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Solid-solution catalysts for CO_2 reforming of methane☆

Yun Hang Hu

Department of Materials Science and Engineering, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931-1295, United States

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ABSTRACT

One of the important developments in CO_2 reforming of methane is highly effective MgO-based solid-solution catalysts. Herein, their high activity and selectivity as well as excellent stability for CO_2 reforming of methane were briefly reviewed. How to inhibit carbon deposition via the formation of NiO–MgO or CoO–MgO solid solution was discussed. The reduction of NiO (or CoO) in the NiO–MgO (or CoO–MgO) solid solution is much more difficult than that of pure NiO (or CoO), which contributes to the formation of very small Ni particles to inhibit carbon deposition. It is generally recognized that the reduction of a metal oxide is determined by its metal–oxygen bond strength. Herein, however, it was showed that the reduction of a metal oxide is strongly dependent on both metal–oxygen bond strength of the metal oxide and the metal–metal bond strength of its metal product. Furthermore, it was proposed that a critical factor to control the reduction of NiO (or CoO) in the solid solution is the isolation effect that NiO (or CoO) is isolated by MgO, which inhibits the metal–metal bond formation during the reduction.

1. Introduction

In the 1980s, Keller and Bhasin reported the oxidative coupling of methane to give ethylene and ethane [1]. This work prompted numerous attempts to convert methane directly to ethylene and ethane [1] as well as other compounds [2]. However, the best result obtained in long-run tests has been a C_{2+} yield of only 15% for methane conversions of 15–40% at a temperature of 1270–1370 K and a pressure of 1–2 atm with a CH_4/O_2 molar ratio of 5–10 [3]. In the early 1990s, a consensus emerged that it would be difficult to achieve a significantly better result than that mentioned above for the oxidative coupling to become an economical industrial process. This is because the formation of CO_2, instead of more desirable products (such as ethylene and ethane), is favored thermodynamically when the reaction of methane and oxygen is fast enough to be of practical interest at temperatures above 973 K. Consequently, in the early 1990s, the emphasis in research on CH_4 conversion returned to three indirect processes producing synthesis gas [4–8]: steam reforming (Eq. (1)), partial oxidation (Eq. (2)), and CO_2 reforming (Eq. (3)):

$$CH_4 + H_2O \rightarrow CO + 3H_2, \quad \Delta H^0_{298} = 206\,\text{kJ mol}^{-1} \qquad (1)$$

$$CH_4 + (1/2)O_2 \rightarrow CO + 2H_2, \quad \Delta H^0_{298} = -36\,\text{kJ mol}^{-1} \qquad (2)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \quad \Delta H^0_{298} = 247\,\text{kJ mol}^{-1} \qquad (3)$$

The steam reforming is a commercial process, which was first developed by Standard Oil of New Jersey (current Exxon Moil Oil Corporation) [9]. Compared to the steam reforming of methane, the methane partial oxidation has two main advantages: (1) the partial oxidation is slightly exothermic instead of being strongly endothermic, and (2) the obtained H_2/CO ratio of about 2 is ideal for methanol synthesis and Fischer–Tropsch syntheses of short-chain hydrocarbons. However, the catalytic partial oxidation of methane requires a pure oxygen feed, which is prepared by expensive air separation.

CO_2 reforming, which is endothermic, can produce synthesis gas with a low H_2/CO ratio (1/1) that is suitable for the Fischer–Tropsch synthesis of long-chain hydrocarbons [10]. Furthermore, it can be carried out with natural gas from fields containing large amounts of CO_2 without the pre-separation of CO_2 from the feed. Because CO_2 is a greenhouse gas that causes warming of the earth, there are incentives for reducing its concentration in the atmosphere. Methane should be also considered as a greenhouse gas, because it can absorb 20 times more heat than CO_2. The CO_2 reforming of methane may provide a practical method for consumption of those two greenhouse gases. However, so far, no industrial technology for CO_2 reforming of methane has yet been developed. One of the main reasons is that no effective, economic catalysts have been discovered. When the conventional Ni-containing catalyst for steam reforming was used for CO_2

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E-mail address: yunhanghu@mtu.edu.

