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Preparation of Onboard Reforming Catalyst for Methanol by Chemical Vapor Deposition

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Abstract. NiO deposited on the wall of the pore of the filter by the reaction with $\text{NiCl}_2(\text{g})$ and $\text{O}_2(\text{g})$. $\text{NiCl}_2(\text{g})$ and $\text{O}_2(\text{g})$ are separately fed at the opposite side of the filter (namely inner and outer side). Used alumina filter is mean pore diameter $1\mu\text{m}$, o.d. 10mm, thickness 1mm. This NiO deposited filter was activated by hydrogen to form $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, then the catalyst was measured methanol decomposition activity. From the results, increment of catalytic component increases the specific catalytic activity, but they have an optimal value of Ni deposition. As the shape of the catalyst is favorable to reduce the pressure drop of reactant through the catalyst, this catalyst may be available to treat massive flow. It was found that it is a great catalyst of promise to onboard cracking for methanol automobile.

1 INTRODUCTION

Many works have studied for densification of preform with applying CVD[1] and CVI[2]. Scarcely studies are to prepare the catalysts. Preparation of membrane catalyst mainly has been coated on surface of the support rather than embedding the catalyst component[3]. We attempted to prepare the membrane catalyst by embedding a catalyst component into the alumina filter (mean pore diameter $1\mu\text{m}$, o.d. 10mm, thickness 1mm and 20mm length). In the embedding chemical vapor deposition, $\text{NiCl}_2(\text{g})$ and $\text{O}_2(\text{g})$ was counter currently poured into the pore of the filter and deposited NiO in the pore of the filter. This catalyst are activated by hydrogen to produce a $\text{Ni}/\text{Al}_2\text{O}_3$, and the rate of methanol decomposition on the catalyst was measured. From the results, the specific catalytic activity increases with the content of the catalytic component NiO, and the optimal Ni content is present. As the shape of the catalyst is favorable to reduce the pressure drop of reactant through the catalyst, this catalyst may be available to treat massive flow. It was found that it is a great catalyst of promise to onboard cracking catalyst for methanol automobile.

2 EXPERIMENT

2.1 Preparation of filter catalyst

Alumina filter (Mitsui Whetstone Co., Multiporelone) of mean pore diameter $1\mu\text{m}$, o.d. 10mm, thickness 1mm and 500mm length, at the preparation, the filter is cut 20mm length. The CVD reactor made by quartz glass, the size is diameter 35mm. The length of evaporation and reaction zone are each 250mm as shown in Fig.1. The alumina filter adheres to oxygen lead pipe (shown in Fig. 1 Cf) using ceramic cement (Toa synthetic

Chemicals; Aronceramics-E). 20g of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ loaded into the evaporation port Eb and, according to the eq.(1), the evaporation temperature was adjusted to desired NiCl_2 vapor pressure.

$$\log P = 12.051 - 11499/T \quad (1)$$

Figure 1 CVD reactor

Ic; Inlet for N_2 Carrier gas of NiCl_2
 In; Out let for Reaction Products
 Io; Inlet for Oxygen
 Ip; Out let for reaction products
 Eb; Evaporation boat
 Cw; Inlet Cooling water
 Cf; Ceramic filter

2.2 Preparation mode.

Because NiCl_2 is ionic compound, the reaction $\text{NiCl}_2(\text{g})$ and oxygen is slow under dry condition the reaction proceeds in a molecular state, and an appropriate reaction rate can be only obtained by more than 30 times of stoichiometric oxygen and the reaction temperature also more than 873K[5,6]. But in presence of water vapor, the reaction becomes ionic reaction. Under the condition of embedding NiO into the pore, the larger the ratio of the reaction to the mass transfer rate, the NiO is difficult to fill deeply and homogeneously into the pore. The deposition must operate by reaction limited regime. Therefore the reaction took in dry condition. Then some reaction modes are devised the desired reaction performance.

2.2.1 Reactants feed with parallel way (Mode 1);

Carrier gas of NiCl_2 (g) introduced to Ic(Fig.1), the gas stream released through scrubber to the atmosphere. Oxygen lead pipe consists of double tube, the outer side connects the filter with the filter with ceramic cement and the inner side of the filter closes.

Oxygen introduces to Io(Fig.1) and pass through the filter sample and releases to atmosphere as the same way as $\text{NiCl}_2(\text{g})$.

In this case, the reactant flow pattern schematically shows as mode 1 in Fig.2. The oxygen flows parallel with $\text{NiCl}_2(\text{g})$ in the pore as shown in Fig.2. The mole ratio of $\text{NiCl}_2(\text{g})$ and $\text{O}_2(\text{g})$ and flow rates show Run 4 and 9 in

Table 1.

2.2.2 Reactants feed into the pore by molecular diffusion (Mode 2)

NiCl_2 introduces from N(Fig.1) to the reaction zone and releases to the outlet In(Fig.1). Oxygen leads from Io and leaves Ip, and so Ip releases. In this case, let open the front side of the filter. In this way, Oxygen does not force to pass through the pores of the filter, oxygen and $\text{NiCl}_2(\text{g})$ diffuse into each side of the pore.

