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Promotional effect of Ce on the activity of In/W–ZrO_2 for selective reduction of NO_x with methane

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The Ce modified In/W–ZrO_2 catalysts were prepared by impregnation and mechanical mix method. Their activities for SCR of NO_x with methane were investigated. The activity of the In/W–ZrO_2 catalyst was enhanced by addition of Ce with both methods, while the promotional effect was more pronounced for catalyst prepared by mechanical mix method compared to impregnation method. The function of Ce was to improve the oxidation of NO to NO_2. The maximum NO_x conversion over the mechanical mixed catalyst can be stabilized at 74% at 450 °C in a dry gas flow and 37% at 500 °C in wet flow (24,000 h^{-1}). For the impregnated catalysts, Ce was found to compete with In to adsorb on strong acid site over W–ZrO_2 support and inhibited the formation of InO^+, which resulted in the lower activity of these catalysts than mechanical mixed catalysts.

KEY WORDS: Ce; In/W–ZrO_2; NO_x; selective catalytic reduction; methane.

1. Introduction

Methane is the most potential reductant used for selective catalytic reduction (SCR) of NO_x because methane is the main component of natural gas [1,2]. Indium catalysts such as In/zeolite [3,4] and In/SZ (sulphated zirconia) [5] have been reported to be effective catalysts for CH_4-SCR. In our previous research, we found that indium supported on tungstated zirconia (WZ) also showed high activity for CH_4-SCR [6], further more, WZ was more stable than that of zeolite and SZ in hydrothermal conditions [7,8], indicating that In/WZr could be a more practicable catalyst in real exhaust condition.

For the In/zeolite and In/SZ catalysts, their catalytic activity for CH_4-SCR can be successfully enhanced by adding additives, such as Co or Ce [5,9,10]. These additives favor the oxidation of NO to NO_2, which is a key intermediate for NO reduction. In this paper, the effect of additives, including Co, Mn and Ce, on the activity of the In/WZr catalyst was investigated. Among the three metals, only Ce showed significantly improvement on the activity of the In/WZr catalyst. The promotional effect of Ce on the activity of the In/WZr catalyst was further investigated, and the enhancement in activity was obviously different with various preparation methods.

2. Experimental

2.1. Catalyst preparation

WZr was prepared as described previously by impregnating $Zr(OH)_4$ (AR grade, Shanghai Agent Company, China) with an aqueous solution of ammonium paratungstate (AR grade, Tianjin Juneng Chemical Company, China). The support was dried at 120 °C overnight and calcined at 600 °C for 5 h. The tungsten contents in all catalyst were 10% by weight. In/WZr was prepared by incipient wetness impregnation of WZr with an aqueous solution of $In(NO_3)_3$ (AR grade, Sinopharm chemical reagent company, China). Ce modified In/WZr catalysts were prepared using two different methods, i.e. impregnation and mechanical mix. The indium loading in all catalysts were 1% by weight.

For impregnation method, the catalysts were prepared by impregnating Ce and In solution together with the WZr support. These samples were all dried at 120 °C overnight and calcined at 650 °C for 5 h. Indium nitrate and cerium nitrate (AR grade, Tianjin chemical reagent company, China) were used as the precursors of In and Ce, respectively. These catalysts are designated as ICe-aInWZr, where I refers as the impregnation preparation method and a refers as the weight content of Ce in catalysts. In addition, Co and Mn modified In/WZr catalysts were also prepared in this method. Cobalt nitrate (AR grade, Beijing modern eastern finechemical company, China) and manganous nitrate (50% solution, Beijing yili finechemical company, China) were used as the source of Co and Mn, respectively.

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Mechanical mixtures of In/WZr and CeO$_2$ were prepared by grinding CeO$_2$ together with In/WZr. These catalysts are designated as MCeaInWZr, where M refers as the mixing preparation method and a refers as the weight content of CeO$_2$ in catalysts. The CeO$_2$ used in the mechanical mixed catalyst was prepared by precipitate cerium nitrate solution with ammonia, it was then dried at 110 °C overnight and calcined in air at 650 °C for 5 h. The BET surface area, pore size, and pore volume of the obtained CeO$_2$ were 38 m^2/g, 9.9 nm, and 0.39 cm^3/g, respectively.

