valuable energy resources if collected and used effectively. A promising approach is to generate syngas stream for Solid Oxide Fuel Cells (SOFCs) application by autothermal reforming of them. However, conventional nickel-based catalysts with whatever promoters/supports or formulations are not very successful for this process for lacking of activities or deactivating quickly due to sintering or carbon deposition at the presence of high percentage of aromatic compounds or sulfur chemicals. By contrast, there also exist many big challenges for precious metal-based catalysts in terms of longevity and cost effectiveness. In this paper, Ruthenium noble metal dispersed in a formulation of pyrochlore structure was explored, and various VOCs with wide range of monoaromatics additives of various species and fairly amount of naphthalene was used as fuels to simulate actual VOCs. It was found that this catalyst not only had quite good initial activity but also showed very good stability during the longevity tests, which was considered as important as, if not more important than, the former for commercialization. Eventually, actual VOC collected from a painting-booth was tested for this autothermal reforming process. The longevity test verified the high activities and good stabilities of this catalyst. Most likely the precious metal atomically dispersed in a stable structure of pyrochlore contributed to the super performance, although fundamental studies to understand the reaction mechanism was much needed.

Keywords: Hydrogen; VOCs; Autothermal reforming; SOFC;Pyrochlore; Catalyst; Longevity test.

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1. Introduction

Nowadays, many industrial coating facilities implement emission reduction technologies to reduce Volatile Organic Compounds (VOCs) emissions. Although effective, VOC abatement systems like the popular regenerative thermal oxidation process, are costly to operate, require substantial maintenance resources and produce extra pollutants like SOx and NOx. On the other end, VOC from these industrial coating operations could be valuable energy resources if collected and used effectively. So in this paper, we put forward an energy recovery concept, i.e., syngas production for fuel cells via autothermal reforming process. In this process, VOCs were collected and then at high temperatures with steam and air were converted into syngas for SOFC application.

However, there still exist formidable challenges facing this reforming process, among which is the development of high efficient and endurable catalysts. The conventional nickel-based catalysts with whatever promoters/supports or formulations are not very successful for this process for lacking of activities or deactivating quickly due to sintering or carbon deposition at the presence of high percentage of aromatic compounds or sulfur chemicals. By contrast, there also exist many big challenges for precious metal-based catalysts in terms of longevity and cost effectiveness. Based on new literatures, Rh-pyrochlore catalysts are very promising for this purpose[1]. In order to further lower the cost, Ruthenium noble metal dispersed in a formulation of pyrochlore structure was explored in this paper, and various VOCs with wide range of monoaromatics additives of various species and fairly amount of naphthalene was used as fuels to simulate actual VOCs.

2. Experimental

2.1. Catalyst development

Pyrochlore catalysts with a formulation of $(La,M)_2(Ru,Zr)_2O_{7-\delta}$ were prepared using a variation of the Pechini method which produces highly uniform non-substituted and substituted catalyst crystals, which was also widely known as the polymerization and combustion method path[2]. The desire amount of metal salts were dissolved in de-ionized water, then was combined with a citric acid (CA) solution in a 1/1 molar ratio of CA/metal. The solution was then heated to 65-70°C while being stirred to ensure complete metal complexation. Once the temperature is stabilized, a 2/3 molar ratio of ethylene glycol to CA was added into the solution. The solution was left stirring on the hot plate until most of the water had evaporated and a transparent and viscous gel formed. At this point, the stir bar was removed from the beaker, and the gel was left on the hot plate to promote the polyesterification reaction between EG and CA and ultimately formed the organic polymeric network. During this time, the gel began frothing and bubbling violently while some NOx were emitted due to the decomposition of the nitrate precursors. The foam-like mass that remained was then placed in an oven at 110-130°C to dry overnight. Finally, the organic precursors were oxidized by calcination at 900-1000°C overnight to form the catalyst powders.

