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# Promoting effect of water vapor on catalytic oxidation of methane over cobalt/manganese mixed oxides

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## Abstract

Methane oxidation was conducted in a fixed bed quartz tubular reactor on a series of mixed oxides of cobalt/manganese prepared by a sol–gel method. A unique promoting effect of water vapor on methane conversion was observed for the first time on these cobalt/manganese mixed oxides calcined at 450 or 600 °C. However, these mixed catalysts lost their catalytic activities after being calcined at 850 °C. The catalytic activity of methane oxidation was significantly improved by supporting the cobalt/manganese mixed species onto the high surface area $SiO_2$ or $Al_2O_3$–$SiO_2$ materials. It was noteworthy that the water enhancement effect was retained on these supported catalysts.

*Keywords:* Methane oxidation; Catalytic combustion; Water vapor effect; Cobalt oxide; Manganese oxide

## 1. Introduction

Catalytic combustion can be used in a variety of natural gas combustion processes, such as electrical utilities and motor vehicles, with significant reduction of the formation of thermal nitric oxides by lowering combustion temperatures. On the other hand, catalytic combustion is also an effective route to purify methane greenhouse gas from several exhaust emission sources, such as incomplete methane combustion from natural gas fueled engines. Pd-based noble metals have been reported as active catalysts for methane combustion. In addition to high cost concerns, supported Pd catalysts are usually deactivated by water vapor regardless of the various supports used, such as $Pd/Al_2O_3$ [1], $Pd/SnO_2$ [2] and $Pd/ZrO_2$ [3–5], particularly at low temperatures below 450 °C [6]. Only few studies have been devoted to single oxides such as Au [7], Ag [8], Fe [9] and Mn [10,11] containing metal oxides partly because of their relatively easy deactivation by sintering. Perovskite oxides have been investigated widely in an attempt to reduce the costs and increase the thermal stability [12–14]. Considering a great number of literatures on methane oxidation, there are few literature reports regarding the inhibition by the reaction products, viz., $CO_2$ and water [1,15], particularly on the transition metal oxide catalysts [16].

In this presentation, the Co/Mn mixed metal oxides were prepared by a sol–gel process, and then the Co–Mn supported catalysts, i.e., Co–Mn/MCM-41, and Co–Mn/Al-MCM-41, were prepared by homogeneous precipitation on hydrothermal stable mesoporous MCM-41. The methane oxidation activities were investigated on these catalysts in the presence of water vapor on these catalysts. A special

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attention was also paid to the thermal stability of these catalysts.

## 2. Experimental

### 2.1. Catalyst synthesis

The bare Co and Mn containing catalysts were prepared as follows [16]: A citrate solution was added to a mixed aqueous solution of $Mn(CH_3COO)_2{\cdot}4H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ under strongly stirring conditions. 2 mol/l aqueous ammonia was slowly added to the above solution until the pH value reached 6.5–7.0. Subsequently, the above transparent solution was water bathed at 95 °C for 10 h and then dried at 120 °C for 12 h to obtain a gel powder, which was further calcined at 450 °C in nitrogen for 1 h and then in oxygen for next 2 h. The available powders were ready for the oxidation activity measurements after being crushed and sieved. The obtained metal oxide samples are denoted as $CoO_x$, $MnO_x$, CoMn and $CoMn_2$, where the subscript number stands for the molar ratio of Mn and Co in the samples.

Siliceous MCM-41 (BET surface area is ca. 1010 $m^2$/g) and Al-MCM-41 (BET surface area is ca. 1000 $m^2$/g) previously obtained in our laboratory were used as catalyst supports, and the synthesis procedure was reported elsewhere [17]. The Co/Mn supported catalyst was prepared from a mixed aqueous solution of $Mn(CH_3COO)_2$ and $Co(NO_3)_2$ and urea through adding an appropriate amount of Al-MCM-41 or MCM-41 into the autoclave at 120 °C. The resulting samples were then obtained after being washed by distilled water, dried at 120 °C and calcined at 450 or 850 °C for 2 h. The powder samples from Al-MCM-41 and MCM-41 were denoted as Co–Mn/SiAl and Co–Mn/$SiO_2$, respectively, which both contained 10 wt.% Co–Mn oxides with the molar ratio of Co to Mn as being 1:1.

### 2.2. Characterization of the catalysts

X-ray powder diffraction (XRD) was conducted by means of a Rigaku D/max RB X-ray diffractometer using Cu Kα radiation. Scanning electron microscope (SEM) was taken on the JSM-6301F instrument with pre-coating samples with gold. The XPS data were acquired with a PHI 5300 ESCA spectrometer with an Al Kα 250 W X-ray source at a pass energy of 37.5 eV. Intensities were estimated by calculating the integral of each peak, and fitting the experimental curve to a Gaussian line of variable proportions. All binding energies (BE) were referred to the C 1s signal line at 284.9 eV.

