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Preparation and characterization of metallic catalyst using wire arc spraying and its application in partial oxidation of methane

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ABSTRACT

The catalyst activity over a series of new metallic catalysts prepared with wire arc spraying (WAS) method was investigated in catalytic partial oxidation of methane (CPOM) to syngas. Comparing with the conventional Ni-based catalyst, the prepared WAS catalysts exhibited significant activity in CPOM. At 850 °C, CH_4 conversion and CO selectivity for the best prepared catalyst were 48.0 and 75.2, respectively. Also, characterization of the WAS catalysts by BET isotherm, XRD and SEM showed that the excellent catalytic performance of the WAS catalysts is related to the high atomizing air pressure and particle cooling rate during the preparation process.

1. Introduction

Synthesis gas is industrially produced through the steam reforming of methane. This process requires too high temperatures as well as a large amount of energy input due to a highly endothermic reaction. Alternatively, the production of synthesis gas through the partial oxidation of methane (CPOM) is preferred because the reaction is an exothermic one [1,2]. Also, the CPOM produces synthesis gas with H_2/CO ratio near 2, where this ratio is suitable for the synthesis to methanol and higher hydrocarbons [2,3].

Among the various noble metal catalysts examined to date [4–6], Rh has been reported to be the most active and stable catalyst in the CPOM. Due to the costs of Rh-based catalysts, it is clear that the development of cheaper and alternative metal-based catalysts such as Fe-, Co-, and Ni-based ones would be desirable [7–10]. Torniainen et al. [11] investigated monolith supported Fe and found that this metal was not successful in converting CH_4 to synthesis gas as it appeared to oxidize rapidly. Meanwhile, Ni catalysts have been widely investigated because of their lower cost and relatively high activity in the CPOM [8,12,13]. However, Mixed Ni–Fe catalysts supported on Al_2O_3 have been reported to show increased stability and resistance to wards carbon deposition [14,15].

In this paper, we employed wire arc spraying (WAS) technique as a novel method for the preparation of metallic catalysts. The WAS system is a branch of thermal spraying methods that is commercially used to produce a wide variety of coatings [16]. Thermal spraying encompasses a group of processes that are capable for rapidly depositing of metals, ceramics, plastics, and mixtures of these materials [17]. In the WAS system, the molten droplet spray is created by forming a direct current (DC) arc between two consumable conductive wires of the raw material. The high temperature of the arc melts, wires and an atomizing gas breaks-up the molten material on the wires tips and propels it in the form of droplets to prepared catalysts [18]. Low running cost, high spray rates and efficiency make it a good process for the preparation of catalysts. However, Rosenzweig et al. [19] was formed a porous nickel coating by using the WAS method, but so far, no report on the application of WAS method for the preparation of surfaces, with catalytic properties has been reported.

The performance of the prepared metallic catalysts was tested in CPOM reaction. For comparing the performance of the WAS catalysts, a sample of nickel catalyst based on alumina, with the same percentage of nickel was prepared. Also, the effects of some operational parameters such as spraying environment (into atmospheric air or cold water), and pressure of atomizing air were investigated [20]. The SEM, XRD and BET analyses were applied for the study of the structure of WAS catalysts. Although, the presence of each of the elemental metals in the WAS wire (alone and together) will be affect the performance of the CPOM catalyst. But, the main purpose of this study is introducing a new type of metal catalysts, which was produced by the WAS method.

2. Experiment

The metal catalysts were synthesized by the WAS method. Commercially available RIMA 410 stainless steel cored wire (*D*

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1.6 mm and containing low amount of Ni, 0.8 wt.%), with air as atomizing gas was used for the spray operation in this research.

The elemental composition of wire is given in Table 1. Principal components of the WAS experimental apparatus are shown in Fig. 1.

After spraying in different atmosphere (air or water), the WAS catalysts were collected and used for this study without any further drying or calcinations pretreatment. These catalysts were labeled as TS_0, TS_1, and TS_2. The preparation conditions of WAS catalysts are summarized in Table 2.

For comparison, 0.8 wt.%Ni/γ-Al_2O_3 catalyst was prepared by wetness impregnation method using Ni $(NO_3)_2 \cdot 6\,H_2O$ as precursor. The γ-Al_2O_3 (Condea Vista Catalox with a surface area of 200 m^2/g and a pore volume of 0.7 cm^3/g) support was dried at 120 °C for 12 h. After Ni metal impregnation, the catalyst was dried at 120 °C and calcined at 700 °C for 3 h, under argon stream.

Each catalyst was tested in a fixed bed quartz microrector (ID 6 × 500 mm). The feed was 10 ml/min (STP), with CH_4:O_2:He = 4:2:4. Typically, 0.5 g of catalyst (particle size 60–120 mesh) was reduced in situ with a flow of hydrogen (30 ml/min (STP)) for at least 12 h at 700 °C, before it was switched to take the reaction feed. The catalytic tests were carried out at atmospheric pressure and at a GHSV of 600 h^{-1}. The reaction temperature was raised from 750 to 850 °C. Products were determined using the commercial gas chromatograph GC-CGCA-1 apparatus equipped with a thermal conductivity detector (TCD). These analyses were done isothermally at 50 °C using a parallel setup of two packed columns (Molecular sieve and Porapak Q).

