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Re-promoted Ni-Mn bifunctional catalysts prepared by microwave heating for partial methanation coupling with water gas shift under low H_2/CO conditions

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ABSTRACT

Re-promoted Ni-Mn bifunctional catalysts were prepared by microwave and conventional heating separately, and tested for partial methanation coupling with water gas shift (WGS) of simulated biomass gas in a fixed bed reactor. A series of characterization techniques including N_2 isothermal adsorption, XRD, H_2-TPR, H_2-TPD, SEM, TEM and XPS were employed to examine the physico-chemical properties of the catalysts. With the reaction condition of 350 °C, $H_2/CO = 0.8$ and $H_2O/CO = 1$, 82.6% CO conversion, 70.0% CH_4 selectivity and 82.8% CO_2 growth rate were obtained on the Ni-Mn/Re-Al_2O_3 (MV) catalyst, which indicated its excellent synergetic effect on partial methanation coupling with WGS. According to the characterization results, it was found that microwave heating was beneficial to increase the dispersion of Ni species in comparison with conventional heating and the addition of Re promoter elevated the catalytic performance from both structural and electronic aspects, which was proven by the lowered reduction temperature of β-type NiO and the intensified electron cloud density of active Ni atoms, respectively. In addition, the sequence of Re impregnation also had impact on the catalytic performance. Step impregnation prepared Ni-Mn/Re-Al_2O_3 (MV) exhibited larger turnover frequency (TOF) than co-impregnation prepared Ni-Mn-Re/Al_2O_3 (MV) in the H_2/CO range of 0.6–1.0, owing to the larger electron cloud density and better anti-coking ability of the former catalyst. The 110-h lifetime test further demonstrated the potential of stable Ni-Mn/Re-Al_2O_3 (MV) catalyst in industrial application.

1. Introduction

The rapid development of urbanization in China has spontaneously urged an increasing demand for centralized energy supply [1–3]. Therefore, the gas supply is naturally endowed with considerable significance. At the present stage, urban gas is principally composed of coal gas generated from coal gasification and pipeline natural gas exploited from gas field. However, excess consumption of coal is disadvantageous to the total environment and pipeline natural gas is occasionally of high price due to market turbulence. Such drawbacks drive people to produce supplementary and/or alternative urban gas that is environmentally friendly and economically feasible. Biomass gas, one type of sustainable and recyclable energy manufactured by gasification of organic materials such as forestry and agricultural residues, could be highly promising as substitute or supplemental gas source for urban gas owing to the extensive existence of raw materials [4,5]. Hence, if fully utilized, the biomass gas would breed great economic and social benefit. Normally, biomass gas comprises CO, H_2, CO_2 and N_2 as well as a small amount of water vapor. Nevertheless, on account of diverse biomass materials [6,7] and gasification agents such as air, H_2O, O_2 [8–11], the H_2/CO ratio of obtained biomass gas varies to a great extent and particularly, biomass gas with low H_2/CO ratio ($H_2/CO < 1$) is rarely mentioned on its applications by reason of its relatively high perniciousness and low heating value. A traditionally effective way to avoid the above shortcomings is to reduce the CO content by water gas shift (WGS) (Eq. (1)) and synthesize CH_4 by methanation (Eq. (2)). Through those two reactions, the content of noxious CO is reduced to safe value and in the meantime the heating value of biomass gas is improved due to the formation of CH_4 (Lower Heating Value for CO: 12.64 MJ/Nm^3, for CH_4: 35.91 MJ/Nm^3).

$$CO + H_2O \rightarrow CO_2 + H_2\ \Delta H^0 = -40.6 kJ/mol \quad (1)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O\ \Delta H^0 = -206.1 kJ/mol \quad (2)$$

Conventionally, WGS reaction and methanation are carried out in separated reactors using specific catalysts and if necessary, such as in

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ammonia synthesis or natural gas production from coal, the two reaction units are merely in linear connection, which is uneconomical in equipment cost and inconvenient in operation. In our previous study [12], a novel idea concerning an integrated unit was proposed. The integrated unit was designed to compress methanation and WGS into one reactor and was applied for urban gas production from biomass gas with low H_2/CO ratio. Above all, the core element of the integrated unit was the Ni-Mn bifunctional catalyst, which was proven to have favorable synergy effect to catalyze methanation and water gas shift simultaneously. As is well known, catalysts with satisfying performance generally encompass several elements including support, active component and indispensable promoter. Take the Ni-Mn bifunctional catalyst we have researched as example. Ni plus Mn act as active component and γ-Al_2O_3 plays the role of support. However, catalyst promoter, which is mainly employed to improve the activity and durability, is remained to be investigated. In this case, it is meaningful and necessary to study the effect of promoter on the Ni-Mn bifunctional catalyst. From the present research status, plenty of exposed literatures have reported the promotion effect of various additives into Ni-based catalyst. Kim et al. [13] probed the promotion effect of four precious metals involving Ru, Rh, Pt and Ir by the means of impregnation onto the Ni-MgO/γ-Al_2O_3 catalysts and revealed that Ir metal had better promotion effect for CO selective methanation than the other three metals, primarily owing to its enhancement in reducibility and CO affinity. Zahra and his co-workers prepared samarium promoted Ni-SBA-15 catalysts by two-solvent impregnation method for dry reforming of methane and according to their research, the catalytic activity and stability was enhanced due to samarium promotion in the interaction of NiO particles with the support and dispersion of NiO species [14]. Moreover, promotion effect of alkali metals such as K on metal-carbon bond strength [15] and alkaline earth metals, for instance, Ca on CH_4 selectivity [16] and Mg on mechanical and chemical property of Ni-based catalysts [17–19] were also investigated. Apart from the above-mentioned metal elements, nonmetal additives have also been studied. Kambolis et al. [20] discovered that boron had excellent performance in carbon resistance due to the effective prevention of carbon diffusion on Ni, resulting in the augmented stability for CO methanation. In spite of the broad range of researches, few investigations focus on the promotion effect of Re, which is a member of VIIB elements in the periodic table but plays an important role in the modern chemical industry. It was only infrequently reported that Re had outstanding promotion effect on Fisher-Tropsch synthesis [21,22] or on methanation reaction [23].