2.2. Catalytic activity measurement

The activity measurements were carried out in a fixed-bed quartz reactor (inner diameter 8 mm) using 0.25 g catalyst with 60–80 mesh. The feed gas mixture contained 1000 ppm NO or NO$_2$, 3000 ppm CH$_4$, 10% O$_2$, 0% or 10% H$_2$O and N$_2$ as the balance gas. The total flow rate of the feed gas was 100 mL/min, corresponding to a space velocity of about 24,000 h^{-1}. NO and NO$_2$ concentration were analyzed with a chemiluminescence NO/NO$_2$ analyzer (Thermal Environmental Instruments, model 42C), and CH$_4$ concentration was detected by gas chromatograph (Shimadzu GC 17A). The activity data were collected when the catalytic reaction substantially reached a steady-state condition for half an hour at each temperature.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained using a Rigaku D/max-RB diffractometer. Analyses were performed with Cu Target (40 KV and 100 mA); a typical scan speed was 6°/min with a step of 0.002° in the range from 20° to 70°. The BET surface area, pore size, and pore volume were measured by N$_2$ adsorption-desorption method using a NOVA 3200e analyzer.

X-ray photoelectron spectroscopy (XPS) measurements were conducted on a PHI15300/ESCA system with Al Ka radiation (1484.6 eV), calibrated internally by carbon deposit C1s binding energy (BE) at 284.6 eV.

3. Results and discussion

3.1. Characterization of the catalysts

Figure 1 shows the XRD patterns of In/WZr, ICeInWZr, and CeO$_2$ used in MCeInWZr catalysts. The CeO$_2$ appeared in MCeInWZr catalysts was in a cubic phase. The In/WZr and ICeInWZr catalysts were all in a combined phase of tetragonal and monoclinic ZrO$_2$. The diffraction lines corresponding to indium or tungsten containing phases were not observed over all of these catalysts. The small peaks in the XRD patterns of the ICe10InWZr catalyst can be identified belong to cubic CeO$_2$.

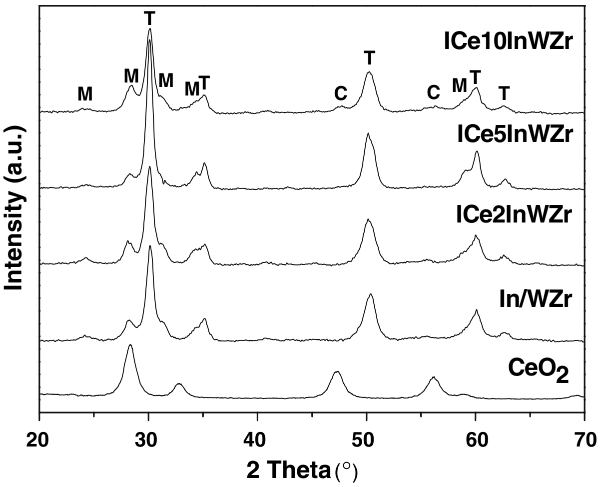

Figure 1. XRD patterns of In/WZr, ICeInWZr and CeO$_2$ used in MCeInWZr. T: tetragonal ZrO$_2$; M: monoclinic ZrO$_2$; C: cubic CeO$_2$.

