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Titania-supported cobalt and nickel bimetallic catalysts for carbon dioxide reforming of methane

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Abstract

Titania-supported cobalt and nickel bimetallic catalysts were investigated for CO_2 reforming of methane to synthesis gas at 1023 K under ambient pressure. Bimetallic Co–Ni/TiO_2 catalysts with an appropriate Co/Ni ratio showed highly stable activities without carbon deposition. Whereas the monometallic Co/TiO_2 catalyst deactivated rapidly because of the oxidation of metal, 10 mol% substitution of nickel for cobalt suppressed the oxidation of metal, providing a high catalytic stability. However, the catalysts with excess nickel content (>80 mol%) underwent carbon formation. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses revealed that a homogeneous alloy of cobalt and nickel was formed from bulk to the surface by the H_2 reduction, and the alloy was stable during reforming. The advantages of the bimetallic catalysts are high resistance to undesirable metal oxidation and coking, through the control of reactions between CH_4 and CO_2.

Keywords: Cobalt; Nickel; Bimetal; Alloy; Titania; Methane; CO_2 reforming; Strong resistance to coking

1. Introduction

Carbon dioxide reforming of methane to synthesis gas ($CH_4 + CO_2 \rightleftarrows 2CO + 2H_2$) has been of great interest for the technology of natural gas conversion, since the reaction can optimize the H_2/CO ratio when combined with, for instance, steam reforming of methane. In general, carbon formation on catalysts is a serious issue for the reaction. Supported noble metals, such as Rh, Ru, Pd, Pt, and Ir, can provide operations with lower carbon deposition in the CH_4/CO_2 reaction [1]. However, from a practical point of view, noble metals are unsuitable for industrial use, considering their high cost and restricted availability. Hence, supported Ni catalysts are commonly applied because of their low cost [2]. The nickel catalysts are known to show high catalytic activity; however, nickel catalysts easily induce formation of graphitic carbon, causing catalyst deactivation and plugging of a reactor tube [1,2].

There have been a number of discussions on how to avoid carbon formation [3,4]. A number of contributions have claimed that the nature of the supports strongly affects the catalytic behavior and carbon deposition for the CH_4/CO_2 reaction [5–10]. Among oxides titania is reported to be an excellent support for suppressing carbon deposition [5–7, 10–16]. It is proposed that during H_2 reduction, the partially reduced TiO_x species would migrate on the metal particle (so-called strong metal support interaction (SMSI) [17,18]), destroy large ensembles of the metal species, and create the highly active sites for the reforming at the boundary between metal and support, resulting in reduction of the amount of carbon deposits [7,11].

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Another idea for minimizing carbon deposits is preventing carbide formation on the metal particles, because carbide formation is suggested to be the essential intermediate for carbon formation [4]. It has been reported that doping Ni catalysts with other metal, such as tin [19], chromium [20,21], or manganese [22,23], has a significant effect on the suppression of carbide formation. Some detailed studies [24,25] have shown that additives like potassium, sulfur, and gold preferentially bind to the step sites working as the coking sites and, hence, suppress graphite formation, without significantly influencing the catalytic activity for the reforming.

It has also been reported that the addition of cobalt to nickel catalysts reduces coke formation during reactions, such as CO methanation [26], partial oxidation of methane to synthesis gas [27,28], and steam or CO_2 reforming of methane [29]. Bartholomew et al. suggested that suppression of coke formation by the addition of cobalt to nickel catalyst for CO methanation would be due to enhancement of the hydrogenation of atomic carbon and/or inhibition of the formation of carbide species in the metal crystal [26]. However, the beneficial effects and the nature/state of the bimetallic catalysts remain unclear and needed to be investigated.

