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MICROWAVE EFFECT ON PARTIAL OXIDATION OF METHANE TO SYNGAS

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Abstract

In this paper the results of the partial oxidation of methane over Ni-based and Co-based catalysts activated by two different heating modes (conventional and microwaves) are reported. Compared with a conventional heating mode, the temperature of the catalytic bed is much lower and there is a higher selectivity of CO and H₂ with microwave irradiation.

Keywords: Microwave, methane, partial oxidation, syngas

INTRODUCTION

Microwave dielectric heating is found to be an alternative procedure to conventional conductive heating for introducing energy into chemical reactions and seems to be a well-suited process for activating solid catalysts [1-3]. The origin of the microwave coupling dielectric heating lies in the capacity of an electric field to polarize charges in a material. The heating effect is more emphasized when the irradiated material has a strong dipolar character. This is particularly the case with those catalysts where the support is an oxide with numerous polar OH groups. Moreover, when polar molecules are present on the surface of the oxide support as active phase, stronger coupling effect with microwave energy will be generated. So we consider that partial oxidation of methane to syngas over supported Ni and Co catalysts will be performed under microwave irradiation. The aim of this work is to investigate the influence of microwave heating effect on the supported Ni and Co catalysts in the title reaction referred to as POM.

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EXPERIMENTAL

The Ni-based catalysts (with 10 wt.% nickel) were prepared by impregnating ZrO_2 and La_2O_3 powders with nickel nitrate solution, respectively. The resulting paste was dried at 383 K, annealed at 673 K for decomposition and calcined at 1023 K for 6 h in air. The calcined oxides were finely ground and pelleted and heated at 1073 K for 8 h. The Co-based catalysts (with 10 wt.% Co) were prepared by solid-state reaction of the oxides Co_2O_3 and ZrO_2 or La_2O_3 . The raw materials, in powder form were mixed well and were calcined at 1023 K for 6 h in air. The calcined materials were finely ground and pelleted, and finally heated at 1073 K for 8 h in air. The X-ray diffraction (XRD) pattern of the oxides was recorded with a D/max-3B diffractometer using $\text{Cu-K}\alpha$ radiation. XPS spectra were recorded using a Perkin Elmer Phi 5600 ESCA system. The binding energies were corrected using the reference value of 284.8 eV of the C1s peak resulting from carbon contamination.

The POM reaction was carried out at atmospheric pressure in a continuous flow fixed-bed quartz tube (5 mm id) packed with the catalyst (particle size: 40~80 mesh). The catalytic bed can be heated either by conventional heating or by microwave radiation. (a) Conventional heating: the reactor was enclosed by a vertical tubular furnace; the reactor temperature (controlled by a temperature controller) was measured by a thermocouple located in the catalyst bed. (b) Microwave radiation: the part of the tube packed with the catalysts was kept in a TE_{103} cavity, perpendicular to the broad wall of the waveguide and parallel to the direction of the electric field; the temperature of the catalyst bed was controlled by adjusting the microwave power and plunger. Temperature measurement within the microwave field is not a trivial matter [4]. Most commonly used measurement techniques are not suitable in the presence of a microwave field due to the metallic nature of the probes involved. Bond and co-workers have proved that the measurement of temperature in the cavity using an infrared pyrometer is acceptable [5]. In our experiment, a comparison of the metallic thermocouple and an infrared pyrometer for measuring the temperature of the sample heated in an electric furnace has been made. The results indicate that there is only a very small difference between the two measurement methods. So, throughout this work, the temperature in the cavity was measured with an infrared pyrometer. Furthermore, the infrared pyrometer was carefully fixed so that the center of the probe always aims at the center of the catalytic bed in all experiments. Therefore, we think the temperature measurement would not affect the evaluation of activity for various catalysts.

A microwave source with power of 0~600 W, continuously adjustable, operating at a frequency of 2450 MHz was used for the experiment. The useful power for heating the sample was varied between 80 and 150 W during the experiment. The microwave power was varied so as to maintain the temperature at the required pre-set value.

Experimental conditions for these two modes were as follows: the amount of catalyst 0.1 g; $\text{CH}_4/\text{O}_2 = 2/1$; flow rate of the feed: 100 mL/min. The reactor effluent gases were analyzed by an on-line gas chromatography equipped with a carbosieve column and a TCD. The conversion and selectivity after 30 min of reaction were calculated on carbon number basis.