### 2.3. Catalytic activity measurements

Catalytic activities were measured in a 10 mm i.d. quartz tubular reactor. The reaction mixture consisting of $CH_4$ (0.5 vol.%), $O_2$ (0–8 vol.%), water vapor (5 vol.%) and argon (balance gas) was passed continuously through a 0.1 g catalyst sample bed with a total feed gas flow rate of 100 ml/min. The inlet and outlet gas compositions were analyzed at the fixed reaction temperatures by on-line gas chromatograph (Shimadzu 14B) with a thermal conductivity detector using a 5A Molecular Sieve column and a Porapak Q column.

## 3. Results and discussion

### 3.1. Catalytic activities on the unsupported $CoMnO_x$ catalysts

Catalytic activities of methane oxidation was measured in the absence or presence of 5% water vapor, with 0.5% $CH_4$ and 1.5% oxygen in the feed stream. Methane conversion as a function of reaction temperature on the Co–Mn mixed oxides was shown in Fig. 1. It is observed that the reaction activities at low temperatures followed the order of $CoO_x > CoMn_2 >$ $CoMn > MnO_x$. For example, methane conversion at 500 °C in the absence of water vapor on $CoO_x$, $CoMn_2$, CoMn and $MnO_x$ was found to be 86, 70, 59 and 47%, respectively. When adding 5% water vapor into the reaction feed, methane conversion on $MnO_x$ was decreased from 47 to 41% at 500 °C, whereas only minor changes were observed on the $CoO_x$ catalyst under the similar conditions. However, it is interesting that a remarkable increase in methane conversion was observed on the CoMn and $CoMn_2$ catalysts when introducing water vapor into the feed gas. For example, methane conversion at 500 °C on $CoMn_2$ was increased from 70 to 83% by the presence of 5% water

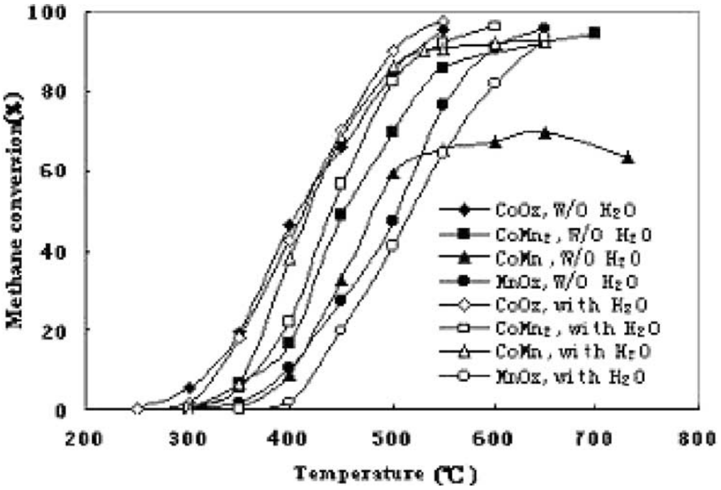

Fig. 1. Methane conversion on $CoO_x$ (diamond), $CoMn_2$ (square), CoMn (triangle) and $MnO_x$ (circle) in the absence (solid symbols) or presence (open symbols) of water vapor. Experimental conditions: 0.5% $CH_4$, 1.5% $O_2$, 5% water vapor and argon as balance gas, 0.1 g of catalyst.

vapor, and the value on CoMn was increased from 59 to 86% under the similar conditions. It was also noted that such a water enhancement effect became weak at high temperatures. Considering the serious deactivation on Pd catalysts at low temperatures below 450 °C reported by Burch et al. [6], such a water enhancement effect on methane oxidation indicates the Co and Mn containing materials are prominent for the methane oxidation reaction.

The structures of the Co and Mn containing mixed oxides were examined by XRD analysis as shown in Fig. 2. The results indicate that the main crystal phases after calcined at 850 °C were $CoCo_2O_4$ in $CoO_x$, and $Mn_2O_3$ in $MnO_x$. In the case of $CoMn_2$ and CoMn, the mixture of $MnCo_2O_4$ and $(CoMn)(CoMn)_2O_4$ (JCPDS 231237) was found on former sample and the mixture of $CoMn_2O_4$ and $CoCo_2O_4$ was found on the later one. For all these samples calcined at lower temperatures such as 450 °C, poorly crystalline structures were found as reported previously [16].