All of the collected data were obtained after at least 24 h on stream CPOM to ensure steady-state conditions. The catalyst performance at the test conditions in the course of the experiments was quite similar. Catalyst activity was calculated on the basis of products selectivity and methane conversion, formulated as follows (Eqs. (1) and (2)):

$$\text{Selectivity of CO }(\%) = \frac{\text{Moles of CO products}}{\text{Moles of CO} + CO_2 \text{ products}} \times 100 \tag{1}$$

$$\text{Conversion of } CH_4\ (\%) = \frac{(\text{Moles of } CH_4^{in} - \text{Moles of } CH_4^{out})}{\text{Moles of } CH_4^{in}} \times 100 \tag{2}$$

Table 1
Elemental specification of commercial stainless steel cored wire RIMA 410 (*D* 1.6 mm).

Element	C	Si	Mn	S	P	Cu	Ni	Mo	Cr	Fe
Wt.%	0.15	1	1	0.02	0.03	0.75	0.8	0.5	12–15	80.75–83.75

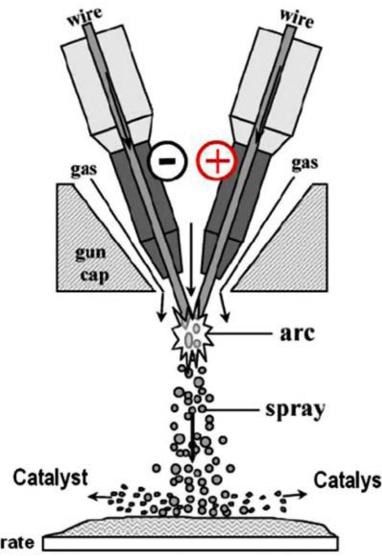

Fig. 1. Schematic diagram showing the wire arc spray process for the catalyst preparation.

Table 2
Preparation condition of the WAS catalysts.

Catalyst	Atomizing gas pressure (bar)	Spraying environment
TS_0	3.5	Air
TS_1	5.5	Air
TS_2	5.5	Cold water

3. Result and discussion

3.1. Catalytic performances

The performance of the catalysts was tested on the CPOM reaction at temperature range 750–850 °C. Table 3 summarizes the results, corresponding to CH_4 conversion, CO selectivity, H_2 yield and H_2/CO ratio obtained over WAS and Ni/γ-Al_2O_3 catalysts. The main aim of the activity test of Ni/γ-Al_2O_3 catalyst was to utilize the results as a basis for comparison with those obtained over WAS catalysts. These observations are consistent with previously reported studies indicating that a higher operating temperature results in a shift in catalyst activity towards higher CH_4 conversion and CO selectivity and to more yield of H_2 and the H_2/CO ratio [2]. A general agreement in the literature is that; the CPOM proceeds through an exo-endothermic sequence of reactions: a first step of oxidation (both partial and total), followed by H_2 oxidation, steam reforming, and Water–Gas shift (WGS) reaction. Due to the exothermic nature of the WGS reaction, temperature is a critical parameter which may limit the efficiency of the reaction [21]. It could be seen that the WAS catalyst samples requires temperature above 750 °C, to show high level of catalytic activity. In this case, the effect of the WGS reaction on performance of the WAS catalysts was negligible. Also, it can be seen that the TS_2 and TS_1 catalysts which were prepared at higher atomizing air pressure and cooled with spraying into the cold water showed higher CH_4 conversion and selectivity to syngas, as compared to the TS_0 catalyst.

By increasing atomizing air pressure, a higher level of porosity was produced over the catalyst due to the trapped gas packets caused by the turbulence of the air flow during the WAS process.

Table 3
Performances of the WAS catalysts and Ni/γ-Al_2O_3 over a temperature range of 750–850 °C.

Catalyst	Temperature (°C)	Catalyst activity			
		X_{CH_4}	Y_{H_2}	S_{CO} (%)	H_2/CO ratio
TS_0	750	20.67	0	15.757	Trace
	800	24.109	0	20.438	Trace
	850	28.12	1.3	26.51	0.35
TS_1	750	25.673	4.207	16.91	Trace
	800	27.70	8.33	30.05	0.46
	850	36.53	19.65	53.78	1.41
TS_2	750	28.16	5.71	20.28	0.47
	800	37.19	23.96	64.43	1.01
	850	47.96	36.08	75.22	1.55
Ni/γ-Al_2O_3	750	46.86	27.82	59.38	2.05
	800	54.36	37.46	68.91	2.08
	850	63.44	50.11	78.97	2.03