



Experimental and kinetic study of methane combustion with water over copper catalyst at low-temperature



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ABSTRACT

In this paper, the effect of water on methane combustion over a copper catalyst in a fixed-bed catalytic reactor was investigated. The activity for methane combustion gradually decreased in the presence of water, whereas when water was turned off, methane conversion recovered completely. The reaction between surface hydroxyls and gas-phase methane was investigated by DRIFTS; high hydroxyls peaks made low methane conversion. Under differential conditions, kinetic studies revealed that oxygen pressure almost had no relationship with the reaction rate ($\beta = 0$), while methane pressure obviously affected the reaction order ($\alpha = 1.07$). As water was added into the feed, the reaction order with respect to methane decreased from 1.07 to 0.86. Water exhibited an inhibitory effect on methane oxidation, and the water poisoning effect was slowly reversible. When the water concentration increased, the reaction order with respect to water decreased from -0.72 to -0.95 . At low temperature (<450 °C), water reacted with chemisorbed oxygen (O^*), which could form hydroxyl groups (OH^*) on the active sites. This interaction inhibited the oxydehydrogenation of methane. Hence, methane needed more energy to combine with oxygen, and the apparent activation energy increased from 81.4 kJ/mol to 153.0 kJ/mol.

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1. Introduction

Large amounts of low-concentration methane exist in mines, particularly in China. However, it is difficult to utilize this low-concentration methane by employing conventional combustion technology. Hence, an attractive alternative for this purpose is catalytic combustion, which involves complete oxidation at low temperature [1,2]. On the other hand, several catalysts, such as Pd and Pt, have been investigated for their activity for methane oxidation [3,4]. Noble metals exhibit excellent performance for catalysis, which adsorb O_2 molecules onto active sites, followed by the dissociation of $O-O$ bonds to afford O^* (chemisorbed O) for methane dehydrogenation [5,6]. However, because of the presence of a large amount of water in coal bed gas, in most cases, methane combustion is inhibited. Water inhibits the activity of catalyst for methane combustion [7,8]. On the active sites, water easily combines with chemisorbed O and generates surface OH groups, which are not suitable for methane combustion [9].

On the other hand, methane can react with water via the reforming reaction at high temperature [10,11]. Reforming reaction utilizes H_2O for the selective conversion of CH_4 to CO and H_2 on the metal surface or oxides at moderate temperatures (900 K–1200 K) [12,13]. However, thus far, reactions between CH_4 and H_2O and the role of chemisorbed oxygen as well as their catalytic consequences still remain unclear [14–16]. With respect to the introduction of water into the feed at low O_2/CH_4 ratios, studies have mainly focused on whether the reforming reaction of methane with water could occur before O_2 depletion. A few researchers [17,18] have hypothesized that in the presence of surface chemisorbed oxygen, methane prefers to combine with chemisorbed oxygen (oxidation). If oxygen is completely depleted, methane undergoes dehydrogenation on the active sites (reforming reaction), which indicates that combustion precedes reforming reactions on the catalyst surface [19,20].

Although several studies on catalytic oxidation or the reforming reaction have been reported, CH_4-O_2/H_2O reactions and the role of chemisorbed oxygen still remain unclear. By taking special precautionary measures to ensure differential conditions during experiments, van Giezen [21,22] has studied the oxidation of methane with water at low temperature. They reported that, when water was introduced into the feed, the reaction order with respect to methane decreased; the reaction order in water was between

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–0.6 and –1. Copper exhibited good catalytic performance in the reforming or combustion of methane, and some researchers have investigated the effect of the loading amount, metal valence, and calcination temperature on methane conversion. They both revealed that copper exhibits good catalytic activity for methane combustion when water was cut off. Gonzalo Aguila [23,24] has studied methane oxidation over a Cu catalyst and hypothesized that water obviously affects oxidation, while CO₂ does not exhibit any activity; an optimal Cu catalyst loading of 10–12 wt% afforded the highest activity. In addition, the activity of the Cu species on γ -Al₂O₃ continuously decreases with Cu loading. Ciuparu [25,26] has conducted in situ DR-FTIR studies and obtained direct evidence for the formation and accumulation of hydroxyl groups at the catalyst surface during experiments. Several well-resolved absorption bands were observed in the wavenumber region, which represented isolated OH groups (bridged and terminal) before recombination and desorption as gas-phase water. Meanwhile, they pointed out that, the adsorption of water weakened with increase in temperature.

Some researchers have employed TPD for investigating the influence of water and oxygen and have found that pre-adsorbed water on the *cus*-Pd sites completely suppressed the adsorption of methane, which limited the activation of methane on the catalyst surface [31,32]. However, they did not focus on the surface reactant, which may change reaction pathways. The activity of several metal catalysts for methane oxidation decreases with the injection of water into the feed [33–35]. Thus, water inhibition is probably not caused by the metal but is rather attributed to the reactions at the surface, which were changed because of the additional water; this additional water may have caused the inhibitory effect. This study has employed the reforming theory to tackle issues related to combustion, which explain the common problems of the inhibitory effect of water in methane oxidation.