The chemical states of Ce over the ICeInWZr catalysts were investigated by XPS and the results are shown in figure 2. The Ce 3d XP spectrum of the MCe10InWZr catalyst is also included in figure 2 as a reference for Ce^{4+}. The bands labeled u1 and v1 represent the 3d^{10}4f^1 initial electronic state corresponding to Ce^{3+}, while the peaks labeled u, u2, u3, v, v2 and v3 represent the 3d^{10}4f^0 state of Ce^{4+} ions [11,12]. In many literatures, the measurement of the area under the u3 peak relative to the total area under the Ce 3d spectra has been used to calculate the fraction of Ce in the +4 state [11]. For the ICe2InWZr and ICe5InWZr catalyst, no u3 peak was found in its XPS spectra, while v1 and u1 peaks for Ce^{3+} were very high. These facts suggested that Ce in these two catalysts were mainly in the valence state of +3, even though Ce^{3+} was usually unstable under an oxidative treatment at 650 °C. For the ICe10InWZr

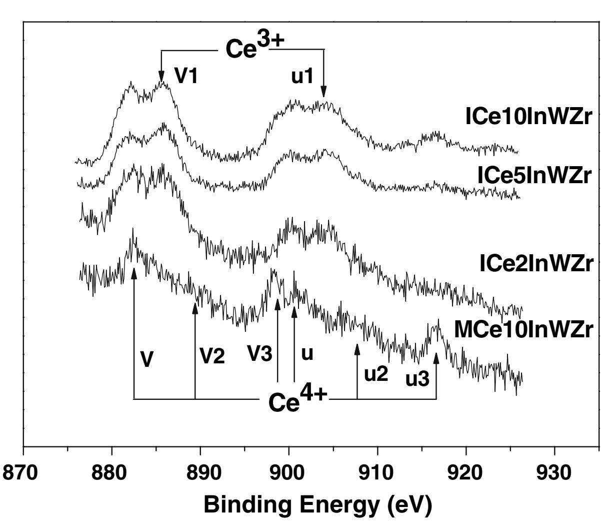

Figure 2. Ce3d XPS spectras for MCe10InWZr, ICe2InWZr, ICe5InWZr, and ICe10InWZr.

Table 1
In3d$_{5/2}$ binding energies derived from XPS

Samples	In3d$_{5/2}$ (eV)
In/WZr	445.2
MCe10InWZr	445.2
ICe2InWZr	445.0
ICe5InWZr	444.8
ICe10InWZr	444.8
In$_2$O$_3$	444.7[a]

[a] From reference [16].

catalyst, a small u3 peak belonging to Ce^{4+} was detected besides the big v1 and u1 peaks for Ce^{3+}. This result suggested the appearance of CeO$_2$ in the ICe10InWZr catalyst, which was consistent with the XRD result. It is known from literature that unstable Co^{2+} or Mn^{3+} can be stabilized by the strong acid site over ZSM-5 or SZr support [13,14]. The Ce^{3+} in these ICeInWZr catalysts may indicate the interaction of Ce atoms with the strong acid sites over the WZr support. It is noticed that the formation of InO$^+$, the active site for CH$_4$-SCR, was also attributed to the interaction between In atoms and the strong acid sites over the WZr support [4,15]. Therefore, there may be a competition between In and Ce atoms for adsorbing on the strong acid sites over the WZr support. This assumption can be confirmed by the In3d$_{5/2}$ binding energies listed in table 1. The binding energy of In3d$_{5/2}$ for In/WZr was 445.2 eV, which was 0.5 eV higher than the value for the In$_2$O$_3$ bulk phase [16]. This result suggested the formation of InO$^+$ species over In/WZr catalyst [6,15]. It can be seen that the binding energy of In3d$_{5/2}$ generally shifted to lower values with the increase of Ce loadings in ICeInWZr catalysts, suggesting that Ce in ICeInWZr catalyst inhibited the formation of InO$^+$.

3.2. CH$_4$-SCR activity test

The effect of Co, Mn, and Ce on the activity of In/WZr catalyst is presented in figure 3. The addition of Co and Mn caused a pronounced decrease in the NO conversion activity of the In/WZr catalyst; on the other hand, the activity of the In/WZr catalyst was remarkably enhanced when Ce was added. The oxidation capacity of Co and Mn oxides were much stronger than that of Ce oxide. It has been reported that Co and Mn oxides were not only active for the conversion of NO to NO$_2$ but also very active for the oxidation of CH$_4$ [17–19]. However, Ce oxide was only active for the conversion of NO to NO$_2$, but its capacity for CH$_4$ oxidation was very poor [17]. These facts suggested that the decrease in activity for conversion of NO by addition of Co and Mn into the In/WZr catalyst might be due to their influence on the activation of CH$_4$. In further investigations, the promotional effect of Ce on the NO$_x$ conversion activity of In/WZr catalyst was compared for two preparation methods: impregnation and mechanical mix.