2.2.3 Oxygen forces to pass through the pore (Mode 3);

The depositions steadily go on as the higher ratio of $\text{O}_2/\text{NiCl}_2(\text{g})$ so that $\text{NiCl}_2(\text{g})$ flows from outer to inner side of the filter. In this case, the carrier gas of $\text{NiCl}_2(\text{g})$ kept constant at 500ml/min, and oxygen flow rates vary 5 to 40ml/min.

Figure 2 Schematic flow pattern reaction zone

2.2.4 $\text{NiCl}_2(\text{g})$ forces to pass through the pore (Mode 4)

Table 1 Reaction condition

mode	Run No.	Flow rate [ml/min]		Reaction Temp.[K]	Partial Pressure[atm]		
		Carrier N ₂	O ₂		N ₂	O ₂	NiCl ₂
1	1	500	50	973	0.896	0.920E-2	1.10E-3
2	2	500	200	1023	0.320	0.289	3.11E-3
3	4	500	200	1023	0.990	9.90E-3	8.15E-3
3	5	500	10	1023	0.800	1.96E-2	8.36E-3
3	6	500	15	1023	0.962	2.09E-2	8.30E-3
3	7	500	20	1023	0.954	3.80E-2	8.20E-3
3	8	500	30	1023	0.936	5.60E-2	8.20E-3
3	9	500	40	1023	0.920	7.36E-2	8.05E-3
4	3	500	5	973	0.739	0.675	4.04E-3

Outlet side of oxygen pass(Fig.1,Ip) opens, outlet side of $\text{NiCl}_2(\text{g})$ pass(Fig.1, In) closes, let leads $\text{NiCl}_2(\text{g})$ stream running from the outside to the inner side of the filter. In this case, Ni component deposits on the outer side of the filter and little NiO deposited observed inner side and within the pore of the filter.

2.3 Measurement of deposited Ni

Radial distribution of deposited NiO measured with EPMA(Shimazu Mnuf Co., EPMA-810) using X-ray length of Ni(1.6572Å), Al(8.005 Å) and Si(7.1245Å) were used by determining the contents, Ni Al and Si, respectively. In the quantitative analysis of deposited NiO, a few mg of the sample dissolved in concentrated nitric acid, and after to heat several hours,

the mixture filtrates and measures with

Induced Coupling Plasma Atomic Flame

Detector(Shimadzu Mnuf. Co., ICP-1000).

2.4 Measurement of Methanol Decomposition Rate

The $\text{NiO}/\text{Al}_2\text{O}_3$ filter sample cements blacked parts of methanol decomposition reactor as shown in Fig.3 the $\text{Ni}/\text{Al}_2\text{O}_3$ was activated with 5 Vol% of hydrogen for 3 hour, and the hydrogen flow rate and the temperature are 40ml/min, 623K, respectively.

After the activation, desired partial pressure of methanol feeds to the reactor then decomposition rate measured with the reaction

temperature range from 623 to 723K. The reaction was followed the

products of hydrogen and carbon dioxide with gas chromatography that was equipped with 2m of active carbon AA-662 30/60 mesh for hydrogen and carbon monoxide, and with 2m of Porapak P 80/100mesh for methanol.

2.5 Measurement of specific surface area and Nickel metal surface area

Fig. 3 Catalytic reactor

The specific surface area of the sample is measured by hydrogen chemisorption method[4]

3 Results

3.1 Preparation mode and the distribution of deposited nickel.

Figure 4 shows the result of preparation mode 1(dashed) and mode 2(solid line), in mode 1, the radial distribution of deposited NiO that was measured with EPMA, NiO deposits is concentrated on the outer side of the filter. And in spite of the oxygen partial pressure varies with one order, but the difference of the deposited amount and distribution does not observed within EPMA. In mode 2, the deposited NiO does not almost detected with EPMA, the fact suggests no deposition occurs in the pore.

The results of mode 3 are shown in **Fig.5a and b**. The deposited amount is the highest at the oxygen rate of 15ml/min. The performance of this mode shows homogeneous NiO distribution in radial direction rather than other reaction modes, deposited NiO are in the pore of the filter. In mode 4, Ni component deposits on the outer side of the filter and little NiO deposited observed inner side and in the pore as shown in **Fig.6**.

3.2 Properties of deposited sample

3.2.1 Ni contents

In order to use deposited NiO sample in methanol decomposition catalyst, the Ni contents are measured and summarized in Table 2. Catalyst are called Cat-x-y, x is number of reaction mode, y means run number in Table 1.