2.2. Catalyst evaluation

A predetermined amount (0.1-2g) of catalyst with desired pellet sizes diluted with some quartz chips was loaded in the quartz reactor tubing between two quartz wool plugs. VOCs and water were injected using HPLC pumps respectively into a vaporizer that was maintained at sufficient temperature, and mixed with air controlled by MFC near the inlet of the reactor. Prior to the reaction, the catalyst was preheated to a temperature slightly lower than the targeted temperature under He or N_2 inert gas purging. During normal runs, further adjustment of temperature to the desired may be needed. Downstream the reactor, water and un-reacted VOC and other possible high boiling point by-products were condensed in a condenser. The product gas was analyzed by an on-line Shimadzu 17A GC and measured by soap film meter. The general operation conditions, unless mentioned otherwise, were listed in Table 1.

Table 1. General operation conditions

Items	Operation Conditions
Catalyst	0.5g
GHSV*	47500 h^{-1}
Temperature	550-850 °C
S/C mole ratio	3.0
O_2/C mole ratio	0.4

* Calculated by total inlet flow at normal conditions divided by catalyst volume

3. Results and discussion

3.1. In-house pyrochlore catalyst and comparison with its NETL counterpart

In order to simplify the catalyst screening process, n-butanol was used as VOCs surrogate initially. Figure 1 presented butanol conversion along with operation temperature. Clearly, when the operation temperature was above 700°C, conversion of butuanol on all the catalyst were close to 100%. However, at lower operation temperatures, Catalyst 3 with only 1wt% Ru loading showed very poor performance, indicating that adequate amount of precious metal loading is indispensable. Moreover, it seems the in-hosue Ru-pyrochlore catatlyst (Catalyst 1) showed much better performance than its NETL counterpart with a similar amount of noble metal loading at an even lower temperature of 550°C, which was quite beneficial for autothermal reforming process in terms of energy saving and catalyst stability.

Meanwhile, less ethylene was produced on the in-house pyrochlore catalyst compared with its NETL counterparts as shown in Figure 2, which indirectly suggested that the former system could be more stable during a normal operation considering that ethylene was a well-known precursor for carbon deposition and coke formation.

H_2 production (Figure 3) is a key index for catalyst activity. Therefore, to maximize H_2 production is a goal. Theoretically, H_2 concentration reaches highest at 650-700°C due to CH_4 concentration (Figure 4) sharply decreases at this temperature. Obviously on in-house catalyst and it counterpart NETL formulation catalyst with 2wt% of Ruthenium achieved similar amount of H_2 concentration, which were always close to equilibrium, indirectly confirming their activities. By contrast, for the NETL formulation with only 1wt% *Ru* the H_2 concentration was greatly compromised by the dilution of N_2 because of the low conversion and by the tradeoff of CH_4 slip (Figure 4) and higher *CO* production (Figure 5) due to less activity to *CO WGS* reaction.

Again, there existed a balance of *CO* and CO_2. For Catalyst 1 and 2, i.e., in-house pyrochlore catalyst and its NETL counterpart with 2wt% *Ru*, the concentration trends of *CO* and CO_2 were right opposite and their concentration were almost complemental considering that production of methane was relatively small. As for the NETL counterpart with only 1wt% *Ru*, obviously the water gas shift reaction was far from equilibrium resulting in a completely different *CO* and CO_2 trend and balance.

