Catalytic Combustion of Methane over Ti-Pillared Clay Supported Copper Catalysts

Xiufeng Xu1*, Yanfei Pan2, Xiaoyan Cui1, Zhanghuai Suo1

1. Institute of Applied Catalysis, Yantai University, Yantai 264005, China; 2. Analysis Center, Yantai University, Yantai 264005, China
[Manuscript received October 09, 2004; revised November 17, 2004]

Abstract: A natural montmorillonite, produced from Laiyang of Shandong Province, was pillared by Ti-polycations to form Ti-pillared clay (Ti-PILC), and characterized by BET surface area, infrared spectra and thermal analysis. The characterization results show that Ti-PILC has a larger surface area and more hydroxyl groups than that of the natural clay, thus was used as the catalytic carriers to prepare supported Cu catalysts (Cu/Ti-PILC). The 20%Cu/Ti-PILC with 10mmol/g of Ti/clay shows a high catalytic performance of methane combustion in the temperature range of 400–500 ºC.

Key words: Ti-pillared clay, characterization, copper, catalytic combustion, methane

1. Introduction

The thermal combustion of methane results in large amounts of pollutants due to its low utilization rate and rather high combustion temperature. In the process of catalytic combustion of methane, very high efficiencies can be achieved at relatively low operating temperatures resulting in considerable economic benefits and less formation of thermal NOx.

Catalysts used for the combustion of methane fall broadly into two series: γ-Al2O3, ZrO2 or TiO2 supported noble metals, typically platinum or palladium, and oxides of transition metals, mainly oxides of copper, manganese and cobalt [1–3].

Montmorillonite with low cost is a potential material for the adsorbents and catalyst supports, but less directly applied in reality due to its low thermal stability and small basal spacing. During the recent years, many researchers have urged to prepare the pillared clays (PILC) by exchanging the charge-compensating polycations present in the interlamellar space of the parent clay, thus largely improve the surface area and basal space of the resulted PILCs [4–8].

In the present study, TiCl4 and Ti(OC4H9)4 was served as the starting materials to prepare the Ti pillaring agents and Ti-pillared clay (Ti-PILC), respectively. The Ti-PILC samples were characterized by performing BET surface area, thermal analysis (TG-DTA) and FT-infrared (FTIR) spectra. Then Ti-PILC was impregnated incipiently with Cu(NO3)2 solution to prepare the supported copper catalysts. The catalytic activity of Cu/Ti-PILC catalysts for methane combustion was evaluated under the reaction temperature of 400–550 ºC.

2. Experimental

2.1. The preparation of Ti-pillared clay (Ti-PILC) and Cu/Ti-PILC catalysts
The parent clay, a purified montmorillonite with a particle size ≤2 μm, was obtained from Laiyang of Shandong Province. This montmorillonite contains a cation exchange capacity (CEC) of 86 meq/100 g.

The starting materials for Ti pillaring agents are TiCl₄ and Ti(OCH₃H₅)₄, and to be expressed clearly, the resulted pillared clay are designated as inorganic and organic Ti-PILC, respectively. The preparation procedure of these two Ti-pillaring agents is described as follows. For the inorganic Ti-pillaring agent, the TiCl₄ was added into 2.0 mol/L HCl solutions, and diluted with distilled water to obtain the final Ti and HCl concentrations of 0.8 and 0.4 mol/L, respectively. Ti(OCH₃H₅)₄ was added to an aqueous solution of CH₃COOH (80%) by peptizing at 50 °C for 1 h to prepare the organic Ti-pillaring agent.

After aging at room temperature for 24 h, an appropriate amount of pillaring solutions, required for the Ti/clay (mmol-Ti/g-clay) ratio of 5, 10, 20 and 30, was slowly added to the parent clay suspension (1% in water), stirred at room temperature for 2 h and separated by a centrifuge. The product was washed several times with deionized water to remove Cl⁻ or excess sol solution and followed by drying in air at 110 °C and calcinations at 500 °C for 2 h.

Ti-PILC was impregnated overnight with Cu(NO₃)₂ solution, dried under vacuum and calcined at 500 °C. The Cu loading was limited to 20% in its metallic state.

2.2. Physicochemical analysis

The measurement of BET surface area ($A_{\text{BET}}$) of Ti-PILC was performed by continuous flowing method with physisorbed N₂ at 77 K using H₂ as carrier gas. The FTIR spectra of Ti-PILC were recorded on a Shimadzu FTIR-8400s spectrophotometer, using the sample pressed in KBr disk, at a spectra resolution of 4 cm⁻¹. TG-DTA spectra of the Ti-PILC samples were recorded with about 10 mg of each sample and a temperature ramp of 10 °C/min.

2.3. Catalytic activity measurements for methane combustion

The catalyst was put in the middle of a horizontal quartz reactor. The reaction temperature was controlled by a K-type thermocouple in the heated zone. The flow rate of reactant gases was controlled by a pressure stabilizer before introducing into the reactor and was recorded by a flow meter at the end of reactor. The composition of gases at the inlet and outlet of the reactor was determined by an on-line GC with a TCD detector. The feed of reactants consists of 0.75%CH₄ and 9.11%O₂ diluted in nitrogen with the gas hourly space velocity (GHSV) of 7200 h⁻¹.

3. Results and discussion

3.1. Surface area of Ti-PILC

The measurement results of BET surface area of Ti-PILC samples are listed in Table 1. It can be seen the surface area of Ti-PILC, which was related to the ratio of Ti to clay, were increased greatly compared to that of the parent clay (26.5 m²/g). This indicated that the use of inorganic hydrated Ti polycations and organic Ti sol cations as pillaring agents provided high surface area. Among the Ti-PILC samples, the one with 10 mmol/g of Ti/clay has the highest surface area, but when the Ti/clay exceeds 10 mmol/g, the surface area of the resulted Ti-PILC decreased evidently.

