

Ceria supported nickel catalysts for CO removal from H₂-rich gas

GAO Zhiming (高志明)^{1,*}, DAI Qianzi (代倩子)¹, MA Hongwei (马宏伟)¹, LI Zhanping (李展平)²

(1. School of Chemistry, Beijing Institute of Technology, Beijing 102488, China; 2. Analysis Center, Tsinghua University, Beijing 100084, China)

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Abstract: CO in H₂-rich gas must be removed to meet various requirements in industrial applications. Four methods, i.e., the precipitation method using aqueous ammonia, the complexing method using urea, the complexing method using citric acid and the precipitation method using ammonium carbonate, were adopted to prepare samples NiO/CeO₂ as catalyst precursors for removal of CO from H₂-rich gas via selective methanation reaction. The sample NiO/CeO₂ prepared by the precipitation method using aqueous ammonia as precipitant exhibited the highest catalytic activity both for CO methanation and for CO₂ methanation after reduction prior to the catalytic reaction. Chlorine ion was then doped to suppress CO₂ conversion. Effect of chlorine doping was investigated. Over the optimal catalyst 40%Ni(Cl_{0.2})/CeO₂, CO in the H₂-rich gas was removed to below 10 ppm with selectivity of 60% or higher at reaction temperatures 230–250 °C in the test period of 75 h.

Keywords: CO selective methanation; nickel; ceria; chlorine doping; adsorption; rare earths

Small stack of proton exchange membrane fuel cell (PEMFC) is commercialized for residential use^[1]. It works after a hydrogen fuel processor, which contains units of steam reforming reaction of hydrocarbons, water gas shift reaction (WGS) and hydrogen purification. In the unit of hydrogen purification, preferential oxidation of CO in H₂-rich gas (CO-PROX) is currently used to remove CO to below 10 ppm to avoid poisoning of the anode of PEMFC by CO. The catalysts for CO-PROX are noble metal catalysts and air is supplied as oxidant externally. In the CO-PROX process, selectivity for CO oxidation is not high, since an appreciable amount of H₂ is oxidized into H₂O.

Selective methanation of CO in H₂-rich gas (CO-SMET) is extensively studied these years as an alternative way to remove CO from H₂-rich gas^[1–9]. This is because CO-SMET reaction does not need any reactant gas supplied externally, and Ni catalyst instead of noble metal catalysts is effective. When CO is hydrogenated into methane, a part of CO₂ may also be hydrogenated, as shown in Eqs. (1) and (2).



It is widely accepted that CO₂ methanation goes through two steps of reaction over transition metal catalysts (e.g., Ru, Ni), i.e., (i) CO₂+H₂=CO+H₂O, (ii) CO+3H₂=CH₄+H₂O^[6–11]. The first step is indeed the reverse water gas shift reaction (RWGS), which leads to CO formation and is undesirable for CO removal. So, a good catalyst for CO-SMET must have a high activity to de-

crease CO to the permissible level and meanwhile have a high selectivity on H₂ basis not less than 50%.

Impregnation method was usually used to prepare catalyst precursor with a proper calcination for CO-SMET reaction^[1,4–6,8,12,13]. Metal supported catalyst was then obtained by reducing the catalyst precursor with hydrogen prior to the catalytic reaction. It is reported that kind of support has a remarkable influence on catalytic activity of Ru catalyst for CO-SMET reaction^[14]. An order of support TiO₂>Al₂O₃>CeO₂>YSZ>>SiO₂ was found both in CO conversion and in CO₂ conversion^[14]. Kind of nickel salts has also an effect on catalytic activity of Ni/TiO₂ catalyst^[12]. It is reported that, when support CeO₂ was impregnated with solution of nickel nitrate, CO₂ conversion was high over the final catalyst Ni/CeO₂. In contrast, CO₂ conversion was suppressed when mixture solution of nickel nitrate and nickel chloride was used to impregnate the support^[15]. The positive effect of chlorine ion doping is ascribed to the suppression effect of chlorine ions on CO₂ dissociation^[13,15]. Chlorine ions can suppress CO adsorption as well^[16,17]. So, curves of the outlet CO and CH₄ concentrations versus reaction temperature were observed to shift towards higher temperature with chlorine ion amount increasing in the series catalysts^[15]. Beneficial effect of chlorine ion doping for CO-SMET reaction was also reported for Ru-Al₂O₃ catalysts^[17], Ni alumina based catalysts^[13] and Ni/TiO₂ catalysts^[8]. It is known earlier that chlorine ions have an inhibiting effect on hydrogenation reactions over metal catalysts^[18]. In those cases, chlorine ions present even as

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* **Corresponding author:** GAO Zhiming (Email: zgao@bit.edu.cn; Tel.: +86-10-81381388)

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impurity in the catalysts are not desirable^[19]. But, fortunately, in the case of CO-SMET reaction, addition of chlorine ions led to a net profit by suppressing adsorption of CO₂ and CO^[8,13,15,17].