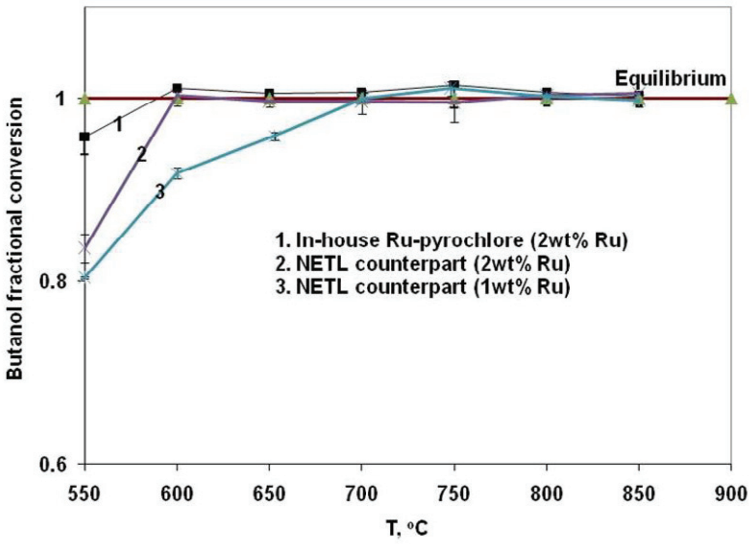

Fig. 1. n-Butanol conversion as a function of operation temperatures

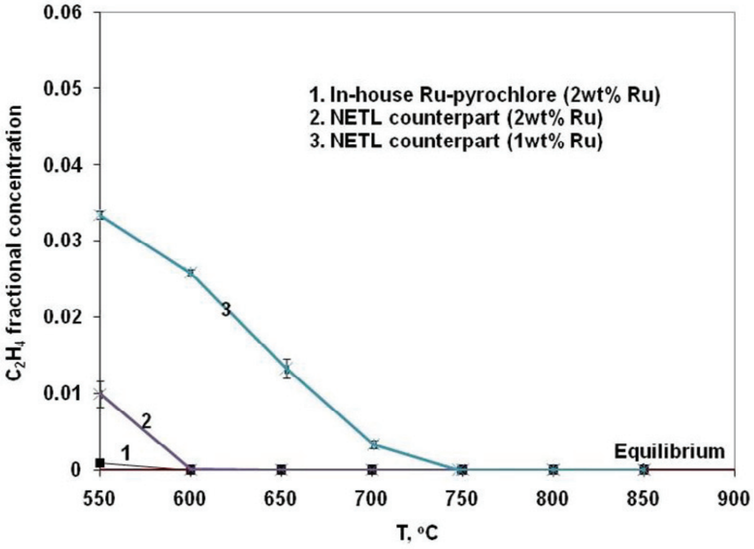

Fig. 2. Ethylene concentration as a function of operation temperatures

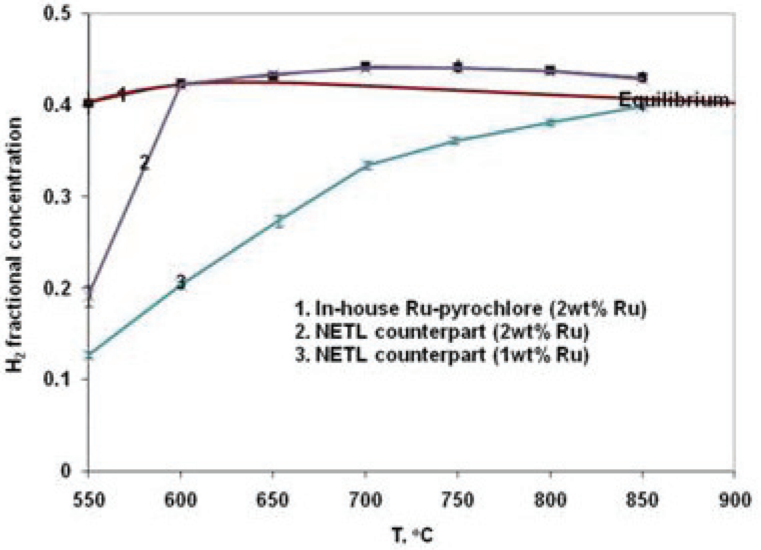

Fig. 3. Hydrogen concentration as a function of operation temperatures

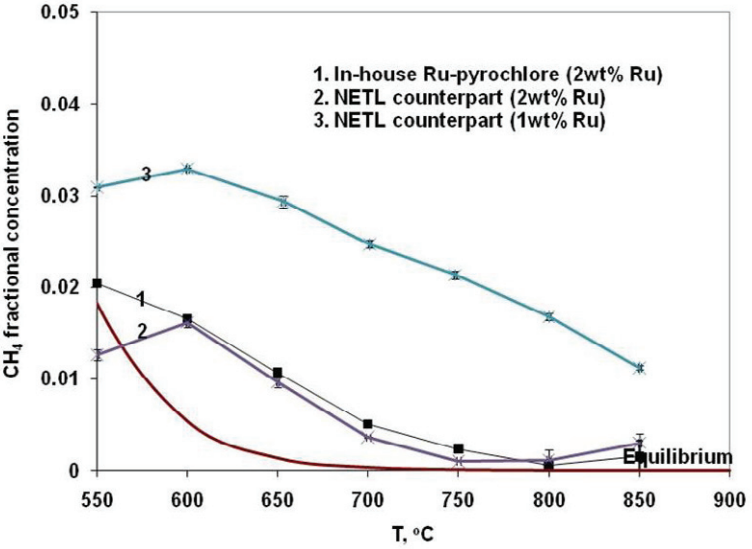

Fig. 4. Methane concentration as a function of operation temperature

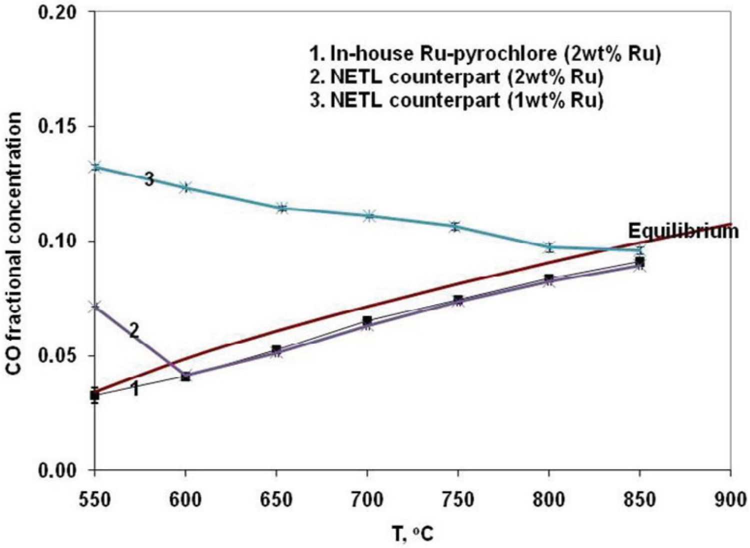

Fig. 5. CO concentration as a function of operation temperature

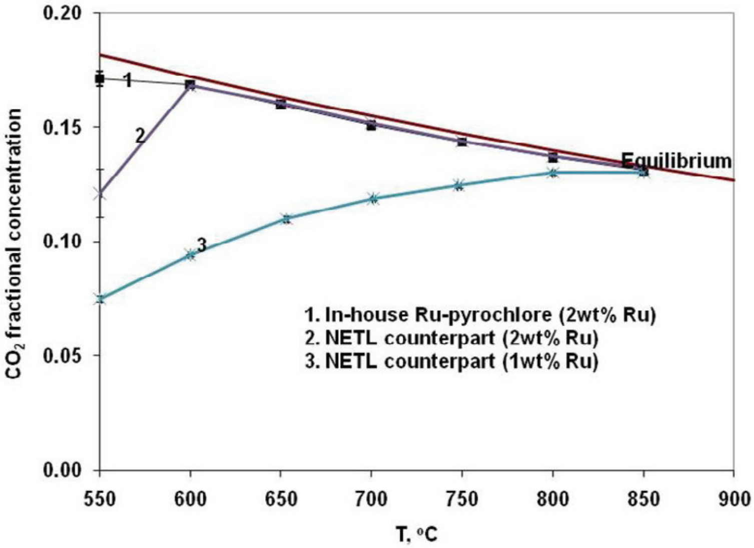

Fig. 6. CO_2 concentration as a function of operation temperature

3.2. Simulated VOCs longevity test on in-house catalyst

Obviously, using the single component n-butanol as surrogate for industrial VOCs was too simplified, therefore a much complex simulated VOC mixture were prepared and its comparison with actual VOCs were shown in Table 2.

It could be expected that it would be harder to reform the simulated VOCs and actual VOCs taking into consideration there are a large amount of aromatics and even a little amount of naphthalene in them. However, the low sulfur existence in the actual VOCs provided a perfect opportunity for reforming process.

