Effect of support ZrO_2 on selective methanation of CO over the nickel supported catalysts

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Abstract: Four supports ZrO_2 were prepared by thermal decomposition method from zirconium oxynitrate and zirconium oxychloride at calcination temperatures of 400°C and 800°C, respectively. It is found that salt kind and calcination temperature affect phase state (tetragonal, monoclinic), crystallite size and specific surface area of the supports, and thus lead to different catalytic performance for selective methanation of CO for the catalysts Ni/ZrO_2. The catalytic performance is also related to the chlorine ion residues in the support prepared from zirconium oxychloride. The chlorine ions suppressed CO_2 adsorption and enhanced catalytic activity of CO removal.

Keywords: Selective methanation, CO, Chlorine ion residues.

1. Introduction

The H_2-rch gas produced from the fossil resources such as natural gas can be used as fuel for proton exchange membrane fuel cell (PEMFC) only after removing CO in the gas mixture to below 10ppm to avoid poisoning of the anode of the fuel cell. Selective methanation reaction of CO in H_2-rich gas (CO-SMET) is a promising way for this purpose. Both ruthenium and nickel supported catalysts can be used for this reaction. The common supports such as TiO_2 and Al_2O_3 are suitable supports for the metal catalysts [1], in which ZrO_2 as support of the nickel catalysts seems better [2, 3]. In the present work, thermal decomposition method was adopted to prepare supports ZrO_2 from zirconium oxynitrate and zirconium oxychloride. Effect of the supports ZrO_2 on selective methanation of CO over the nickel supported catalysts was studied.

2. Experimental

Four supports ZrO_2 were prepared by thermal decomposition method from zirconium oxynitrate and zirconium oxychloride at calcination temperatures of 400°C and 800°C, respectively. The ZrO_2 powder was impregnated with aqueous solution of nickel nitrate at the set feed atomic ratio of Ni/Zr equal to 0.4. After drying in an oven, the dried samples were calcined in static air in a muffle furnace for 2h at 500°C. The pellets (200mg, 60-80mesh) of the calcined samples were loaded into the quartz tube reactor and reduced at 450°C for 2h in 30%H_2/N_2 gas prior to the catalytic reaction. The feed reactant gas was composed of 1% CO, 70%H_2, 18% CO_2 and 11% N_2 (volume percent). Characterizations were carried out for the supports, the calcined samples and the spent catalysts.

3. Results and discussion

Table 1 lists crystallite size of the main phase (tetragonal or monoclinic, denoted as *t*-ZrO_2 or *m*-ZrO_2, respectively) and specific surface area of the supports ZrO_2. It is seen that thermal decomposition of oxychloride led to larger crystallites' formation (of the main phase) and smaller specific surface areas for the decomposition products (i.e., ZrO_2-Cl-T-400 and ZrO_2-Cl-T-800, in which the letter T stands for thermal decomposition, the letter Cl for the salt of oxychloride and the digital for the calcination temperature). Such the properties influenced dispersion of NiO and metallic Ni on the supports and catalytic activity for CO removal of the nickel supported catalysts finally. Table 2 lists weight percent and crystallite size of Ni phase in the spent catalysts Ni/ZrO_2. Notably the Ni crystallites on the supports Ni/ZrO_2-Cl-T are larger. Theoretic phase composition of metallic Ni in the catalysts is 16.7wt%, corresponding to the atomic ratio of N/Zr equal to 0.42 measured by TPR and XRF.

Figure 1 shows CO concentration in the effluent gas after the catalytic reaction. It is seen that the catalyst Ni/ZrO_2-Cl-T-400 exhibited a wider temperature range 240-300°C of removing CO to below 10ppm. The superior performance is related with dispersion of metallic Ni and chlorine ion residues on and in the support ZrO_2-Cl-T-400. Chlorine ion residues in the support were detected by EDX analysis, corresponding to an atomic ratio of Cl/Zr equal to 0.07. The chlorine ions suppressed CO_2 adsorption/dissociation and enhanced the catalytic activity of CO removal.

Table 1. Crystallite size of the main phase of the supports calculated by the Rietveld method, and specific surface area (SSA) of the supports.

Sample	Main phase	Crystallite size (nm)	SSA ($m^2 \cdot g^{-1}$)
ZrO_2-N-T-400	*t*-ZrO_2	9.7±0.1	85
ZrO_2-N-T-800	*m*-ZrO_2	51.0±0.6	9
ZrO_2-Cl-T-400	*t*-ZrO_2	15.5±0.2	57
ZrO_2-Cl-T-800	*m*-ZrO_2	76.7±1.2	<5

Table 2. Weight percent and crystallite size of Ni phase in the spent catalysts Ni/ZrO_2 calculated by the Rietveld method.

Sample	Ni phase (wt%)	Size of Ni (nm)
Ni/ZrO_2-N-T-400	9.3	25±2
Ni/ZrO_2-N-T-800	14.5	47±2
Ni/ZrO_2-Cl-T-400	12.1	65±3
Ni/ZrO_2-Cl-T-800	14.2	178±9

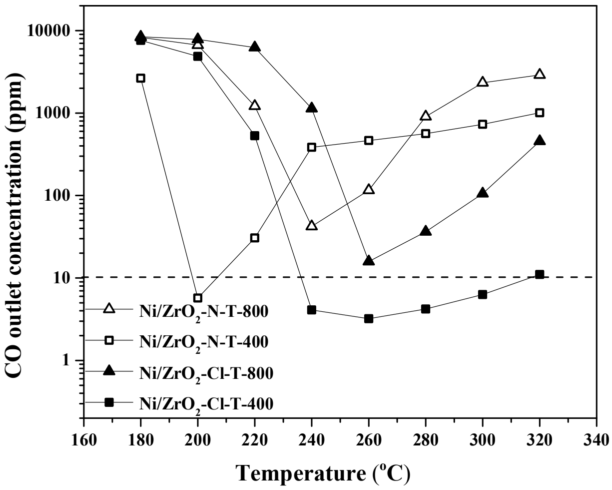

Figure 1. Catalytic activity for CO-SMET of the catalysts Ni/ZrO_2.

4. Conclusions

Kind of the salts influenced crystallite size and specific surface area of the decomposition products ZrO_2. A little amount of chlorine ions was remaining in the ZrO_2 prepared from the thermal decomposition of zirconium oxychloride at calcination temperature of 400°C. The catalyst Ni/ZrO_2-Cl-T-400 thus exhibited a high catalytic activity of removing CO to below 10ppm in a wide temperature range.

References

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