Table 2 Ni contents of Catalyst

Catalyst	Ni content[wt%]
Cat-3-4	3.37
Cat-3-5	11.18
Cat-3-6	21.21
Cat-3-7	60.21

3.3.2 Catalytic properties

NiO deposited sample adhered to C site in conventional flow reactor as shown in **Fig.3** by ceramic cement. Methanol introduced inner side of the sample filter (as shown in **Fig.3** with inlet) and the decomposition rates were measured. In spite of closing the front end side the catalyst, the extent of methanol decomposition was not largely changed. This mean that the rate determining step is in reaction limited step. Then, the rates were measured under the open state of the catalyst, because it can be escape pressure drop during the methanol feed into the catalyst. The measured results are shown for each samples in **Fig.7**, with the conversion [X] as ordinate and W/F [Kg sec/mol] as abscissa.

Sample of Cat-3-4 shows about 80% of methanol conversion at the reaction temperature 573K with $W/F=4000$ [Kg sec/mol]. All of the other results show about 100% conversion at the same temperature, therefore discriminating between these catalytic activities, the reaction rates were measured at 503K, the results are shown in **Fig.8**.

4 Discussion

4.1 Reaction mode and deposited amounts of NiO

Mode 1; According to $\text{NiCl}_2(\text{g})$ and $\text{O}_2(\text{g})$ both force to introduce from outside into inner side of the filter, the outer side concentrations of $\text{NiCl}_2(\text{g})$ and $\text{O}_2(\text{g})$ are higher value than that of the inner side, therefore the amount of NiO deposited becomes higher outside of the filter.

Figure 4 Radial distribution of NiO deposit from EPMA in case of mode 1 and 2

Figure 5a Radial distribution of NiO deposited from EPMA in case of mode 3

Figure 5b Radial distribution of NiO deposited from EPMA in case of mode 3

Figure 6 Radial distribution of NiO deposited from EPMA in case of mode 4

Figure 7 Methanol decomposition activity shown by W/F and conversion x at 503K

Figure 8 Methanol decomposition activity shown by W/F and conversion x at 573K

Mode 2; $\text{NiCl}_2(\text{g})$ passes through the outer part of the filter, $\text{O}_2(\text{g})$ also passes through inner part of the filter, so that each component can only penetrate into the pore by pore diffusion, therefore may not expect higher reaction performance.

Mode 3; Stoichiometrically excess of oxygen feeds from inside to outside of the filter, oxygen concentration was higher than that of $\text{NiCl}_2(\text{g})$ at the inner side of the filter. In this case, NiO homogeneously deposits in the pore.

Mode 4; $\text{NiCl}_2(\text{g})$ feeds from outside to inner side of the filter. In this case, $\text{NiCl}_2(\text{g})$ fills up in the pore and but because of insufficient oxygen concentration, large amount of $\text{NiCl}_2(\text{g})$ solidifies at inner side of the filter.

Above these facts, the mode 3 is the best way to prepare uniform deposition.

4.2 Methanol decomposition Activity

Utilization of methanol to automobile fuel possesses several advantages over fossil fuels, one of them is that methanol is free from nitrogen components, there are little NO_x in the exhaust gas, and second, thermal efficiency is high because the exhaust heat can be recovered by evaporation process of the methanol. Third, the methanol as fuel must not completely decompose to hydrogen and carbon monoxide, because methanol is also burned in the engine. These advantages have already been known as an onboard cracking system. Here, the effectiveness of this $\text{Ni}/\text{Al}_2\text{O}_3$ filter catalyst to the onboard cracking is described below.

4.2.1 Low head loss

Figure 7 shows catalytic activity of the filter catalyst containing nickel (Cat-3-4) 3.3wt% at the reaction temperature 573K. Cat-3-5, Cat-3-6 and Cat-3-7 show all almost about 100% of extent of decomposition at 573K. It is desirable to be able to react at 503K as an onboard cracking catalyst. These reaction activities are shown in Fig.8. The order of resultant activity is Cat-3-5 > Cat-3-6 > Cat-3-7, even at 503K, 60% of methanol decomposes at $W/F=1000[\text{Kg sec}/\text{Mol}]$. From these capacities, if the catalyst loads on 2000ml of displacement capacity of engine, the feed rate required 235~285ml/(STP)/min of methanol. At this time, the amount of demanding catalyst is about 1.5Kg (abs 5 l). And if we use this catalyst for 50ml of displacement engine, the needed catalyst is about 40g (36ml). These weights and volumes are in the range of carrying capacity for scooter and bicycles.

5. Conclusion

Nickel supported cylindrical filter catalyst was prepared with $\text{NiCl}_2 + \text{O}_2$ gas phase vapor deposition on an alumina filter which has a mean pore diameter 1.5 μm . The homogeneous deposition had not been prepared easily with conventional way, so various ways of reaction systems were attempted. As the results, the best way that nickel chloride(g) and oxygen(g) are separately fed at the opposite side of the filter. These reactions can be appreciated over thirty times of oxygen on the stoichiometrical amount of the reaction, and the optimal reactant's ratio exists.

This NiO deposited sample was activated by hydrogen at 623K and was employed for decomposition of methanol as a catalyst. The extents of reactions were almost the same in different two reaction conditions where one is opened and the other closed end of the catalyst. This means the reaction is not influenced by the mass transfer effect. Therefore it can be maintained constant extent of decomposition at any largely fluctuating intake of engine fuel.

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