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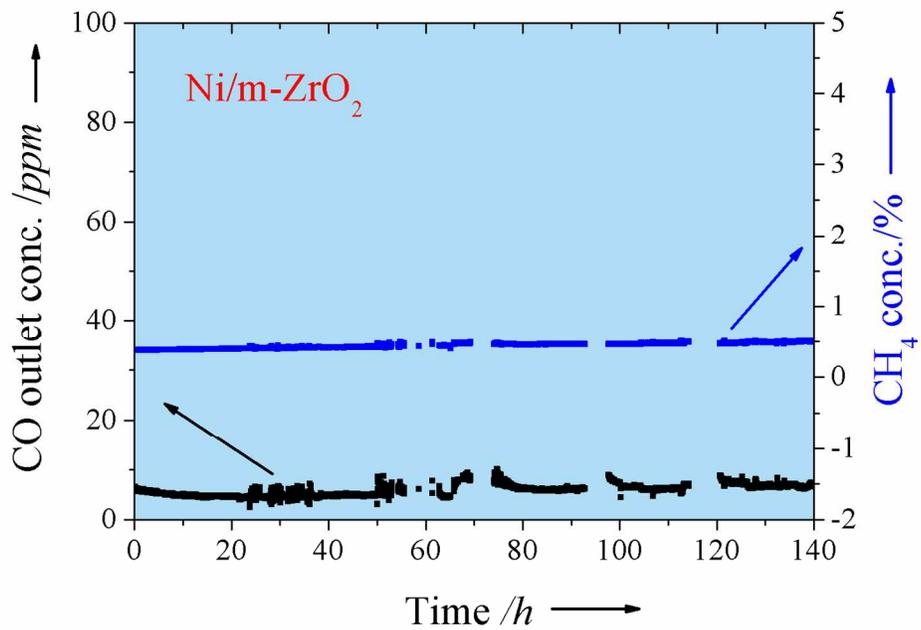


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COMMUNICATION

High catalytic performance of mesoporous zirconia supported nickel catalysts for selective CO methanation

Aihua Chen, † Toshihiro Miyao, Kazutoshi Higashiyama*, Mashiro Watanabe

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Deep-cleaned hydrogen can be produced for fuel cells directly through selective CO methanation over nickel-based mesoporous ZrO₂ catalysts without precious metals. 5000 ppm CO contained in hydrogen was removed to less than 10 ppm, with wide working temperature window and superior long-term stability.

Proton exchange membrane fuel cells (PEFC), fueled by hydrogen-rich reformat gas mixture, have been considered as the most promising candidates for the power sources of residential generators among the fuel cells. The technology of deep removal of carbon monoxide (CO) in the reformat gas is increasingly important because the PEFC is poisoned readily if the CO concentration is higher than 10 ppm.¹⁻⁴ Presently, the preferential oxidation of CO (PROX) is widely utilized for deep removing CO in the reformat gas and successfully meets the requirements of PEFC.⁵⁻¹⁰ However, the reported effective catalysts for this reaction are precious metal based, such as Ru, Au, Pt, and Rh, which lead to high cost. On the other hand, this process requires external air supplier and a mixer for reformat gas and air, causing the complication of the apparatus. Therefore, it is necessary to explore other cost-effective and simple approaches.

The process of CO methanation, i.e., direct hydrogenation of CO to methane and water via consumption of three moles of hydrogen, has been investigated as a less costly, space-saving substitute for PROX, requiring no additional reactants.¹¹⁻¹⁸ Moreover, the CH₄ produced by this reaction can be reused by recirculating the anode off-gas into the reformer as a combustion fuel for the reforming. High selectivity, as well as the high activity, are important parameters to evaluate the newly explored catalysts. This is because about 20 vol% of CO₂ are present in reformat hydrogen fuels, and one mole CO₂ consumes four moles of hydrogen at relatively high temperatures. Moreover, the reaction is often accompanied by another side-reaction of the reverse-water-gas-shift (RWGS) by converting CO₂ to CO. Therefore, the development of catalysts for selective CO methanation with high activity and selectivity is an important subject to make the simple catalytic fuel processors.¹⁹⁻²³ Numerous studies have been conducted on selective CO methanation over Ru,²⁴ Ni,²¹ and Ru-Ni^{25,26} catalysts. However, the main research of this field is on the stage of exploring of new catalysts with high performance to meet the requirements of PEFC, which is still major challenge to date. Hence, there are very few reports on stability test of newly explored catalysts.