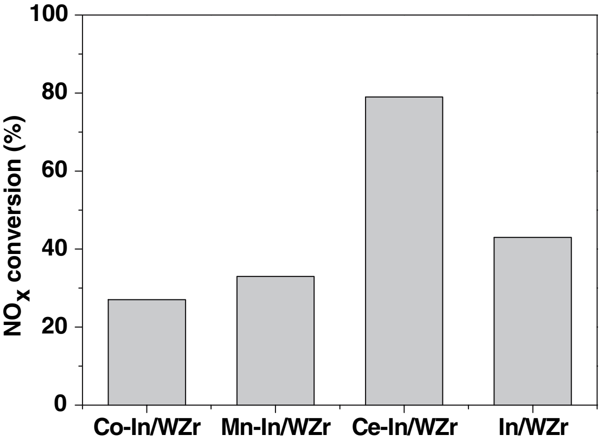

Figure 3. NO$_x$ conversion activities of Co, Mn and Ce modified In/WZr catalysts at 450 °C. The contents of Co, Mn and Ce were 2 wt%. Reaction conditions: 1000 ppm NO, 3000 ppm CH$_4$, 10% O$_2$, N$_2$ as balance; GHSV = 24,000 h^{-1}.

Figure 4 shows the NO$_x$ conversion activities of the Ce/WZr, In/WZr and ICeInWZr catalysts. The activity of Ce/WZr for CH$_4$-SCR was very low, it means that Ce species over the WZr support was not active for the reduction of NO$_x$. However, addition of Ce to In/WZr by co-impregnation can significantly influence the activity of the In/WZr catalyst. The maximum NO$_x$ conversion activity was greatly improved from 40% to 80% with the increase of Ce loading from 0% to 2%. Further increasing the Ce loading led to a decrease of the activity and when Ce loading reached 10%, the NO conversion was even lower than that of the In/WZr catalyst above 450 °C. Therefore, the optimal Ce loading for provided maximum promotion of CH$_4$-SCR

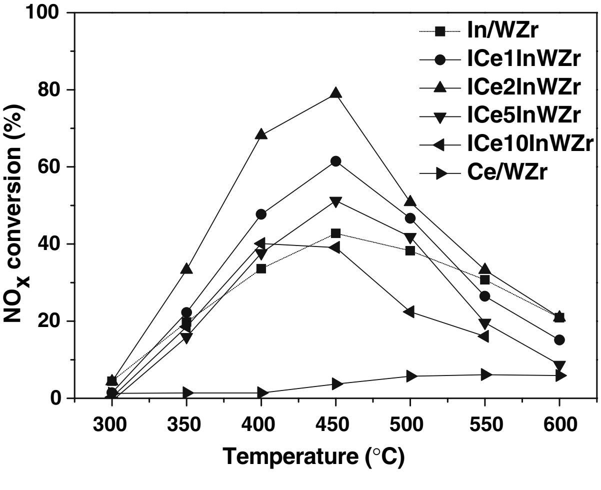

Figure 4. NO$_x$ conversion activities of In/WZr, Ce/WZr and ICeInWZr with various Ce loadings. Ce content in Ce/WZr was 2 wt%. Reaction conditions: 1000 ppm NO, 3000 ppm CH$_4$, 10% O$_2$, N$_2$ as balance; GHSV = 24,000 h^{-1}.