Table 2. Actual and Simulated VOCs composition

Actual paint VOCs component (wt%)		Simulated VOCs component (wt%)		
Oxygenates and Alphatic HCs	35.66	n-Butanol	14.89	49.35
		Butylacetate	24.75	
		Heptane	9.71	
Monoaromatics	64.24	p-Xylene	29.22	50.60
		1,3,5-Trimethylbenzene	5.69	
		1,2,4-Trimethylbenzene	15.69	
Naphthalene	0.10	Naphthalene	0.05	0.05
Sulfur	~2.3 ppmw	Sulfur	-	-

Figure 7 showed a 900h longevity test of simulated VOCs on the in-house catalyst. As shown in Fig. 7a, the total conversion of simulated VOCs kept unchanged and close to 100%. The reformate composition as shown in Fig. 7b, although slightly changed along with time on stream, the overall composition shifting was relatively small, indicating that the catalyst had a very good stability. As mentioned before, in the reforming process, stability is as important as, if not more important than, the initial activities. It should be noted that there was an unknown sharp shifting of the reformate composition in the middle of the run. Likely, a suddenly catalyst bed shifting at that time for some reason cause the big changes.

3.3. Actual VOCs longevity test on in-house catalyst

A 700h longevity test for actual VOCs on the in-house catalyst was carried out as shown in Figure 8. During the whole time on stream, both actual VOCs conversion and reformate concentration stayed almost unchanged, which was a good indication of the catalyst stabilities. It seems that the high aromatics and low concentration sulfur presence did not have manifest effect on the performance of the catalyst.

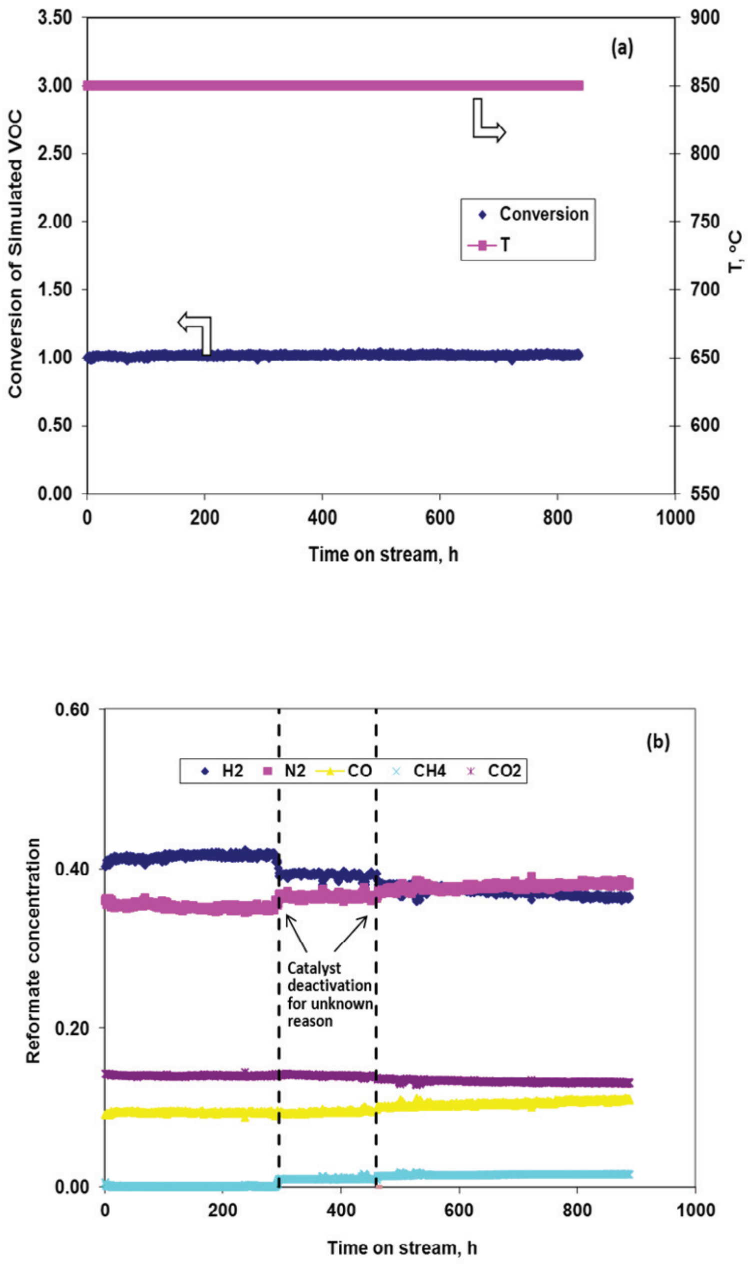

Fig. 7. Simulated VOCs longevity test on in-house catalyst (a) VOCs conversion and (b) reformate concentration