RESULTS AND DISCUSSION

The XRD pattern confirmed that Ni/ZrO₂ has only NiO and ZrO₂ phase. Ni/La₂O₃ has La₂O₃, La₂NiO₄ and La₂Ni₄O₇ phase. Co/ZrO₂ also has only Co₃O₄ and ZrO₂ phase. Co/La₂O₃ has Co₃O₄, LaCoO₃ and La₂O₃ phase. Compared with the fresh oxides, there are no changes in the bulk phase of the oxides used after treatment by the two heating modes, but the surface composition of the oxides changed slightly. However, there is no obvious difference between the oxides irradiated by microwave and the oxides heated by the conventional method.

Table 1
Comparison of methane conversion and product distribution over
10% Ni/ZrO₂ under two activation modes

| Treating method | T (K) | CH ₄ conv.(%) | Selectivity (%) | | | H ₂ /CO |
|-------------------------|----------|-----------------------------|-----------------|------|-----------------|--------------------|
| | | | H ₂ | CO | CO ₂ | |
| Microwave heating | 673 | 69.8 | 85.9 | 84.3 | 15.7 | 2.04 |
| | 713 | 77.4 | 90.2 | 89.7 | 10.3 | 2.01 |
| | 733 | 80.5 | 91.5 | 92.5 | 7.5 | 1.98 |
| | 753 | 82.6 | 93.8 | 93.9 | 6.1 | 2.00 |
| | 773 | 88.9 | 94.8 | 94.7 | 5.3 | 2.00 |
| | 823 | 92.6 | 96.5 | 96.2 | 3.8 | 2.01 |
| | 873 | 97.1 | 97.6 | 97.3 | 2.7 | 2.01 |
| | 923 | 99.5 | 99.7 | 99.7 | 0.3 | 2.00 |
| Conventional heating | 873 | 65.5 | 92.9 | 90.1 | 9.9 | 2.06 |
| | 923 | 83.7 | 94.2 | 92.7 | 7.3 | 2.03 |
| | 973 | 89.2 | 95.8 | 95.2 | 4.8 | 2.01 |
| | 1023 | 91.2 | 96.0 | 96.2 | 3.8 | 2.00 |
| | 1073 | 93.8 | 98.3 | 98.0 | 2.0 | 2.01 |

The products from the POM reaction are H₂, CO, CO₂ and H₂O for both activation modes (see Tables 1-4). The amount of water formed in the reaction is not negligible. Obviously, the important point is that at the same methane conversion level, the temperature of the catalyst bed is much lower with microwave irradiation than with the conventional heating mode. This is due to the "hot-spot effect". Booske and co-workers have proposed that the microwave can localize resonant coupling of microwave energy to point defects or a weakly

bonded surface [6]. In other words, under microwave irradiation the energy distribution is nonuniform on the catalyst. The microwave energy could be concentrated at some spots, which are known as "microwave hot spots". Since the late 1960s, it has been recognized that the critical energy for initiating detonation is insufficient to start any chemical reaction if that energy were to be uniformly distributed. So, "microwave hot spots" can be reasonably regarded as the active centers for the catalytic reaction. In this work, the oxygen vacancy is the "hot spot" and the reaction can be initiated there.

Table 2

Comparison of methane conversion and product distribution over 10% Ni/La₂O₃ under two activation modes

| Treating method | T (K) | CH ₄ conv.(%) | Selectivity (%) | | | H ₂ /CO |
|----------------------|-------|--------------------------|-----------------|------|-----------------|--------------------|
| | | | H ₂ | CO | CO ₂ | |
| Microwave heating | 673 | 58.3 | 74.2 | 73.6 | 26.4 | 2.02 |
| | 723 | 79.1 | 84.8 | 83.9 | 16.1 | 2.02 |
| | 773 | 80.4 | 93.0 | 92.5 | 7.5 | 2.01 |
| | 823 | 81.3 | 95.2 | 95.8 | 4.2 | 1.99 |
| | 873 | 88.5 | 96.8 | 96.0 | 4.0 | 2.02 |
| | 923 | 97.4 | 98.8 | 96.2 | 3.8 | 2.05 |
| | 973 | 99.5 | 99.8 | 99.7 | 0.3 | 2.00 |
| Conventional heating | 873 | 40.3 | 78.3 | 76.7 | 23.3 | 2.04 |
| | 923 | 49.3 | 81.0 | 80.8 | 19.2 | 2.01 |
| | 973 | 69.8 | 84.7 | 84.0 | 16.0 | 2.02 |
| | 1023 | 89.6 | 90.9 | 91.2 | 8.8 | 1.99 |
| | 1073 | 90.8 | 92.7 | 92.2 | 7.8 | 2.01 |