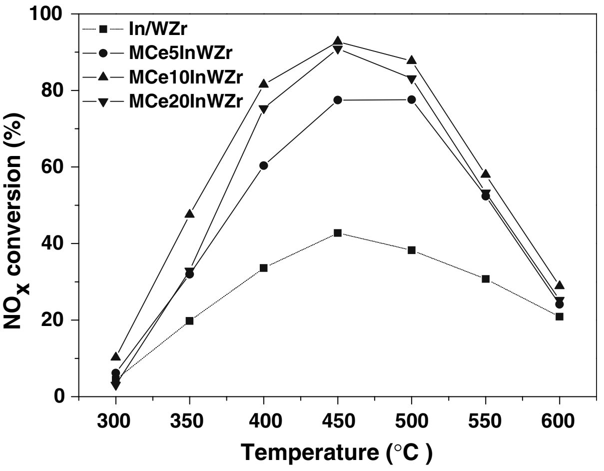

Figure 5. NO$_x$ conversion activities of MCeInWZr catalysts with various contents of CeO$_2$. Reaction conditions: 1000 ppm NO, 3000 ppm CH$_4$, 10% O$_2$, N$_2$ as balance; GHSV = 24,000 h^{-1}.

reaction was 2%. Ce can improve the activity of In/WZr catalyst by enhancing the conversion of NO to NO$_2$, while loading of Ce on WZr inhibited the formation of InO$^+$ species simultaneously (as shown in XPS result). With the increase of Ce loading, the inhibition effect became more and more serious, as a result, the activity of the ICeInWZr catalysts decreased with high Ce loadings.

Figure 5 shows the NO$_x$ conversion activity over MCeInWZr catalysts with CeO$_2$ contents ranging from 5% to 20%. All of the MCeInWZr catalysts showed improved activity than In/WZr catalyst in the entire temperature range, and the optimal CeO$_2$ content for the maximum promotion of activity was 10%. The maximum NO$_x$ conversion activity over MCe10InWZr reached 92% at 450 °C and more than 50% NO$_x$ conversions were obtained in the temperature of 350–550 °C. The CeO$_2$ particles in the MCeInWZr catalyst would not influence the textural structure of In/WZr and so MCeInWZr could reach much high NO$_x$ conversion ratio to compare with the ICeInWZr catalyst shown in figure 4.

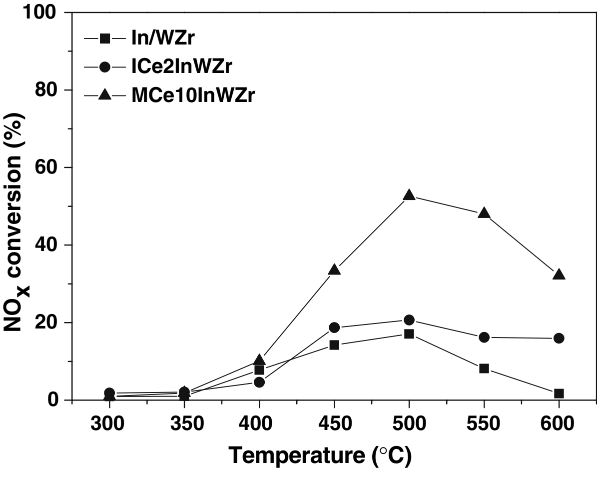

Figure 6. Effect of water vapor on the activities of In/WZr, ICe2InWZr, MCe10InWzr. Reaction conditions: 1000 rpm NO, 3000 rpm CH$_4$, 10% of O$_2$, 10% H$_2$0, N$_2$ as balance GHSV = 24,000 h^{-1}.

Influence of water vapor on the NO$_x$ conversion activities of In/WZr, ICe2InWZr, MCe10InWZr are shown in figure 6. The addition of 10% water vapor to the feed gas reduced the catalytic activities of all of the three catalysts, and the maximum NO$_x$ conversion temperatures over the three catalyst all shifted from 450 °C to 500 °C. This deactivation was probably due to the adsorption of H$_2$O on InO$^+$ sites and forming inactive In(OH)$_2{}^+$ species [6]. The maximum NO$_x$ conversion over In/WZr and ICe2InWZr decreased to 17% (from 43%) and 20% (from 79%), respectively. In comparison, MCe10InWZr showed much higher activity than that of In/WZr and ICe2InWZr. The maximum conversion for the catalyst could still reach 52%. Therefore, the MCe10InWZr catalyst exhibited a higher resistance against H$_2$O than other catalysts.

