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Pretreatment as the crucial step for biogas reforming over Ni–Co bimetallic catalyst – A mechanistic study of CO$_2$ pretreatment

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ABSTRACT

H$_2$ and CO$_2$ pretreatment over the Ni–Co/La$_2$O$_3$–Al$_2$O$_3$ catalyst has been shown to lead to significant increase in catalytic performance. A mechanistic study was investigated by a series of catalytic activity measurements. Ni was found to be the main metal that interacted with CO$_2$. Meanwhile, H$_2$ reduction is an indispensable step of the pretreatment route and CO$_2$ cannot be replaced by O$_2$. FT-IR spectroscopy investigations were used to confirm that carboxyl was created during the CO$_2$ pretreatment of the Ni–Al$_2$O$_3$ catalyst. The result proved that bicarbonate of Ni was formed during the CO$_2$ pretreatment. During CO$_2$-reforming of methane, the bicarbonate of Ni could decompose into CO and provide oxygen species. The oxygen species will react with accumulated carbon on Ni crystallites to produce CO and in turn protect the active sites. Thus, the performance of the catalyst was significantly improved.

Introduction

At present, steam reforming of methane (CH$_4$ + H$_2$O → CO + 3H$_2$, SRM) is a well-established and the most widely method for the manufacture of syngas [1–4]. However, because of some limitations of SRM itself, there are many defects for its future application. For instance, the main raw material for SRM is primarily natural gas, which is known as unsustainable fossil fuel; besides, the H$_2$/CO ratio of the produced syngas is 1:3, which is suitable for the synthesis of compound like ammonia, but not for C1-chemistry. On the other hand, the increasing interest for C1-chemistry has created a need for syngas with low H$_2$/CO ratio. This task can be fulfilled by biogas reforming. In essence, biogas reforming is carbon dioxide reforming of methane (CDRM, CH$_4$ + CO$_2$ → 2CO + 2H$_2$). The main components of biogas are CH$_4$ (40–70%) and CO$_2$ (30–60%). Desulphurized biogas can be used as the fuel of CDRM.

CDRM is attracting more and more attention and researches [5–14]. It is well-known that CH$_4$ has a global warming potential of 25 CO$_2$-equivalents over a 100 year time

horizon [15]. Using CDRM to produce syngas, through its ability to utilize both CH4 and CO2, provides a solution to the green house effect caused by CO_2 and CH_4 [16,17]. Moreover, gas fields sometimes contain CO_2 (=25 vol%), which may be an incentive to apply in CDRM rather than separating methane and CO_2 [18].

However, the presence of CO_2 in the feedstock results in more critical conditions for carbon formation to occur and deposit on the catalyst surface because of lower H/C ratio [19]. Carbon formation may lead to breakdown of the catalyst and the build-up of carbon deposits and degraded catalyst may cause partial or total blockage of some tubes [20,21].

In the previous work [22], pretreatment by H_2 and then by CO_2 was proved to have excellent ability to not only improve the activity and avoid the long induction period, but also enhance resistance to both sintering and coke formation during the reaction compared with the catalyst pretreated only by H_2. The present work focuses on the mechanism of the new pretreatment under a series of catalytic testing in a fixed—bed vertical quartz reactor. The catalyst was also characterized by X—ray diffraction (XRD), Fourier transform infrared spectrometer (FT-IR) and thermogravimetry coupled to differential scanning calorimetry (TG—DSC) with respect to crystal structure, morphology, resistance to sintering and coking.