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reforming, carbon deposits formed on the catalyst, which deactivated rapidly. A high molar ratio of CO_2 to CH_4 (≥ 3) could be used to reduce the carbon deposition by inhibiting CO disproportionation, but the selectivity to synthesis gas could become much lower than that for the stoichiometric CO_2 reforming ($CO_2/CH_4 = 1$). Therefore, the inhibition of carbon deposition without extra cost and loss of catalyst performance constitutes a major challenge for CO_2 reforming of methane. In the past 20 years, one of important developments in this area is MgO-based solid-solution catalysts [11–19]. In this article, the excellent catalytic performance of the solid-solution catalysts will be briefly reviewed. How to inhibit carbon deposition by using solid-solution catalysts will be discussed. Finally, the isolation effect of solid solution will be proposed as a critical factor to control the reduction of NiO in NiO/MgO solid solution, which plays an important role in inhibiting carbon deposition.

2. Catalytic performances of solid-solution catalysts

MgO is widely selected as a catalyst support due to its high thermal stability and low cost. The surface area of the metal oxide powders at high temperatures depends on their intrinsic properties, particularly melting point and phase transformation. MgO has a very high melting point (2850 °C), which can allow MgO to maintain a relatively large surface area at high temperatures compared to most oxides used as catalyst supports. Furthermore, MgO, NiO, and CoO have a face centered cubic structure with almost the same lattice parameters: 4.2112 Å for MgO, 4.1684 Å for NiO, and 4.2667 Å for CoO. As a result, the combination of MgO and NiO (or CoO) leads to the formation of solid solution (NiO–MgO or CoO–MgO). Several groups reported the excellent results of CO_2 reforming of methane in the presence of NiO–MgO and CoO–MgO solid-solution catalysts [11–19]. As shown in Fig. 1, a 20 wt.% NiO/MgO solid-solution catalyst for CO_2 reforming of methane, which was prepared by impregnation and was calcined at 1073 K, was reported [11]. The reduced solid-solution catalyst exhibited almost 100% conversion of CO_2, >91% conversion of CH_4, and >95% selectivities to CO and H_2 at 1063 K, atmospheric pressure, and the very high space velocity of 60,000 ml (g of catalyst)$^{-1}$ h^{-1} for a CH_4/CO_2 (1/1) feed (Fig. 1) [11]. The conversion and selectivity remained unchanged during the entire reaction time employed (120 h), indicating that the reduced NiO/MgO catalyst had a high stability. In contrast to MgO, the other alkaline-earth oxides, such as CaO, SrO, and BaO, were found to be poor supports for NiO, as they provided catalysts with low activities, selectivities, or stabilities [11]. Furthermore, although the reduced NiO/Al_2O_3 catalyst provided high initial conversions (CH_4, 91%; CO_2, 98%) and selectivities (>95% for both CO and H_2), it suffered a rapid carbon deposition, resulting in the complete plugging of the reactor after 6 h of reaction [12f]. It is reasonable to conclude that the excellent catalytic performance of NiO/MgO should be attributed to the formation of a solid solution [12]. The performance of NiO/MgO solid-solution catalysts are dependent on their composition, preparation conditions, and even the properties of the MgO [12]. High and constant H_2 and CO yields (>95%) occurred with NiO/MgO catalysts having NiO contents between 9.2 and 28.6 wt.% [12g]. No activity was observed, however, for a NiO content of 4.8 wt.%. At the high NiO content of 50 wt.%, the CO yield decreased from 91 to 53% after 40 h due to carbon deposition. This indicates that too-small amounts of NiO in the NiO/MgO catalysts provided too-small numbers of Ni sites, and too-large amounts supplied numerous nickel metal particles that could easily sinter and generate large particles, which facilitated carbon deposition. Furthermore, the MgO surface area, pore size distribution, and lattice parameters exhibited significant effects on the performance of NiO/MgO solid-solution catalysts [12e].