Recently, we reported that Ni-Al mixed oxides modified by 1 wt% Ru, synthesized by a solution-spray plasma technique, show high catalytic performance for selective CO methanation with H₂ in reforming gas. The best catalyst can decrease CO levels from 1 vol% to 13 ppm.²⁵ Moreover, the same Ni-Al based catalyst with mesoporous structure exhibiting excellent catalytic property has been studied, which can remove CO from 1 vol% to less than 10 ppm, with working temperature window more than 50 °C.²⁶ Nevertheless, it is still necessary to explore suitable catalysts without any precious metals. It is well known that Ni/ZrO₂ is one of most effective catalysts for selective CO methanation. Takenaka et al.¹⁹ reported that Ni/ZrO₂ showed the highest catalytic activities among a series of catalysts studied for this reaction, reducing CO levels from 0.5 vol% to 20 ppm and the reaction was accompanied by low CO₂ conversion in the presence of 25 vol% CO₂, but in a narrow reaction temperature range. Herein, we demonstrate for the first time that highly ordered mesoporous ZrO₂ (denoted as m-ZrO₂) with crystalline state, loaded with a small amount of Ni through an incipient-wetness impregnation process, show excellent catalytic activity for the selective CO methanation and long-term stability at 240 °C.

Mesoporous zirconia, was prepared by a sol-gel method using evaporation-induced self-assembly, as that reported by Yan et al.²⁷ Fig. 1a, b show typical TEM images of m-ZrO₂. It is clear that highly ordered mesoporous structures were observed from the [001] and [110] orientations, respectively. The high-resolution TEM (HRTEM) image (inset in Fig. 1b) show that the walls are highly crystallized with a lattice spacing of 0.296 nm, consistent with the value of the (101) planes of tetragonal ZrO₂. The regular mesoporous structure has been maintained after loading nickel and calcination at 400 °C, as shown in Fig. 1c, which is a representative TEM image of m-ZrO₂ loaded with 5%Ni. This indicates that the mesoporous ZrO₂ exhibits excellent thermal stability. However, NiO particles were not observed, indicating the high dispersion of loaded particles among mesoporous frameworks, even on 7%Ni/m-ZrO₂ (Fig. S1 in the ESI*). For comparison, 5% Ni loaded on commercial ZrO₂ (denoted as ZRO-5, from Catalysis Society of Japan, JRC) was prepared. Fig. 1d is a TEM image of 5% Ni/ZRO-5. It is obvious that no mesoporous structure was observed. The BET surface areas of all catalysts were listed in Table 1. The specific surface area of m-ZrO₂ is similar with that of the reported data²⁷, which decreased slightly with increase of the Ni loading. This indicates that some blockage was formed after metals were introduced into pores. Furthermore, the surface area decreased remarkably when the loading amount of nickel increased to 7%, implying severe blockage. Moreover, it is noteworthy that 5% Ni/ZRO-5 shows higher specific surface area, even with no mesoporous structure.

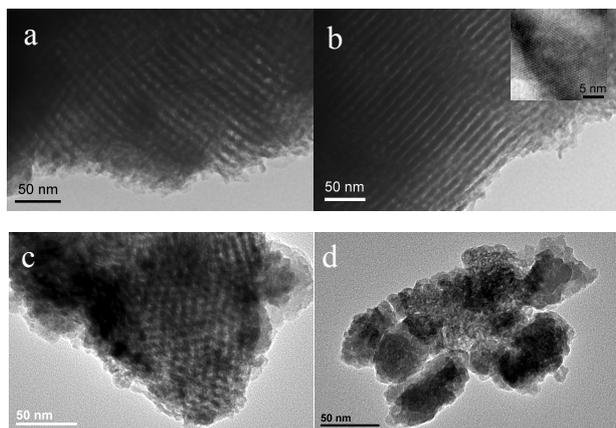


Fig. 1 TEM images of m-ZrO₂ (a, b) 5%Ni/m-ZrO₂ (c) and 5%Ni/ZRO-5 (d). The inset in Fig. 1b is HRTEM image of m-ZrO₂.

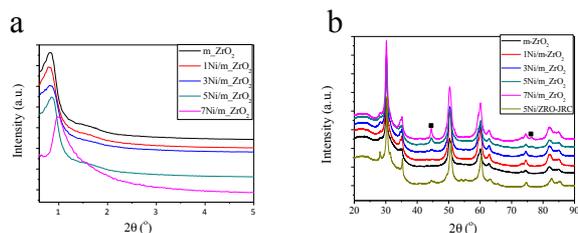


Fig. 2 Small-angle and wide-angle XRD patterns of m-ZrO₂ and Ni/m-ZrO₂ after calcination with different Ni content fraction.