It is well known that oxygen content is essential for the methane oxidation reaction; therefore the effect of oxygen content on methane conversion over the Co–Mn catalyst was shown in Fig. 3. It is demonstrated that methane conversion was increased linearly with an increase in oxygen concentration in the feed gas below 1.5 vol.%, and then reached a plateau up to 8 vol.% oxygen. Hereafter, 1.5% oxygen was chosen for the following experimental tests.

The XPS technique was employed to characterize the catalyst samples in order to investigate the possible mechanism of the water effect. Table 1 shows the quantitative data of the XPS spectra on the CoMn sample after pretreatment at 450 °C in air or in the presence of 5% water vapor. The data of XPS spectra on the sample calcined at 700 °C in air were also tabulated

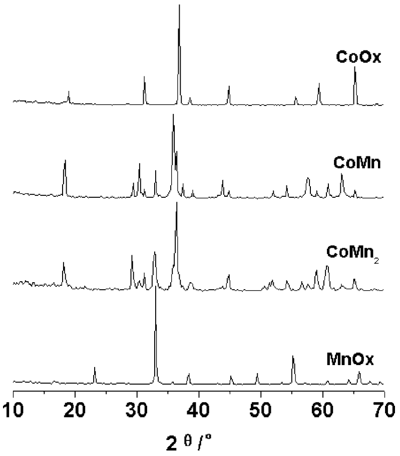

Fig. 2. XRD patterns of the various Co and Mn containing catalysts calcined at 850 °C.

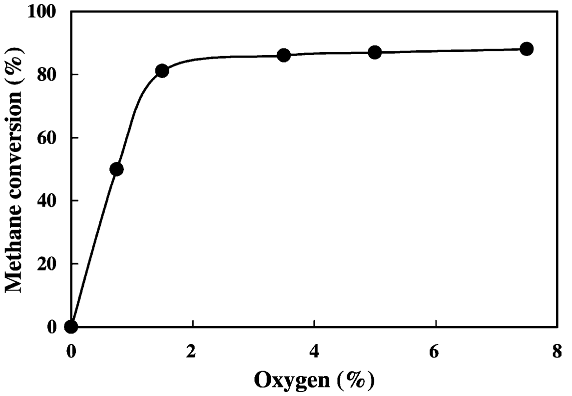

Fig. 3. Effect of oxygen concentration on the Co–Mn catalyst measured at 550 °C. Experimental conditions: 0.5% $CH_4$, 0–8% $O_2$, 5% water vapor and argon as balance gas, 0.1 g of catalyst.

in Table 1 [16]. As can be seen, O 1s spectra clearly exhibit two strong peaks at ca. 529.63 and 531.78 eV, the former peak can be ascribed to lattice oxygen in the form of $O^{2-}$ ion in the oxides, while the latter may relate with adsorbed non-stoichiometric oxygen species in the form of –OH or as $O^-$ [18] associated with surface defect oxides [19]. Co 2p at 779.98 eV and Mn 2p at 641.74 eV are very close to the values of 780.0 and 641.5 eV for $CoMn_2O_4$. It was obvious that after pretreatment in water vapor the intensity ratio of lower BE O 1s peak to higher BE O 1s peak became higher, and meanwhile the atomic ratio of Mn to Co became lower, indicating cobalt species could segregate onto the sample surface, which were possibly related with the increase in the activity of methane oxidation upon exposure to water vapor [16]. Further work to understand the enhancement mechanism may help to develop a type of water-resistant catalysts for methane combustion.

However, when the above Co–Mn catalyst was pretreated at a higher temperature such as 600 °C, the methane oxidation activity was remarkably decreased to 27% at 500 °C on the Co–Mn catalyst as compared to the value of 59% on the sample calcined at 450 °C as shown in Fig. 1. Further heating the above Co–Mn catalyst at 850 °C led to a remarkable decrease in the methane oxidation activity, e.g. 25% at 750 °C on the Co–Mn catalyst.

The deactivation is believed to be mainly due to the sintering of the active transition metal oxide components. Fig. 4 shows the SEM images of the CoMn sample calcined at 450 and 850 °C for 3 h, respectively. As expected, it can be seen that the spherical particles sizing around 60 nm were observed on the sample calcined at 450 °C. These particles become bigger, i.e., around 480 nm upon heating at 850 °C, and the aggregation between them was clearly evidenced, which was the possible reason for the deactivation of the Co–Mn catalyst at high temperatures.

On the other hand, the deactivation of the sample calcined at high temperatures was also related with a decrease in the intensity ratio of lattice oxygen to adsorbed oxygen as well as an increase in the Mn/Co ratio as show in Table 1.