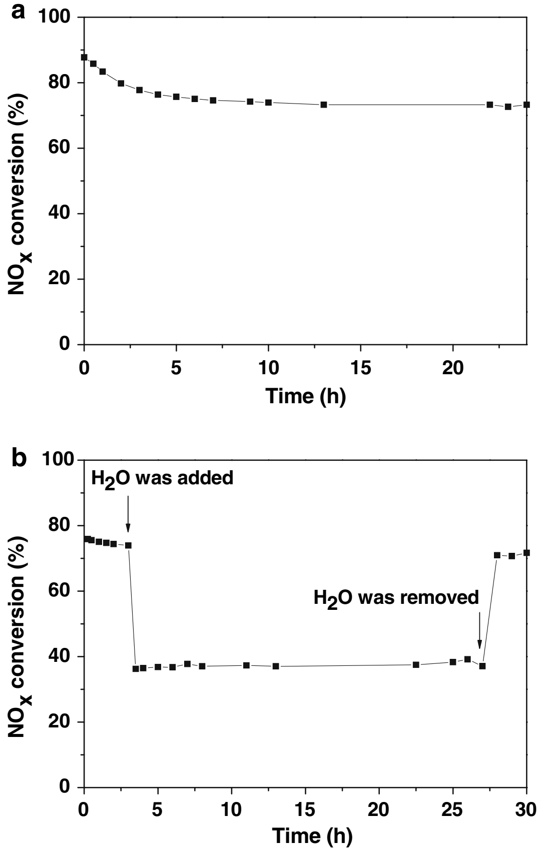

Figure 7. (a) Stability of MCe10InWZr catalyst at 450 °C; (b) effect of H$_2$O on the performance of MCe10InWZr catalyst at 500 °C. Reaction conditions: 1000 ppm NO, 3000 ppm CH$_4$, 10% O$_2$, 0% or 10% H$_2$O, N$_2$ as balance; GHSV = 24,000 h^{-1}.

Since MCe10InWZr catalyst showed much higher NO$_x$ conversion activity than ICe2InWZr, the stability of MCe10InWZr in the absence and presence of water vapor was further investigated and the results were shown in figure 7. Under a dry flow, the NO$_x$ conversion activity over MCe10InWZr was generally decreased from 90% to 74% in the testing process of first 10 h, and then fixed at 74% in the next 14 h. It needs to be emphasized that the decrease of activity under long-term test was also found over In/ZSM-5 catalyst [2]. After 24 h stability test, experiment temperature was increased from 450 °C to 500 °C, it can be seen from figure 7a that the NO$_x$ conversion can still stabilized at about 74%. When 10% water vapor was added, the NO$_x$ conversion was decreased to 37% immediately, and absolutely unchanged in the next 24 h. After removing the water vapor the catalyst recovered its activity. It can be seen that the stationary NO$_x$ conversion of 37% over the MCe10InWZr catalyst was still much higher than ICe2InWZr showed in figure 6.

4. Conclusion

In this paper, Ce was introduced into the In/WZr catalyst by two methods: impregnation and mechanical mix. Both methods showed remarkably promotional effects on the activity of the In/WZr catalyst for CH$_4$-SCR. The function of Ce was to improve the oxidation of NO to NO$_2$. The optimum loading of Ce species prepared by impregnation and mechanical mix method prepared catalysts were 2% (Ce) and 10% (CeO$_2$), respectively. The catalyst prepared by mechanical mix method showed much higher activity for NO$_x$ conversion than that of the catalyst by impregnation in both dry and wet flow. For impregnated Ce–In/WZr catalyst, Ce would compete with In to adsorb on the strong acid site over WZr support. This fact inhibited the formation of InO$^+$ and resulted in a inferior activity to the catalyst by mechanical mix method.

Acknowledgments

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