A Novel Spinel-Type Co/Mn Catalyst for Methane Oxidation at Low Temperatures

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A Spinel-type Co/Mn catalyst prepared in a sol-gel process has been investigated for catalytic oxidation of methane. The reaction activity was significantly improved by either pretreating the catalyst in the presence of water vapor or addition of water vapor into the feed gas. XPS spectra show that the oxidation activity was closely related with surface Co species and the intensity ratio of lattice oxygen to adsorbed oxygen on the sample.

Catalytic combustion of methane has the potential to improve the energy efficiency and substantially reduce thermal nitric oxides by lowering combustion temperatures. Pd based noble metals have been reported as active catalysts for methane combustion. Besides high cost concerns, supported Pd catalysts usually deactivated by water vapor regardless of the type of the supports used, such as Pd/Al_2O_3,[1] Pd/SnO_2[2] and Pd/ZrO_2.[3,4] Most of the research works on metal oxides have been focussed on perovskite oxides[5] in an attempt to lower the costs and increase the thermal stability. Only few studies have been devoted to single oxides such as Au,[6] Ag,[7] Fe,[8] and Mn[9] containing metal oxides partly because of their relatively easy deactivation by sintering. On the other hand, considering a great number of literatures on methane oxidation, inhibition by the reaction products, viz., CO_2 and water has not been given much attention.[1]

In this paper, a novel spinel type catalyst was prepared by a sol-gel process to achieve good chemical homogeneity for spinel precursors, and a special attention was paid to the effect of water vapor on methane oxidation activities on the prepared catalysts. XPS was employed to analyze the possible reactive sites of the catalyst.

The Co/Mn oxides were synthesized as follows: 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.

Powder X-ray diffraction (XRD) data were collected on Bruker D8 Advance instrument with nickel-filtered Cu Kα radiation. The step scans were taken over the range of 2θ angels from 10 to 70° in steps of 0.02°, the intensity data for each step were collected for 5 s. Figure 1 shows the powder XRD patterns recorded for the sample calcined at different temperatures. The weak peaks partly overshadowed by the background profiles indicate a poor degree of crystallization below 450 °C. An increase in the calcination temperature led to a great increase in the peak intensity of the sample. The spinel structure of $CoMn_2O_4$ and $CoCo_2O_4$ was detected at the calcination temperature of 600 °C and 800 °C. The pattern at 600 °C shows a strong peak at $2\theta = 36.4°$, which is more close to the $CoCo_2O_4$ pattern; and the pattern at 800 °C shows a strong peak at $2\theta = 36.1°$, which is close to the $CoMn_2O_4$ pattern. Other possible manganese oxides, cobalt oxides and $CoMnO_4$ were excluded according to the JCPDS data-fitting program. In fact, it is possible that the mixture of $CoMn_2O_4$ and $CoCo_2O_4$ existed particularly at lower temperatures as detected by XRD, whereas $CoMn_2O_4$ are possibly dominant at high temperature.

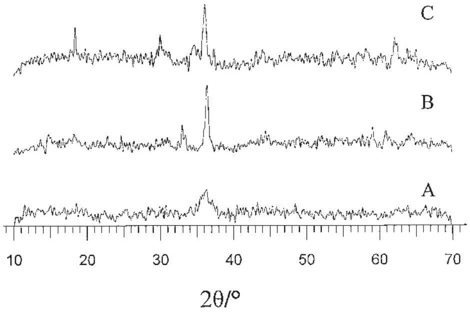

Figure 1. XRD patterns of the sample calcined at 450 °C (A), 600 °C (B) and 800 °C (C).

Catalytic activities were measured in a fixed bed quartz tubular reactor. A gas mixture of CH_4 (0.5% by volume), O_2 (1.5% by volume) and argon was passed continuously through a 0.1 g catalyst sample bed with a total flow rate of 100 ml min^{-1} of argon. The inlet and outlet gas compositions were analyzed by on-line gas chromatograph.

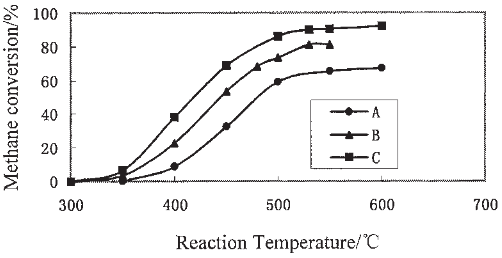

Figure 2. Methane conversion versus reaction temperatures on the Co/Mn spinel-type catalyst activated at 450 °C in pure Ar (A), in 5% H_2O in Ar (B), and activated at 450 °C in Ar and followed by indroducing 5% H_2O into the feed gas (C).