It was reported that the addition of a noble metal could promote both the activity and the stability of NiO/MgO solid-solution catalysts [13e]. The resistance of the $Ni_{0.03}Mg_{0.97}O$ solid-solution catalyst to carbon deposition was retained by the bimetallic catalysts [13e]. The improved stability of the catalyst was attributed to the increased catalyst reducibility caused by noble metal promotion. Furthermore, the water treatment of the $Ni_{0.03}Mg_{0.97}O$ solid-solution catalyst increased the catalytic activity and stability for CO_2 reforming of CH_4 [13d]. This promoting effect was inferred to be the consequence of a structural rearrangement of the solid solution by the formation of nickel and magnesium hydroxides [13d]. Very recently, Liu and Ge et al. revealed the effect of water on CO_2 adsorption on γ-Al_2O_3 by using density functional theory (DFT) calculations [20]. Their interesting results would be useful for ones to explain the effect of water on CO_2 reforming of methane.

The catalytic performance of NiO/MgO solid-solution catalysts for CO_2 reforming of methane is also affected by reactor type [18]. It was found that the methane and CO_2 conversion in the fluidized bed reactor was higher than those in the fixed bed reactor over $Ni_{0.15}Mg_{0.85}O$ catalyst at a pressure of 1.0 MPa. It was suggested that the promoting effect of catalyst fluidization on the activity is related to the catalyst reducibility. The oxidized and deactivated catalyst can be reduced with the produced syngas and the

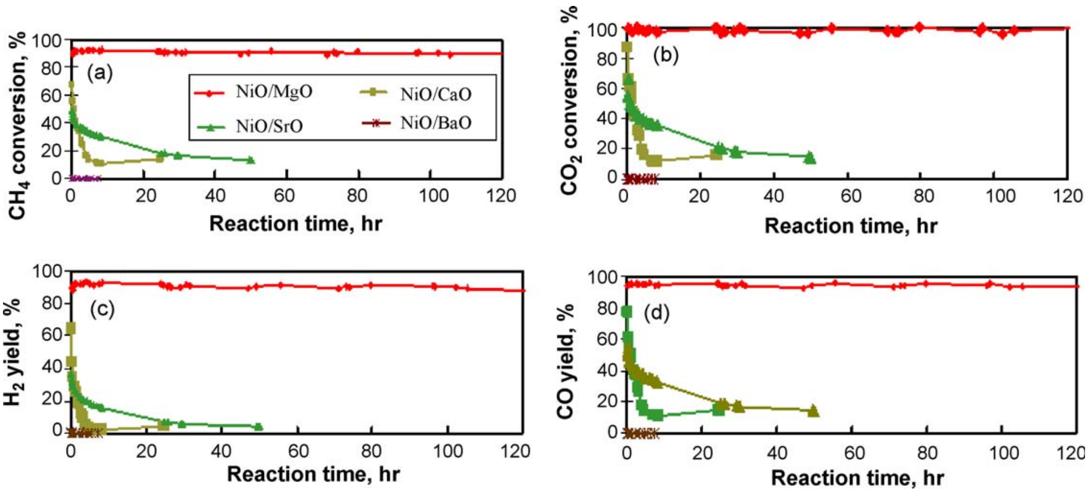

Fig. 1. CH_4 conversion (a), CO_2 conversion (b), H_2 yield (c), and CO yield (d) in the CO_2 reforming of CH_4 catalyzed by reduced 20 wt.% NiO/alkaline-earth metal oxides. Before reaction, each catalyst was reduced in flowing H_2 at 773 K for 14 h. Reaction conditions: pressure = 1 atm, T = 1063 K, CH_4/CO_2 = 1/1, GHSV = 60,000 ml (g of catalyst)$^{-1}$ h^{-1} [11].