In the present work, four preparation methods, two precipitation methods and two complexing methods, were adopted to prepare catalyst precursor NiO/CeO₂ instead of the impregnation method frequently used in literatures. It is desired to find an efficient preparation method to obtain a catalyst with a high catalytic activity. Then, chlorine ions can be doped to suppress CO₂ conversion and meanwhile to keep or improve the high efficiency for CO removal from the H₂-rich gas. In order to reveal effects of preparation method and chlorine ion doping, emphases were laid on phase formation of NiO and metallic Ni and their crystallites' growths in the samples. Moreover, dynamic adsorption isotherms of CO and CO₂ on the reduced samples were measured to study suppression effect of chlorine ions on adsorption of CO₂ and CO. At last, catalytic stability of the optimal catalyst in CO-SMET reaction was tested.

1 Experimental

1.1 Preparation of catalyst precursor NiO/CeO₂

1.1.1 Precipitation method using aqueous ammonia (denoted as A)

Aqueous solution of mixture of cerium(III) nitrate hydrate and nickel nitrate hydrate (Ce(NO₃)₃·6H₂O, Ni(NO₃)₂·6H₂O, Guoyao Chemicals, China) was prepared at first. Aqueous ammonia in stoichiometrical amount to the metallic ions was added dropwise into the solution of the metallic ions under stirring. The slurry obtained was heated in a rotator at 80 °C and 0.02 MPa for 1 h to evaporate the excess water, and then dried at 80 °C for 5 h and subsequently at 110 °C for 14 h in an oven. Calcination was done at 500 °C for 2 h in a muffle furnace. The calcined sample, named as sample (A), is denoted as *y*%NiO/CeO₂. The variable *y*% is the feed atomic ratio of Ni/Ce and equal to 20% unless stated otherwise.

1.1.2 Complexing method using urea (denoted as B)

Complex solution of urea with the metallic ions was prepared by mixing aqueous solution of urea with the solution of the metallic ions. Molar ratio of urea to the total metallic ions was set at 1.3/2. The excess water in the complex solution was evaporated in a rotator at 80 °C and 0.02 MPa for 1 h. The followed drying in the oven and calcination in the muffle furnace were the same as the method (A).

1.1.3 Complexing method using citric acid (denoted as C)

Similarly to the method (B), citric acid was used to make complex with the metallic ions. Molar ratio of citric acid to the total metallic ions was set at 1.3/3.

1.1.4 Precipitation method using ammonium carbonate

(denoted as D)

Similarly to the method (A), aqueous solution of ammonium carbonate in stoichiometrical amount to the metallic ions was used as precipitant.

1.2 Preparation of catalyst precursor 20%NiO(Cl_x)/CeO₂

The preparation method (A) was adopted with partial substitution of nickel nitrate hydrate by nickel chloride hydrate to keep feed atomic ratio of Ni/Ce at 20% (unless stated otherwise) and meanwhile feed atomic ratio of Cl/Ce(*x*) at *x*=0.05–0.40. The final calcined sample is denoted as 20%NiO(Cl_{*x*})/CeO₂.

1.3 Characterizations

Nickel element content in the samples was analyzed with ICP-AES (Thermo Scientific, iCAP 6000 Series).

XRD patterns of the samples were recorded on an X-ray diffractometer (D8 Advance, Bruker) with Cu K α irradiation at 40 kV and 40 mA. Phase composition was calculated by use of the Rietveld method implemented in the TOPAS software package. Thickness (*D*) of NiO or Ni crystallites normal to a given crystal plane was estimated by the Scherrer equation ($D=0.89\lambda/(\beta\cos\theta)$), where $\beta=B-b$, the *B* is the full width at the half maximum of the given XRD peak, and the *b* is the XRD instrumental line broadening at the diffraction angle.

Specific surface area (SSA) of the calcined samples was measured on an SSA analyzer (JW-DA, Beijing JWGB, China). The samples were degassed at 150 °C for 1 h at first, and then allowed to adsorb N₂ at liquid nitrogen temperature (77 K) under the relative pressure of *p/p*₀=0.06–0.30. The BET equation was used to calculate SSA value.

Temperature programmed reduction (TPR) experiment was done on a TPR instrument (PX200, Tianjin Pengxiang, China) equipped with a thermal conductivity detector (TCD). 50 mg of sample was heated in 10%H₂/Ar gas (40 mL/min) from room temperature to 680 °C at 10 °C/min. Deviation of TPR peak area of a measurement to the average of the repeated measurements is within 5%. Response factor of the TPR instrument under the experiment condition was determined by using a NiO powder according to reaction NiO+H₂=Ni+H₂O. If a sample NiO/CeO₂ had a TPR peak area larger than that of reduction of NiO contained in the sample, it implies that the excess TPR peak area was due to the partial reduction of CeO₂ into CeO_{2-d}. The *d* value can then be estimated by use of the response factor of the TPR instrument.

Surface atom composition was analyzed on an X-ray photoelectron spectrometer (PHI Quantera) with monochromatized Al K α radiation. Binding energies of the core electrons were calibrated with adventitious carbon C1s=284.8 eV.

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