Cobalt has attracted interest as an active metal for the CO_2 reforming of methane [13–16,30]. The authors have studied the CO_2 reforming of methane over 0.5 wt% Co/TiO_2 at 2.0 MPa, where carbon formation is highly favored, as predicted by thermodynamic equilibrium [13,14]. The Co/TiO_2 catalyst showed a high tolerance to carbon deposition but gradually deactivated because of the oxidation of the metallic cobalt. In fact, a partial substitution of nickel for cobalt (typically $Co/Ni = 90/10$) enhanced catalytic stability dramatically [15]. It is speculated that, by accelerating methane decomposition, the nickel provides reductive hydrogen to the cobalt via spillover phenomena [31,32], thus inhibiting oxidation of the cobalt. However, it is difficult in practice to clarify the state of the bimetals because of the necessity for low metal loading (0.5 wt%) for high-pressure operations.

At atmospheric pressure, higher loading of the metal can also be applied for stable operations [13], and 10 wt% Co/TiO_2 was investigated thoroughly [16]. It is proposed that, during CH_4/CO_2 reforming, the reactions between CH_4 and CO_2 should be balanced appropriately [16,30]. The coke species formed by decomposition of CH_4 on the metal has to be removed by the activated oxygen species derived from CO_2. The cobalt catalysts tended to be deactivated by oxidation of the metal, implying that the oxygen species derived from CO_2 reacts more preferentially than the coke species derived from CH_4.

This contribution pertains to the carbon dioxide reforming of methane over the bimetallic $Co–Ni/TiO_2$ catalysts (metal loading 10 wt% in total) at atmospheric pressure. The purpose of this work is to combine the nature of cobalt (stronger affinity for oxygen species) and with that of nickel (stronger affinity for carbon species) and to suppress both metal oxidation and carbon formation. Catalysts with various Co/Ni ratios have been prepared and tested for CO_2 reforming of CH_4. To clarify the beneficial effects of the bimetallic catalysts, the state and nature of the $Co–Ni/TiO_2$ catalysts have been extensively characterized.

2. Methods

2.1. Catalyst preparation

$Co–Ni/TiO_2$ catalysts were prepared by incipient wetness co-impregnation of an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemical Industries Ltd.) with TiO_2 (Ishihara Sangyo; A-100, anatase phase), which is pre-calcined at 773 K for 15 h. The metal loading was set at 10 wt% for Co/TiO_2, and cobalt was replaced with the same moles of nickel. The catalysts were dried at room temperature and then at 373 K overnight, followed by calcination at 673 K for 4 h in flowing air to remove ligands from the cobalt and nickel precursors. The powder-form catalysts were pressed into pellets, crushed, and sieved to obtain grains with diameters between 600 and 900 µm. Catalyst with the ratio $Co/Ni = m{:}n$ are denoted $CoNi(m{:}n)/TiO_2$.

2.2. Catalyst characterization

Temperature-programmed reduction (TPR) measurements were carried out over 0.1 g of the calcined catalysts from room temperature to 1223 K, at a rate of 10 $K\,min^{-1}$ in flowing H_2/Ar gas (5:95 vol/vol mixture with a total flow of 30 $ml\,min^{-1}$). The hydrogen consumption was monitored with a TCD.

The specific surface area of the catalysts after H_2 reduction was determined by the BET method. The amounts of chemisorbed CO were determined by a pulse method. Typically 0.1 g of catalyst was reduced in situ at 1123 K for 1 h in a H_2 flow and flushed with He (>99.999% purity) at each temperature for 15 min. Pulses (pulse volume 1.08 ml) of 1% CO in He gas were injected through the catalysts at room temperature until no further adsorption of CO was detected with a TCD.

XRD analysis was performed with a Rigaku Multiflex X-ray diffractometer with monochromatized Cu-K_α. Metal crystallite sizes were calculated from line broadening with the Scherrer equation [33].

X-ray photoelectron spectroscopy (XPS) was performed with an ULVAC-PHI model 3057 ESCA system with a monochromatized Al-K_α (1486.7 eV, 200 W) under a pressure of approximately 10^{-9} Torr. After the reduction, the catalysts were flushed with helium gas and kept in a closed vial, then transferred into the spectrometer without exposure to the ambient air. The measurements were carried out under approximately 1.0×10^{-6} Pa, and the C 1s peak at 284.8 eV was used as a reference. To compensate for lost electrons