Journal of Industrial and Engineering Chemistry 20 (2014) 1677–1683

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Effects of preparation methods on the properties of cobalt/carbon catalyst for methane reforming with carbon dioxide to syngas

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ARTICLE INFO

Article history:
Received 25 April 2013
Accepted 17 August 2013
Available online 24 August 2013

Keywords:
CH_4–CO_2 reforming
Syngas
Cobalt
Carbon catalyst

ABSTRACT

The effect of different preparation methods on the physicochemical property, reforming reactivity, stability and carbon deposition resistance of cobalt/carbon catalyst was investigated through fixed bed flow reaction. The catalysts were prepared by the impregnation and characterized by the XRD and scanning electron microscopy (SEM). The result indicated that the active components of cobalt/carbon catalyst prepared by using ultrasonic wave distributed evenly, activity was high and the loading time was short. The Co/Carbon catalyst prepared by incipient-wetness impregnation, 10 wt% loading and 300 °C calcination, achieved the best activity. Furthermore, the effect of reaction temperature, air speed and CH_4/CO_2 ratio on the catalyst activity and CO/H_2 ratio in products was investigated. It was found that the conversion of CO_2 and CH_4 increased with the increasing of reaction temperature. However, the conversion of CO_2 and CH_4 increased first and then decreased with the increasing of air speed. With the increasing of CH_4/CO_2 in feed gas, both the catalyst activity and the CO/H_2 ratio in products decreased.

1. Introduction

CH_4–CO_2 reforming can effectively convert CO_2 and CH_4 (the main greenhouse gas) into synthesis gas. This not only provides a feasible approach for resource utilization and environmental management, but also its synthesis gas is also chemical raw materials needed for many manufacturing processes [1]. Thus CH_4–CO_2 reforming has a wide application prospect. Developing a practical catalyst with high activity and good stability, it is not only the research hotspot of catalyst field, but also the key of achieving CH_4–CO_2 to synthesis gas reforming industrialized [2–5].

Current research results indicated that the noble metal catalyst has good activity and carbon deposition resistance to the reforming reaction [6,7]. However, researches have been devoted to use non-noble metals, such as Ni and Co, instead of noble metals due to the high cost of noble metal catalyst [3,8–16]. For the current research situation, Ni/Al_2O_3 was the most studied metal active component and carrier [17–20]. However, this catalyst is easy to lose activity because of the serious carbon deposition. Besides, metal Ni and Al_2O_3 produced $NiAl_2O_4$ compound during their reaction, which was not only disadvantageous to the synthesis generation and difficult for restoration and regeneration, thus influencing its industrialization [17,18,20]. To solve this problem, many domestic and foreign scholars had carried out a lot researches [3–20]. Researches on the development of new catalyst and the activation mechanism of CH_4 and CO_2 had achieved important progress [21–23]. Our research group also had thrown great endeavor on these aspects [7,24–28]. However, deep researches on how to prevent catalyst deactivation by carbon deposition and improve the stability of catalyst are still required.

Cobalt oxide was an alkaline oxide rich in oxygen. Metal catalyst taking cobalt oxide as an assistant or active component showed a good catalytic activity in automobile tail gas clean-up, water-gas shift reaction, CO oxidation, CH_4 partial oxidation, synthesis gas production through combustion, and other reactions [29–32]. Compared to the Ni-based catalyst, there's less research on Co-based catalyst. Applied carriers generally were Al_2O_3, SiO_2, molecular sieve, etc., few reports on the Co/Carbon catalyst [4,6,10,21–23,33]. In this paper, the effect of different preparations on the physicochemical property, reforming reactivity, stability and carbon deposition resistance of cobalt/carbon catalyst was investigated through fixed bed flow reaction. These catalysts were prepared by the impregnation method and characterized by the XRD and scanning electron microscopy (SEM). Furthermore, the effect of reaction temperature, air speed and CH_4/CO_2 ratio on the catalyst activity and CO/H_2 ratio in products was investigated.

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http://dx.doi.org/10.1016/j.jiec.2013.08.016

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by successive aqueous incipient wetness impregnations. Carbon used in the experiment was prepared by pyrolysis of coal at 1150 °C for 1.5 h and crushing the catalyst mass to 30–60 mesh-size particles [7]. The proximate analysis and ultimate analysis of carbon catalysts were shown in Table 1. The carbon sample was impregnated with a cobalt salt ($Co(NO_3)_2{\cdot}6H_2O$) for 12 h under atmospheric pressure. For ultrasonic incipient-wetness impregnation, the carbon sample was impregnated with a cobalt salt ($Co(NO_3)_2{\cdot}6H_2O$) or 4 h under the use of ultrasonic wave, then impregnated with a cobalt salt ($Co(NO_3)_2{\cdot}6H_2O$) for 2 h under atmospheric pressure. The catalyst was then dried at 110 °C for 4 h and calcined at different temperature for 4 h.