Table 3

Comparison of methane conversion and product distribution over 10% Co/ZrO₂ under two activation modes

| Treating method | T (K) | CH ₄ conv.(%) | Selectivity (%) | | | H ₂ /CO |
|----------------------|-------|--------------------------|-----------------|------|-----------------|--------------------|
| | | | H ₂ | CO | CO ₂ | |
| Microwave heating | 723 | 48.0 | 79.2 | 78.7 | 21.3 | 2.01 |
| | 773 | 58.7 | 80.8 | 80.1 | 19.9 | 2.02 |
| | 823 | 66.8 | 86.2 | 86.3 | 13.7 | 2.00 |
| | 873 | 79.8 | 88.5 | 87.5 | 12.5 | 2.02 |
| | 923 | 86.5 | 90.7 | 89.9 | 10.1 | 2.02 |
| | 973 | 89.2 | 94.9 | 96.2 | 3.8 | 1.97 |
| | 1023 | 96.8 | 96.9 | 97.5 | 2.5 | 1.99 |
| | 1073 | 100 | 98.1 | 98.9 | 1.1 | 1.98 |
| Conventional heating | 873 | 62.9 | 67.8 | 66.0 | 34.0 | 2.06 |
| | 923 | 77.8 | 83.1 | 81.1 | 18.9 | 2.05 |
| | 973 | 82.6 | 85.2 | 83.9 | 16.1 | 2.03 |
| | 1023 | 88.3 | 90.3 | 90.2 | 9.8 | 2.00 |
| | 1073 | 94.4 | 91.5 | 92.6 | 7.4 | 1.98 |

Table 4
Comparison of methane conversion and product distribution over
10% Co/La₂O₃ under two activation modes

| Treating method | T (K) | CH ₄ conv.(%) | Selectivity (%) | | | H ₂ /CO |
|-------------------------|----------|-----------------------------|-----------------|------|-----------------|--------------------|
| | | | H ₂ | CO | CO ₂ | |
| Microwave heating | 723 | 33.8 | 58.9 | 57.0 | 43.0 | 2.07 |
| | 773 | 57.4 | 82.3 | 81.1 | 18.9 | 2.03 |
| | 823 | 74.2 | 91.1 | 88.8 | 11.2 | 2.05 |
| | 873 | 87.9 | 92.3 | 91.3 | 8.7 | 2.02 |
| | 923 | 91.4 | 94.0 | 94.3 | 5.7 | 1.99 |
| | 973 | 94.9 | 95.1 | 96.5 | 3.5 | 1.97 |
| | 1023 | 97.4 | 96.6 | 97.9 | 2.1 | 1.97 |
| | 1073 | 99.3 | 98.9 | 99.3 | 0.7 | 1.99 |
| Conventional heating | 873 | 27.6 | 48.6 | 47.6 | 52.4 | 2.04 |
| | 923 | 41.7 | 61.5 | 61.7 | 38.3 | 1.99 |
| | 973 | 50.7 | 68.3 | 68.7 | 31.3 | 1.99 |
| | 1023 | 55.9 | 70.8 | 71.7 | 28.3 | 1.98 |
| | 1073 | 60.1 | 73.1 | 73.2 | 26.8 | 2.00 |

Compared with the conventional heating mode at the same temperature, the CO and H₂ selectivity is higher under microwave irradiation. This may be attributed to the suppression of homogeneous reaction and to changes in the oxygen ion mobility and the defect diffusion of the solid induced by microwave irradiation. Further study is necessary to separate the influence of these two aspects.

Tables 1–4 show that Ni-based catalysts have higher activity and selectivity for CO and H₂ than Co-based catalysts under both activation modes. Torniainen *et al.* [8] studied methane oxidation to synthesis gas over nine noble metal catalysts on Al₂O₃ monoliths. Their result indicates that Rh and Ni are the only metals giving high and stable syngas yields, Co appears to have serious problems with deactivation and gives lower syngas selectivity. The result in this paper is similar with Torniainen's. Our result is also consistent with the fact that LaCoO₃ is a good combustion catalyst [9,10].

Based upon the above results, we think that the reaction pathways for CH₄ oxidation under microwave irradiation might be different from that with conventional heating. This viewpoint needs to be confirmed furthermore.

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