### Table 1. BET surface area of Ti-PILC as synthesized

<table>
<thead>
<tr>
<th>Ti/clay (mmol/g)</th>
<th>Inorganic Ti-PILC</th>
<th>Organic Ti-PILC</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>85.9</td>
<td>82.0</td>
</tr>
<tr>
<td>10</td>
<td>168.0</td>
<td>80.6</td>
</tr>
<tr>
<td>20</td>
<td>132.0</td>
<td>55.4</td>
</tr>
<tr>
<td>30</td>
<td>111.4</td>
<td>58.3</td>
</tr>
</tbody>
</table>

3.2. IR spectra of Ti-PILC

Figure 1 shows the FTIR spectra of the inorganic and organic Ti-PILC, respectively. The FTIR spectrum of the parent clay exhibits two peaks at 3440 and 3660 cm⁻¹ at the OH stretching region. This pattern is typical of water adsorption in montmorillonite and is ascribed to the —OH stretching vibration. Compared with the parent clay, an increase in the 3440/3660 cm⁻¹ intensity ratio of Ti-PILC samples is visible and attributed to the increase of —OH groups. A shoulder around 3250 cm⁻¹ can be ascribed to an overtone of the water bending vibration at 1645 cm⁻¹. A broad peak around 1030 cm⁻¹ can be assigned to the in-plane stretching vibration of surface Si—O—Si in parent clay and Ti-PILCs. The peak at 720 cm⁻¹ together with those at 520 and 460 cm⁻¹ is associated with Si—O bending vibration in all samples [9].
As stated before, the Ti-PILCs were synthesized by exchanging the charge-compensating cations (Na\(^{+}\)) present in the interlamellar space of the parent clay with the Ti polycations, thus increase the surface area and —OH groups of the resulted samples, which will be beneficial for the dispersion of Cu species in the prepared Cu/Ti-PILC catalysts.

3.3. TG-DTA curves of organic Ti-PILC

Typical TG and DTA curves of organic Ti-PILC as synthesized are shown in Figure 2.

Figure 1. FTIR spectra of raw clay, inorganic Ti-PILC (a) and organic Ti-PILC (b) as synthesized
Ti/clay (mmol/g): (1) raw clay, (2) 5, (3) 10, (4) 20, (5) 30

Figure 2. TG (a) and DTA (b) curves of organic Ti-PILCs as synthesized
Ti/clay (mmol/g): (1) 5, (2) 10, (3) 20, (4) 30
A weight loss with an endothermic peak near 100 °C is attributed to dehydration of adsorbed water. It is followed by a gradual weight loss with a small exothermic peak at about 150 °C and can be assigned to the combustion of organic compounds adsorbed on the sample. Then a drastic weight loss with a large exothermic peak in the range 200–600 °C is attributed to the combustion of the titanium organic complex existed in the Ti-PILC [10]. The results show there are two types of titanium organic compound in the organic Ti-PILCs, one is the organic species adsorbed on the surface and the other is the titanium organic complex contained in the Ti-PILC.

3.4. The catalytic performance of 20%Cu/Ti-PILC for methane combustion

The methane combustion conversion over Cu catalysts supported on inorganic Ti-PILCs is shown in Figure 3(a). As it can be seen, the 20%Cu/Ti-PILC has a high catalytic performance in the reaction temperature range from 400 to 550 °C. Among these catalysts, the one with 10 mmol Ti/g clay exhibits the highest activity. Figure 3(b) gives the methane combustion conversion over organic Ti-PILC supported copper catalysts. Similar to the activity order of inorganic Ti-PILC catalysts with different Ti/clay, the catalyst with 10 mmol Ti/g clay presents the highest activity in terms of the same catalysts series. Furthermore, the order of the catalytic activity of Cu/Ti-PILC catalysts is in accordance with the surface area of the corresponding Ti-PILCs.

![Figure 3. The methane conversion over Cu catalysts supported on inorganic Ti-PILC (a) and organic Ti-PILC (b)](image)

The methane combustion conversion over Cu catalysts supported on inorganic Ti-PILCs is shown in Figure 3(a). As it can be seen, the 20%Cu/Ti-PILC has a high catalytic performance in the reaction temperature range from 400 to 550 °C. Among these catalysts, the one with 10 mmol Ti/g clay exhibits the highest activity. Figure 3(b) gives the methane combustion conversion over organic Ti-PILC supported copper catalysts. Similar to the activity order of inorganic Ti-PILC catalysts with different Ti/clay, the catalyst with 10 mmol Ti/g clay presents the highest activity in terms of the same catalysts series. Furthermore, the order of the catalytic activity of Cu/Ti-PILC catalysts is in accordance with the surface area of the corresponding Ti-PILCs.

4. Conclusions

There are two types of organic Ti-compound in the organic Ti-PILCs, one is the organic species adsorbed on the surface and the other is the titanium organic complex contained in the Ti-PILC. The surface area of all Ti-PILC samples, dependent upon the ratio of Ti to clay, is higher than that of the parent clay. With respect to the parent clay, the 3440/3660 cm\(^{-1}\) intensity ratio in the FTIR spectra of Ti-PILC samples increased indicating the increase of —OH groups in Ti-PILC. The larger specific surface area and more —OH groups of Ti-PILCs was beneficial for the dispersion of Cu species in the prepared Cu/Ti-PILC catalysts and led to the high catalytic performance for methane combustion under the reaction temperature of 400–550 °C.

References

Chem, 2001, 175: 111