2.2. Catalytic activity measurements

The catalytic CH_4–CO_2 reforming experiments were carried out at a normal pressure in a fixed-bed reactor. High-purity gases were used throughout all experiments. The volumes of CH_4, CO_2 and N_2 were exactly controlled into the reactor by mass flow controllers. About 2 g of the catalyst was used in reaction runs. The apparatus consisted of a fixed-bed quartz reactor (2.0 cm inner diameter) inside an electric furnace. The temperatures at the top and the bottom of the catalyst bed were monitored with a platinum-rhodium thermocouple, and the difference between the two temperatures was less than 2 °C for catalyst beds. Before the activity tests, the catalysts were reduced with the addition of 10% H_2/N_2 flow (50 $cm^3\ min^{-1}$) at a constant heating rate of 5 °C min^{-1} from room temperature to 950 °C, this temperature was kept for 60 min then cooled to the reaction temperature, the reaction run was started by introducing CH_4/CO_2 mixture into the reactor.

After reaching steady-state conditions, the mixture of reactant gases and products was periodically analyzed by a gas chromatography. Prior to analysis, the effluent was passed through a water-trap at 0 °C to remove the reaction water. The error of each data point was less than 3%, and all experiments with large errors were rejected. The steady-state activity was calculated from the constant conversion value at each reaction temperature and each steam/gas ratio. The content of gaseous products in the reactor effluent was analyzed with a gas Chromatography -960 equipped with a TCD detector. Methane and CO_2 intake can be measured using a mass flow meter. And the output of product gas flow can be measured using soap liquid meter. No catalyst deactivation was observed during reactions.

After the catalyst had served the reaction for a specified period of time, the reaction feed was switched to inert nitrogen, followed by cooling in nitrogen flow of the reactor to room temperature at which the used catalyst was unloaded for various characterizations.

2.3. Catalyst characterization

The crystalline structures of the catalysts were determined by X-ray powder diffraction (XRD) with a computer-controlled Shimadzu XRD-6000 apparatus equipped with a monochromator for the Cu Ka radiation, operating at 40 kV and 30 mA. The patterns were recorded in steps of 0.01° with the scanning rate at 8°/min from 10 to 80° under atmospheric pressure.

The catalysts powders were characterized by thermogravimetric analysis by using Netzsch STA409C instrument, which measures mass changes when temperature increases.

SEM images of the catalyst were performed with a scanning electron microscope JSM-4800 (Japan, JEOL Ltd.). Gold was sputtered onto the catalysts to ensure sufficient conductivity.

3. Results and discussion

3.1. Effects of the impregnation method on the catalyst activity

The catalyst prepared through excessive impregnation method was recorded as 1#, while the catalyst prepared through incipient-wetness impregnation method was recorded as 2#. The effect of different impregnation methods on the catalyst activity was shown in Fig. 1. It revealed that the activity of catalyst prepared through incipient-wetness impregnation method was higher than that of catalyst prepared through excessive impregnation method, viewed from the conversion of reaction feed gas and selectivity of synthesis gas. This may be because that the catalyst prepared by using the excessive impregnation method left quite part of active substances in the impregnation residue. In other words, the active component of the catalyst prepared through excessive impregnation is lower than the metal components carried by the catalyst prepared through incipient-wetness impregnation. Therefore, catalyst made by excessive impregnation achieved lower activity and selectivity than that made by incipient-wetness impregnation.

Incipient-wetness impregnation was generally used to make catalyst without strict requirement on particle size since it could conveniently control the load capacity of active component and the load capacity was easy to be calculated. However, it has various shortcomings, such as poor dispersity of active component, uneven distribution of particle size, etc. To overcome these shortcomings, researchers had made a lot of improvements on it, among which the most common one is to increase the disperse uniformity by using ultrasonic wave.

3.2. Effect of ultrasound on the catalyst activity

3.2.1. Effect of ultrasound

Currently, it is a very hot research topic in both domestic and foreign countries by making catalyst through ultrasound wave whose main motive power comes from the “cavitation” of ultrasound wave [34]. The breakdown of cavitation bubble nuclear brings a local high temperature, high pressure and strong impact wave as well as micro jet, which provides a new unique physical and chemical environment for the chemical reaction that is difficult to be achieved or impossible to be achieved under general conditions. To explore the effect of ultrasound treatment on the activity of Co/Carbon catalyst, the activity of metal/Carbon catalyst treated by incipient-wetness impregnation (2#) and ultrasound incipient-wetness impregnation (3#, vibration frequency: 40 kHZ) was investigated, as shown in Fig. 2.

Table 1
Proximate and ultimate analysis.

Sample	Ultimate analysis (%, ad)			Proximate analysis (%, daf)				
	M	A	V	C	H	N	S	O (diff)
DT coal	3.10	12.20	29.00	87.70	4.96	1.27	0.42	5.36
Carbonaceous	1.20	13.30	4.50	94.60	1.47	0.99	0.17	2.36

DT: Datong.