Methane conversion was investigated between 300 °C and 700 °C. No other reaction products besides water and carbon dioxide were detected during the reaction. The water effect on the reaction was presented in Figure 2. In the absence of water vapor, methane conversion was 65.6% at 550 °C, and the value reached 81.1% at 550 °C after the catalyst was pretreated in 5% H_2O/Ar (v/v) at 450 °C. It is noteworthy that even higher methane conversion of 90% was observed at 550 °C upon adding 5% H_2O by volume into the feed gas. Such a water enhancement effect was also observed for the sample calcined at 700 °C as shown in Figure 3, where methane conversions were 29.1% at 550 °C and 53.5% at 700 °C, and the values were 50.6% and 94.1% at 550 °C and 700 °C, respectively, after the sample was pretreated in 5% H_2O at 700 °C. Similarly, addition of 5% H_2O into the reaction stream will lead to 54.8% and 88.4% of methane conversion at 550 °C and 700 °C, respectively. Such a water promoting effect is unique on the spinel catalyst as compared to the deactivation on Pd-based catalysts for methane oxidation.[1–4,10]

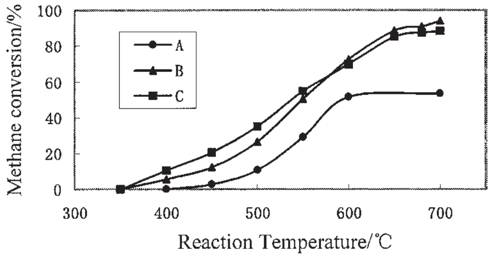

Figure 3. Methane conversion versus reaction temperatures on the Co/Mn spinel-type catalyst activated at 700 °C in pure Ar (A), in 5% H_2O in Ar (B), and activated at 700 °C in Ar and followed by indroducing 5% H_2O into the feed gas (C).

However, methane conversion was decreased from 88% to 75% in the first 1.5 h in the presence of 5% water vapor at 500 °C, and then no significant changes were found in the next 24 h. On the other hand, by comparing Figure 2 and 3, it can also be seen that methane conversion was decreased when the sample was calcined at much higher temperature (700 °C versus 450 °C). X-ray photoelectron spectra (XPS) data were collected on the sample calcined at 450 °C and 700 °C to differentiate surface compositions of the spinel catalyst pretreated at different temperatures. 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 C1s signal line at 284.9 eV.

The BE data of Mn $2p_{3/2}$, $Co2p_{3/2}$, O1s for the samples are discussed as follows. For the sample calcined at 450 °C, O1s spectra clearly exhibit two strong peaks at 529.63 eV (70.97%) and 531.78 (29.03%) (the number following BE value in parenthesis hereafter refers to molar ratio of the peak intensity). 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^{-11} associated with surface defect oxides.[12] 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 $CoMn_2O_4$.[13] The similar BE peak positions were also observed for the sample calcined at 700 °C, where O1s spectra split into two strong peaks at 529.91 (54.24%) and 532.34 (45.76%) eV. Obviously, the relative intensity of the two types of O1s peaks was significantly different. It is seen that the intensity ratio of lower BE O1s to higher BE O1s is 1.18 at the sample calcined at 700 °C as compared to the value of 2.44 for the sample calcined at 450 °C. Considering the different activities shown in Figure 2 and 3, it is postulated that the intensity ratio of the two O1s peaks is closely related with the methane oxidation activity, and the two type of O1s species together may be responsible for the oxidation activity at this temperature range.[5] In other words, increasing the relative molar ratio of the lattice oxygen species on the surface may decrease the light-off temperature of methane oxidation on the catalyst presented here.

Another determinant factor affecting the oxidation activity of the catalyst is possibly the Mn/Co ratio on the sample surfaces. The molar ratio of Mn to Co is 1.59 and 1.81 for the sample activated at 450 °C and 700 °C, respectively, and the ratio is 0.75 for the sample acitivated at 450 °C in the presence of 5% water vapor. It implies that relatively more cobalt species on the surface are possibly related with the active sites at lower reaction temperatures. Moreover, it seems that water vapor may further promote cobalt species segregation on the sample surface and hence increase the activity of methane oxidation. An attempt to introduce more Co species onto the surface and improve the thermal stability of the catalyst is in progress in our laboratory, and the result will be reported later.

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