Experimental

Catalyst preparation

Ni—Co/La$_2$O$_3$—Al$_2$O$_3$ bimetallic samples were prepared by excessive impregnation of γ-Al$_2$O$_3$ pellets (2.5—3.5 mm) with an aqueous solution of Ni(NO$_3$)$_2$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, and La(NO$_3$)$_3$·6H$_2$O. M—Al$_2$O$_3$ (M = Ni, Co, La) samples were prepared by excessive impregnation of γ-Al$_2$O$_3$ pellets (2.5—3.5 mm) with an aqueous solution of Ni(NO$_3$)$_2$·6H$_2$O or Co(NO$_3$)$_2$·6H$_2$O or La(NO$_3$)$_3$·6H$_2$O. Ni—SiO$_2$ samples were prepared by excessive impregnation of an aqueous solution of Ni(NO$_3$)$_2$·6H$_2$O with commercial SiO$_2$. The samples were dried at 120 °C for 6 h and then calcined at 850 °C for 2 h in air. The prepared Ni—Co/La$_2$O$_3$—Al$_2$O$_3$ samples contained 7 wt% Ni, 3 wt% Co and 6 wt% La$_2$O$_3$ promoter. The prepared M—Al$_2$O$_3$ samples contained 10 wt% M and designated 10 M/Al. The prepared Ni—SiO$_2$ sample, containing 10 wt% Ni, was pressed into flakes, crushed, and sieved to 10—20 mesh (1—2 mm) and denoted as 10Ni/Si.

Catalyst characterization

XRD was conducted using a D/max 2550 (Rigaku) diffractometer with Cu-K$_\alpha$ radiation (λ = 0.154056 nm), operated at 40 kV and 100 mA, to detect the crystalline phases of the catalyst. The diffraction patterns were recorded in the 2θ range 10°—100°, with a scanning rate of 0.02° min^{-1}.

The carbon deposits were analyzed using TG (STA449C, NETSCHZ) coupled with DSC. About 10 mg of used catalyst was placed in an alumina crucible, and heated from room temperature to 1000 °C at a rate of 10 °C min^{-1}, in a mixture of 5% O$_2$/N$_2$ at a flow rate of 120 ml min^{-1}; an empty alumina crucible was used as a reference.

FT-IR of the catalyst was obtained on a Fourier transform infrared spectrometry (Bruker company, model EQUINOX 55) equipped with a deuterated triglycine sulfate (DTGS) detector using the KBr pellet technique to determine the chemical structure of the catalyst. Samples of FT-IR analysis were prepared by mixing the catalyst powders with KBr (1:300 by weight ratio) in a steel die.

Catalysts pretreatment and catalytic reactions

The catalysts pretreatment and catalytic assay was carried out under atmospheric pressure in an immobilized-bed vertical quartz reactor (i.d. 25 mm) packed with 4 g of catalysts. All the catalysts were pretreated in situ. The pretreatment routes referred to in this article are listed in Table 1. Catalysts without pretreatment, pretreated using route a, b, c and d were designated Cat-N, Cat-H, Cat-HCD, Cat-HO and Cat-CD, respectively.

The catalytic tests were performed at 850 °C, feeding a stream of 200 ml min^{-1} of methane and carbon dioxide (CH$_4$/CO$_2$ = 1/1 mole ratio) without any diluted gas as model biogas (GHSV 6000 mL g (cat)$^{-1}$ h^{-1}). Temperature at the center of catalyst bed was measured using K-type thermocouple thermometer with a stainless-steel thermocouple well, of which the standard error range is ±0.75%. The temperature at the center of the catalyst bed was measured using a K-type thermocouple thermometer with a stainless-steel thermocouple well. The gaseous products leaving the reactor passed through an ice-cold trap to remove water formed during the reaction. The feed flow rates were controlled using mass flow controllers (Alicat Company), of which the standard error range is ±0.25%. And the exhaust flow rate was measured using a primary flow calibrator (Gilian, Sensidyne Company), of which

Route	Step 1	Step 2	The corresponding catalyst
a	Reduced for 2 h in pure hydrogen at a flow rate of 30 ml min^{-1} at 700 °C	/	Cat-H
b	Reduced for 2 h in pure hydrogen at a flow rate of 30 ml min^{-1} at 700 °C	Treated for 2 h in pure carbon dioxide at a flow rate of 200 ml min^{-1} at 850 °C	Cat-HCD
c	Reduced for 2 h in pure hydrogen at a flow rate of 30 ml min^{-1} at 700 °C	Treated for 2 h in pure oxygen at a flow rate of 200 ml min^{-1} at 850 °C	Cat-HO
d	Treated for 2 h in pure carbon dioxide at a flow rate of 200 ml min^{-1} at 850 °C	/	Cat-CD
e	/	/	Cat-N

Table 1 — Pretreatment routes of the catalyst referred to in this article.