At the moment, the most pervasive way to heat catalyst precursors is conducted in the muffle furnace. Such conventional heating usually takes several hours which could cause unnecessary waste on energy. Besides, the lengthy heating process will induce the movement and aggregation of surface crystals, leading to a reduction in the dispersion of active components. Microwave heating, a novel technique to prepare catalysts, has recently attracted much attention and is shown to be promising for developing well-performed catalysts because of its unique heating characteristic. Compared to traditional heating way by external conduction or convection, microwave heating is internally generated [24], which causes fast and uniform heating. This phenomenon results in evenly distributed active components and promoter on the surface of the support [25,26] as well as mechanically enhanced pore structure [24]. Considering its multiple advantages and relatively few researches, it is worthwhile to apply this method in the preparation of Ni-Mn bifunctional catalysts.

The purpose of this work concentrated on the application of microwave heating to the simple and rapid preparation of Re-promoted Ni-Mn bifunctional catalysts, along with comparing their performance with catalysts prepared by conventional heating. In addition, with the intention of discerning the influence of Re impregnation sequence on the performance of partial methanation coupling with WGS, Re-promoted Ni-Mn catalysts separately using step impregnation and co-impregnation method were correspondingly prepared. The catalysts were roundly characterized by N_2 isothermal adsorption, XRD, H_2-TPR, H_2-TPD, SEM, TEM and XPS. Through above characterization and activity tests, the effect of microwave heating, Re promotion and its impregnation sequence were emphatically discussed.

2. Experimental

2.1. Catalyst preparation

The Re-promoted Ni-Mn bifunctional catalysts supported by γ-Al_2O_3 granules were prepared using the step impregnation and co-impregnation method, respectively. The whole preparation process was elucidated in the following two sections.

2.1.1. Preparation by co-impregnation method

The γ-Al_2O_3 support (Henan Chuangmei Environmental Protection Co., Ltd.) was firstly added to the aqueous solution containing an appropriate amount of $Ni(NO_3)_2{\cdot}6H_2O$, $Mn(NO_3)_2{\cdot}4H_2O$ (Sinopharm Chemical Reagent Co., Ltd.) and NH_4ReO_4 (Guangdong Wengjiang Chemical Reagent Co., Ltd.). The heterogeneous mixture was then maintained in water bath at 60 °C for 12 h in order to disperse the Ni, Mn and Re species uniformly. The acquired precursors were dried at 110 °C in a drying oven and subsequently divided into two equal portions. The first part was calcined in a temperature programmed muffle furnace at 400 °C for 5 h to prepare catalyst by the conventional heating method. Resulting catalysts were denoted as Ni-Mn-Re/Al_2O_3 (MF). The second portion was subjected to microwave heating in a self-designed experimental apparatus as shown in Fig. 1 (introduced specifically in the S1 section of supplementary material). The correspondingly obtained catalysts were marked as Ni-Mn-Re/Al_2O_3 (MV). For comparison, Ni-Mn/Al_2O_3 (MF) and Ni-Mn/Al_2O_3 (MV) were prepared in the same manner.

2.1.2. Preparation by step impregnation method

First of all, an equivalent amount of NH_4ReO_4 as mentioned above was dissolved in distilled water and followed by the addition of γ-Al_2O_3 support. Likewise, the mixture was kept in water bath at 60 °C for 12 h and dried at 110 °C. Then the catalyst precursors were split into two equal parts. The first part was firstly calcined in a muffle furnace at 400 °C for 5 h and followed by the mixing with the solution of $Ni(NO_3)_2$ and $Mn(NO_3)_2$. After the same impregnation and drying period, the products were once again calcined in a muffle furnace at 400 °C for 5 h. Resulting catalysts were denoted as Ni-Mn/Re-Al_2O_3 (MF). The second part was first subjected to microwave heating as mentioned above and subsequently mixed with the solution of $Ni(NO_3)_2$ and $Mn(NO_3)_2$. After the maintenance in water bath and drying, the precursors were second time transferred to microwave heating. The corresponding catalysts were marked as Ni-Mn/Re-Al_2O_3 (MV). The nominal loading of nickel, manganese and/or rhenium in each of the acquired catalyst was devised as 15, 3 and/or 1 wt.%, respectively.

2.2. Catalyst characterization

The actual metal loading in the obtained catalysts were determined by inductively coupled plasma (ICP) for elemental analysis (Optima 8000, PerkinElmer, USA). Nitrogen adsorption-desorption isotherms were recorded with an Autosorb-iQ apparatus (Quantachrome, USA). Prior to N_2 adsorption, the samples were degassed under vacuum at 100 °C for 5 h. The specific surface areas of the support and catalysts were calculated using BET method and the pore diameters as well as pore volumes were calculated on the basis of the standard BJH algorithm. XRD spectra were recorded on an X-ray diffractometer (Xpert powder DY5030, PANalytical Co., Netherlands), operating with Cu Kα radiation ($\lambda = 0.154056$ nm, 40 kV, 100 mA). The samples were scanned with Bragg's angles ranging between 5° and 80° with a speed of