### 3.2. Catalytic activities on the supported catalysts

In order to overcome the sintering problem, the high surface area siliceous MCM-41 and Al-MCM-41 materials were used to support the Co–Mn oxides for methane oxidation. Fig. 5 shows methane conversion as a function of reaction temperature for the CoMn/SiAl and CoMn/$SiO_2$ samples calcined at 450 °C. It can be seen that methane conversion was higher on CoMn/$SiO_2$ than that on CoMn/SiAl, i.e., 55% viz. 41% at 450 °C, while minor differences were observed above 500 °C for the two samples. It was also clear that the promoting effect of water vapor was remained on these two samples, whereas

Table 1
BE (eV) of the CoMn sample

| Catalyst pretreatment condition | O 1s[a] | $O_L/O_S$[b] | Mn $2p_{3/2}$ | Co $2p_{3/2}$ | Mn/Co[c] |
|---|---|---|---|---|---|
| At 450 °C in air | 529.63 (70.97%), 531.78 (29.03%) | 2.44 | 641.74 | 779.98 | 1.59 |
| At 450 °C in 5% $H_2O$ | 529.86 (77.74%), 531.89 (22.26%) | 3.49 | 641.79 | 780.04 | 0.75 |
| At 700 °C in air | 529.91 (54.24%), 532.34 (45.76%) | 1.18 | 641.68 | 780.4 | 1.81 |

[a] The number in the parenthesis is the molar ratio of the peak intensity.
[b] $O_L/O_S$ is the intensity ratio of lower BE O 1s peak to higher BE O 1s peak.
[c] Mn/Co is the atomic ratio of Mn to Co.

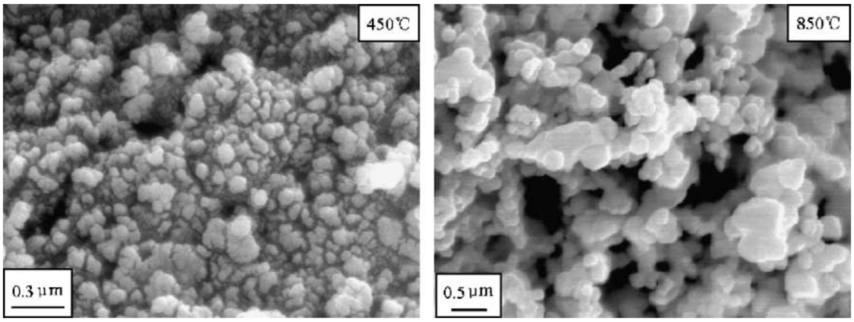

Fig. 4. SEM images of the CoMn sample calcined at 450 °C (left) and 850 °C (right).

the more pronounced effect was observed on the CoMn/SiAl sample, for example, methane conversion was increased from 66 to 91% on CoMn/SiAl upon introducing the water vapor into the feed gas; while the value was 70–77% on CoMn/$SiO_2$ under the similar conditions. As compared with the results on the CoMn sample in Fig. 1, it can also be seen that the reaction activities were improved on CoMn/SiAl in the absence or presence of water vapor, which might be related with the better dispersion of Co and Mn species on the high surface area support.

As shown in Fig. 6, no significant differences of the oxidation activities were found on the Co–Mn catalyst and the CoMn/SiAl catalyst when these two catalysts were calcined at 600 °C. However, when these samples were further calcined at a still higher temperature such as 850 °C, the methane conversion was decreased to 25% at 750 °C remarkably on the Co–Mn catalyst; while the methane conversion could reach 96% at 750 °C on CoMn/SiAl calcined at 850 °C. It is noted that after the sample being calcined at 850 °C for 2 h, a similar water enhancement effect was still found on the CoMn/SiAl sample. For example, methane conversion at 700 °C reached ca. 100% in the presence of 5% water vapor as compared to the value of 74% in the absence of water vapor. Comparing the lower catalytic activities of methane oxidation on the bare CoMn sample after calcinations at 850 °C, it was obvious that the thermal stability was improved after Co–Mn oxides being supported on an $Al_2O_3$–$SiO_2$ support.