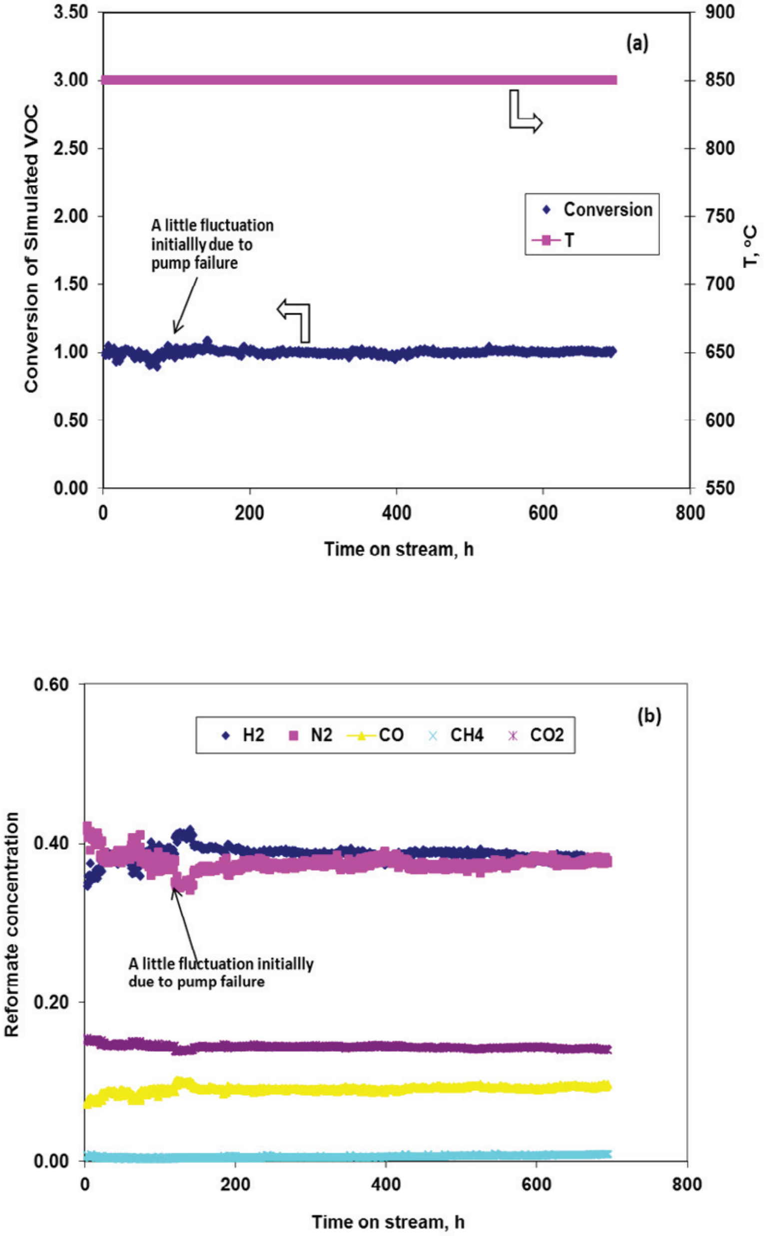

Fig. 8. Actual VOCs longevity test on in-house catalyst (a) VOCs conversion and (b) reformate concentration

4. Conclusion

A Ru-substituted pyrochlore catalyst was developed and successfully used for autothermal reforming of n-butanol, simulated VOCs and actual paint VOC samples. The durability test for autothermal reforming of actual paint VOC was steadily carried out for 700h. Therefore, it is safe to conclude that the metallically dispersed ruthenium in the stable pyrochlore structure contributed to the chemical and thermal stability of the catalyst as well as it high activity in the harsh VOCs autothermal reforming system

Acknowledgements

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