For methane oxidation under wet air, studies have mainly focused on the use of noble metal catalysts, which exhibit high activity but poor stability. Because of their widespread applicability (oxidation and reforming), several studies have focused on the use of transition metal catalysts such as copper. In this paper, a Cu/ γ -Al₂O₃ catalyst was prepared, and the effect of water on methane oxidation was investigated in terms of apparent activation energy and reaction order.

2. Experiment

2.1. Catalyst preparation and characterization

γ -Al₂O₃ powder (specific surface area, 177.6 m²/g; pore volume, 0.44 cm³/g; pore diameter, 188.3 Å; metal dispersion, 80.6%) was treated under ambient air by increasing the temperature to 400 °C at 2 K/min. First, γ -Al₂O₃ powder was held in air at 400 °C for 3 h before cooling to room temperature. Second, copper clusters were introduced into the catalyst system by incipient wetness impregnation. Third, the Cu/ γ -Al₂O₃ catalyst was prepared using an aqueous solution of Cu(NO₃)₂ so as to achieve a metal loading of 5 wt% for γ -Al₂O₃ powder. The surface reaction required more surface metal atoms on the metal clusters. Hence, we fixed the metal amount (0.05 g) and investigated different loading amounts of 3 wt%, 5 wt%, 7 wt%, 10 wt%, and 15 wt% to attain the maximum catalyst activity. As loading amounts of 3 wt% and 5 wt% exhibited the maximum catalytic activity, we chose a metal loading of 5 wt% on the support. (These experimental details have not been discussed herein.)

First, the impregnated sample was treated at 100 °C for 20 h under ambient air and then in flowing dry air by increasing the temperature to 400 °C at 2 K/min. Second, the dried sample was

calcined in a muffle furnace for 6 h at 500 °C under N₂. The calcination of the catalyst under nitrogen is conducted for removing free radicals, such as OH and NO₃⁻, and other volatile matter. In addition, calcination at 500 °C can help to maintain the surface structure of the catalyst. Most of the working conditions in this paper have been employed at temperatures below 500 °C. The self-made catalyst was cooled to room temperature in a muffle furnace (save under N₂ atmosphere). For attaining differential conditions, the catalyst thus prepared was diluted by adding γ -Al₂O₃ powder to the catalyst system to limit temperature fluctuations in the reactor [27]. The diluting ratio was 1:75 (Cu: γ -Al₂O₃).

The activity of the Cu/ γ -Al₂O₃ catalyst was determined by methane conversion. According to carbon balance, methane conversion *x* can be expressed as follows:

$$x = \frac{[\text{CO}_2]}{[\text{CO}_2] + [\text{CH}_4]} \quad (1)$$

where [CO₂] and [CH₄] was volume percentage of carbon dioxide and methane in the exit gas.

2.2. Experimental devices and system

Methane combustion was conducted in a fixed-bed reactor, which is a ceramic reaction tube with an inner diameter of 10 mm and length of 1200 mm. The loading length of the catalyst is 100 mm. The reaction mixture gas (0–8 kPa CH₄, 0–20 kPa O₂, 0–10 kPa H₂O, and N₂ balance), controlled by a mass flow meter, was injected into the fixed-bed reactor at a rate of 200 mL/min. Water vapor, which was generated by a vapor generator (W-202A-220-K), was carried by N₂ at 150 °C and mixed with CH₄ and O₂ before entering into the reactor. The reactor was heated by a resistance-heated furnace, which was connected to a data acquisition and control system; this system was responsible for controlling the reaction temperature. Gas chromatography was employed to measure the concentrations of CH₄ and CO₂ in the effluent gas. Data such as the reactant concentration were analyzed in triplicate in terms of specific reactant pressure and temperature, and the average was calculated to plot the figures. The error was limited to below 5%. The gas hourly space velocity was 12,000 h⁻¹.

During the reaction, DRIFT spectra were recorded on a Spectrum 100 FTIR instrument, which was equipped with a diffuse reflectance accessory containing a reaction cell. The Cu/ γ -Al₂O₃ catalyst was placed in the reaction cell, where the pressure and temperature were controlled by the instrument. A total of 36 spectra were collected in the range of 2200–4100 cm⁻¹. A resolution of 16 cm⁻¹ and a mirror velocity of 1.67 cm/s were employed. Powder X-ray diffraction (XRD) patterns of the catalyst were recorded on a D/Max-3C diffractometer (200 mA, 50 kV). The experiment was conducted in the 2 θ range of 10–90°.

3. Results and discussion

3.1. Experimental study

Fig. 1 shows the curves of conversion vs temperature for Cu/ γ -Al₂O₃, which is indicative of the effect of water on methane combustion. The reaction conditions were 3 kPa CH₄, 20 kPa O₂, 0–10 kPa H₂O, and N₂ balance. As shown in Fig. 1, the black curve represents methane oxidation under dry air; the catalyst activity was high. When water was added into the feed, methane conversion clearly decreased. On the other hand, under wet air, at 525 °C, the catalyst loses most of its activity. Furthermore, when the temperature was increased to 650 °C, the deactivation effect was weakened, and conversion curves under dry and wet conditions revealed the same behavior. As compared with a temperature

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