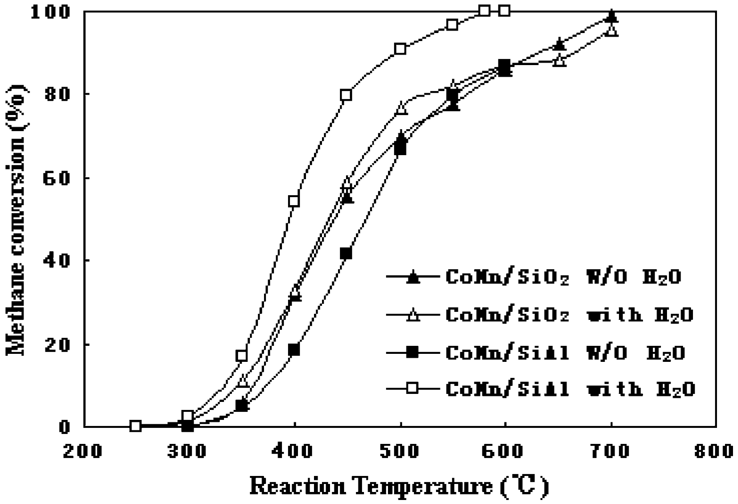

Fig. 5. Methane conversion on CoMn/$SiO_2$ and CoMn/SiAl calcined at 450 °C in the absence (solid symbols) and presence (open symbols) of water vapor. Experimental conditions: 0.5% $CH_4$, 1.5% $O_2$, 5% water vapor and argon as balance gas, 0.1 g of catalyst.

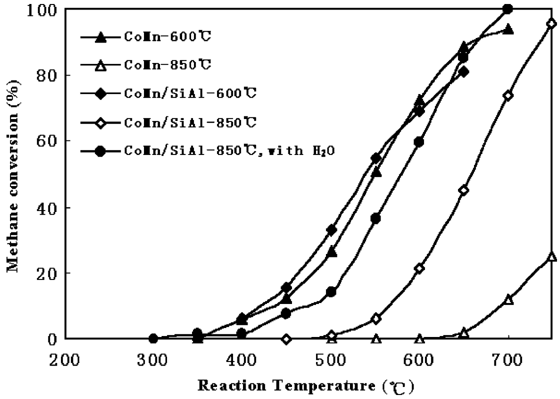

Fig. 6. Methane conversion on CoMn and CoMn/SiAl calcined at various temperatures in the presence (circle symbols) or absence of water vapor. Experimental conditions: 0.5% $CH_4$, 1.5% $O_2$, 5% water vapor and argon as balance gas, 0.1 g of catalyst.

### 3.3. *Catalytic activities on the supported catalysts versus time on stream*

The catalytic activities of methane oxidation at 500 °C in the presence of 5% water vapor versus reaction time on stream on both CoMn/SiAl and CoMn/$SiO_2$ were shown in Fig. 7. Both samples were decreased in the initial reaction period and then stabilized to an almost constant value. For example, methane conversion on CoMn/SiAl first slightly decreased from 96 to 89% after the reaction running for 1.5 h, and then the methane conversion remained at ca. 85% for the next 24 h. Methane conversion on CoMn/$SiO_2$ decreased from 86 to 68% after the reaction running for 3 h, and then the value remained at ca. 68% for the next 24 h. The two supported catalysts showed better stability as compared to that on the bare Co–Mn catalyst reported previously in our laboratory [16]. The results indicate that a better thermal stability in the presence of water vapor might be achieved by supporting Co–Mn mixed components onto a high surface area support. An attempt to further improve the thermal stability of the catalyst is in progress in our laboratory.

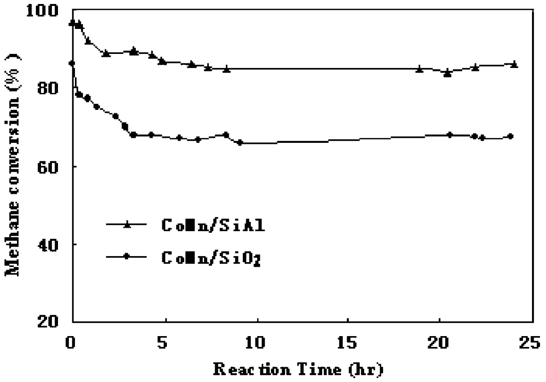

Fig. 7. Methane conversion versus reaction time on stream over the CoMn/SiAl and CoMn/$SiO_2$ catalysts. Experimental conditions: 0.5% $CH_4$, 1.5% $O_2$, 5% water vapor and argon as balance gas, 0.1 g of catalyst.

## 4. Conclusion

In conclusion, both supported and bare Co–Mn mixed oxides show a pronounced promoting effect of water vapor on the methane oxidation at lower reaction temperatures. Moreover, the supported Co–Mn mixed catalysts show a good thermal stability as compared to the pure Co–Mn mixed oxide catalyst at higher temperatures. Further investigations on the mechanism of the promoting effect of water vapor may be helpful to develop a catalyst with a much higher activity in the presence of water vapor.

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