Table 1 Physicochemical properties of m-ZrO₂ and Ni/m-ZrO₂ catalysts.

	S _{BET} (m ² /g)	Ni crystallite size /nm (200)
m-ZrO ₂	79	-
1%Ni/m-ZrO ₂	69	-
3%Ni/m-ZrO ₂	66	4.8
5%Ni/m-ZrO ₂	68	11.4
7%Ni/m-ZrO ₂	53	12.5
5%Ni/ZRO-5	131	9.2

This may be caused by different precursors and preparation procedures.

Fig. 2a shows small-angle XRD patterns of m-ZrO₂ and Ni/m-ZrO₂ with different metal loading amounts after calcination at 400 °C. A very sharp diffraction peak appears around 1.0 °, and one weak peak around 1.6 ° is observed on the curve of m-ZrO₂, which could be attributed to p6mm hexagonal symmetry based observation in TEM images. The peaks are also observed on other XRD patterns, implicating that the ordered mesoporous structure is maintained after loading nickel. Fig. 2b are the wide-angle XRD patterns of Ni/ZrO₂ after reduction at 400 °C by hydrogen. The diffraction peaks observed at 2θ of 30, 34, 35, 43, 50, 59, 60, 63, 73, 74, 82, 84, 85 ° are assigned to tetragonal phase (JCPDS card no. 80-0784), indicating the same crystalline phase of m-ZrO₂ and ZRO-5. The diffraction peaks for Ni metal phase at 2θ of 44.5, 51.9 ° (JCPDS card no. 04-0850, marked with square symbols) become apparent with the increase of Ni loading amount. The crystallite size of Ni particles calculated from XRD patterns (2θ = 44.5 °) are summarized in Table 1. It is clear that Ni crystallites become larger with the increase of Ni loading. Compared with Ni/ZRO-5 of the same Ni loading amount, the Ni species in mesoporous samples is slightly larger.

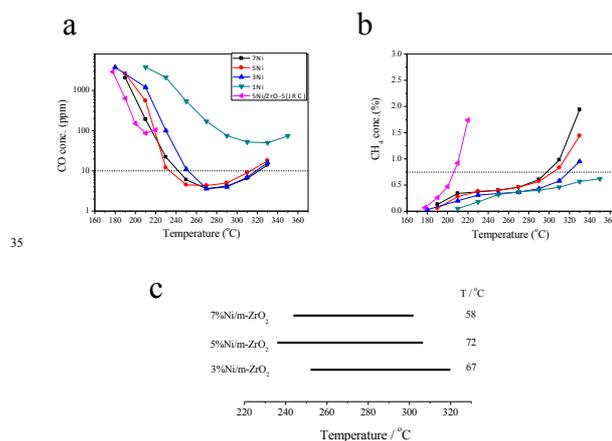


Fig. 3 Temperature dependence of a) CO, b) CH₄ outlet concentrations, and c) temperature window over Ni/ZrO₂ catalysts for selective CO methanation. Feed gas composition: 0.5 vol% CO, 20 vol % CO₂, 5 vol % N₂, H₂ balance, H/C = 15, SV = 10000 h⁻¹.

The catalytic activities for selective CO methanation over as-prepared catalysts were investigated with a fixed-bed flow reactor at atmospheric pressure with GHSV of 10,000 h⁻¹. The temperature dependence of CO and CH₄ outlet concentrations are shown in Fig. 3a, b. On every catalyst examined, the CO outlet level decreased with increasing temperature and exhibited a minimum, as shown in Fig. 3a. For the mesoporous catalysts, the catalytic activity increased significantly with Ni loading amount increase from 1% to 3%, which successfully removed CO levels to less than 10 ppm, with the reaction temperature from 252 ~ 320 °C. However, the curve shifts to lower temperature with Ni loading amount increased to 5%, while shift contrarily over 7%Ni/ZrO₂. It is also noteworthy that the CH₄ levels were nearly constant under these lowered CO level conditions over mesoporous catalysts, as shown in Fig 3b. After the appearance of the minima in the CO levels, the CH₄ levels increased with increasing temperature due to the occurrence of the RWGS, as well as the methanation of CO₂. The highest activity for CO methanation is at 210 °C over the 5%Ni/ZRO-5 catalyst, removing CO to 80 ppm, whereas the amount of the formed CH₄ increased severely with increase of temperature, implying the inferior selectivity for CO methanation.

It is required that CO levels contained in hydrogen should be lower than 10 ppm for direct feeding for PEFC. Moreover, the methanation of CO₂ should be as low as possible considering of consumption of hydrogen. According to the considerations above, we defined a working temperature window, ΔT, in which CO is removed to less than 10 ppm, and the formed CH₄ is lower than 0.75 vol %. Under these conditions, the conversion of CO and CO₂ are 99.8 % and 1.25 %, respectively, and the selectivity of CO methanation is 67 % (See ESI[†] in detail). Fig 3c illustrates the working temperature windows of the studied catalysts. It is clear that 5%Ni/ZRO-JRC and 1% Ni/m-ZrO₂ failed to meet the requirements of the definition of the working temperature window. For practical application, catalysts for selective CO methanation are required to have a wide temperature window at a relatively low temperature range for practical application. From Fig. 3c, it is obvious that the window of 5%Ni/m-ZrO₂ is the

widest and located at low temperatures compared to other catalysts, indicating that 5%Ni/m-ZrO₂ is the most suitable candidate for selective CO methanation among the studied catalysts.

The specific surface area of 5%Ni/ZRO-JRC is larger than that of 5%Ni/m-ZrO₂, whereas the catalytic performance of latter one is much better than that of the former. It is proposed that chlorine residue in the framework of the m-ZrO₂ has a significant effect on the dramatic improvement of selectivity of catalysts.²⁸ In addition, the confinement effect from the mesoporous structure play an important role on the catalytic performance for selective CO methanation. Furthermore, the larger size of nickel species is preferable for this reaction.^{19,26} For mesoporous catalysts, when the loading amount of nickel reaches 7%, the blockage become serious, which induce the decrease of the catalytic performance to some extent.

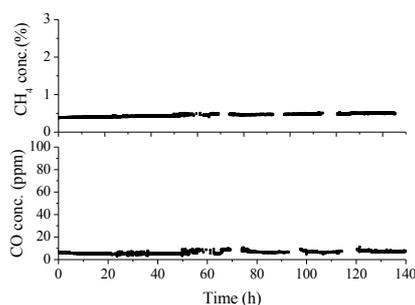


Fig. 4 Durability test for selective CO methanation over 5 wt%Ni/m-ZrO₂ at 240 °C.

It is well known that long-time stability test is very important for a new catalyst. A durability test was carried out over 5 wt%Ni/m-ZrO₂ at 240 °C under the standard reaction conditions. Fig. 4 shows the time courses of the changes in the CO and CH₄ outlet concentrations. It is clear that CO levels of less than 10 ppm were maintained for 140 h with a nearly constant CH₄ concentration of 0.5 %, exhibiting nearly 100% selectivity of CO methanation at this temperature. To the best of our knowledge, it is the first time that the low-cost catalysts without precious metals have been reported that meet the requirements for high purity hydrogen to remove CO from 0.5 % to less than 10 ppm in high space volume with long-time stability under standard reaction conditions.

Conclusions

In summary, we have successfully demonstrated that mesoporous ZrO₂ loaded with nickel through an incipient-wetness impregnation process show excellent catalytic performance for the selective CO methanation in the presence of excess CO₂ under high gas hourly space velocity. The working temperature windows, in which CO was removed to less than 10 ppm with greater than 67% selectivity for CO methanation, were wider than 70 °C over 5% Ni/m-ZrO₂ catalysts. Furthermore, long-term stability (140 h) was demonstrated, with no detectable change in the outlet CO as well as CH₄ concentration, with about 100% selectivity of CO methanation at 240 °C. The facile synthesis of the low-cost catalysts makes them promising candidates for practical application.

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Notes and references

Fuel Cell Nanomaterials Center, University of Yamanashi, 6-43 Miyamae-cho, Kofu, Yamanashi 400-0021, Japan Fax: 81 55 254 7091; Tel: 81 55 254 7091; E-mail: kazutoshih@yamanashi.ac.jp
 † Present address: School of Materials Science and Engineering, Beihang University, No. 37 Xueyuan Road, Haidian District, Beijing 100191, China. Fax: 86 10 8231 7738; Tel: 86 10 8231 7738; E-mail: chenaihua@buaa.edu.cn

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