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Partial oxidation of methane by O_2 and N_2O to syngas over yttrium-stabilized ZrO_2

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Abstract

Catalytic partial oxidation of methane to synthesis gas over ZrO_2 and yttrium-stabilized zirconia (YSZ) is studied using O_2 and N_2O as oxidants. ZrO_2 is much more active than YSZ in oxidation of methane with N_2O. In contrast, YSZ is significantly more active than ZrO_2 when O_2 is used as an oxidant. The presence of O_2 does not influence the rate of N_2O decomposition over ZrO_2 and YSZ, while the presence of H_2O in the system decreases N_2O conversion significantly. O_2 and N_2O are activated at different active sites. Y-induced oxygen vacancies are active for O_2 activation, whereas oxygen co-ordinatively unsaturated Zr cations (Zr-CUS) located at corners, edges, steps and kinks are responsible for N_2O activation. These sites are also capable of dissociating H_2O, resulting in competition between H_2O and N_2O. As compared with N_2O, molecular O_2 is easier to be activated over YSZ and ZrO_2.

Keywords: Oxygen vacancies; Partial oxidation of methane; Yttrium-stabilized ZrO_2; N_2O

1. Introduction

The conversion of methane to value-added products has attracted a lot of attention. While study continues on oxidative coupling [1,2] and selective oxidation [3] processes, significant attention has been directed to the production of synthesis gas [4–6] as well as the application of oxidants other than oxygen [7]. Synthesis gas is conventionally produced via methane steam reforming. Catalytic partial oxidation of methane to synthesis gas (CPOM) is particular attractive because of its mild exothermic reaction heat and the suitable H_2/CO ratio for downstream processes, such as methanol and Fischer–Tropsch syntheses. Metal catalysts, e.g. Ni, Co and noble metals (Pt, Rh), are very active for CPOM. However, the stability of metal catalysts is still a concern, despite intensive investigation of CPOM over metallic catalysts [8,9]. As we discussed previously [10], metallic catalysts are suffering from deactivation due to sintering and metal loss via the formation of volatile metal oxides [11]. Study on CPOM over thermal stable oxides is rather limited [12–14]. CPOM over ZrO_2-based oxides has been intensively studied in our laboratory [10,13–17]. Yttrium-stabilized zirconia (YSZ) appears to be a promising catalyst for CPOM [12], despite its insufficient reforming activity, which can be compensated with a reforming catalyst in a dual bed system, as proposed previously [10]. Based on the results of isotopic oxygen exchange and transient experiments under the reaction conditions, it was proposed that CPOM over ZrO_2 and YSZ proceeds via a surface Mars–van Krevelen mechanism [16]. TPD on ZrO_2 and YSZ revealed the formation of two types of oxygen from N_2O, desorbing at 370 and 600 °C, respectively. In contrast, oxygen is only able to form more thermally stable species, desorbing at 600 °C [17].

In the present work, we investigate the activation of N_2O and O_2 on YSZ and ZrO_2 during oxidation of methane with N_2O and O_2 as reactants.

2. Experimental

2.1. Catalysts

Catalysts ZrO_2 and YSZ were prepared by calcining zirconia and yttrium-stabilized zirconia (14 wt.% Y_2O_3 in ZrO_2, TOSOH, Japan) in air at 900 °C for 15 h, respectively, resulting in BET surface areas of 15.4 and 13.7 m^2/g for ZrO_2 and YSZ,

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respectively. The YSZ sample used in this study is identical to the catalyst YSZ14A described in our previous work [14]. Only traces of TiO_2 and HfO_2 were detected in the bulk, whereas no inorganic contamination could be detected in the outermost layer by low-energy ion scattering [14].

2.2. Catalytic measurement

Catalytic performance of the catalysts was examined in a fixed-bed reactor made of an alumina tube (inner diameter, 4 mm; length, 450 mm) at atmospheric pressure. A mixture of 0.3 g catalyst and 0.3 g α-Al_2O_3 particles (0.3–0.6 mm) was positioned in the isothermal zone of the reactor by quartz wool. The mixture of reactants, CH_4 and O_2 or N_2O, were diluted with helium (CH_4:O_2:He = 2:1:14 or CH_4:N_2O:He = 2:2:13), and total flow rate was 170 ml/min (STP); GHSV was about $6 \times 10^3\ h^{-1}$.

On-line gas chromatography with Carboxan 1000 and Haysep N columns was used to analyze the effluent gas from the reactor. N_2 was used as an internal standard in order to calculate the flow rate of the compounds (N) in mol/s. Conversions (X) and yields (Y) were calculated according to:

$$X_{CH_4} = \frac{N_{CH_4^{in}} - N_{CH_4^{out}}}{N_{CH_4^{in}}}; \qquad X_{O_2} = \frac{N_{O_2^{in}} - N_{O_2^{out}}}{N_{O_2^{in}}};$$

$$X_{N_2O} = \frac{N_{N_2O^{in}} - N_{N_2O^{out}}}{N_{N_2O^{in}}}$$

$$Y_{CO} = \frac{N_{CO^{out}}}{N_{CH_4^{in}}}; \qquad Y_{CO_2} = \frac{N_{CO_2^{out}}}{N_{CH_4^{in}}}; \qquad Y_{H_2} = \frac{N_{H_2^{out}}}{2N_{CH_4^{in}}};$$

$$Y_{H_2O} = \frac{N_{H_2O^{out}}}{2N_{CH_4^{in}}}$$

3. Results

3.1. Oxidation of CH_4 by N_2O

Catalytic partial oxidation of methane was carried out over ZrO_2 and YSZ catalysts using N_2O as oxidant. Methane and N_2O conversions are shown in Fig. 1. The conversions of N_2O and CH_4 increase with reaction temperature for both catalysts. Clearly, ZrO_2 is more active than YSZ catalysts, although both catalysts have similar surface areas. CO, CO_2, H_2 and H_2O are major products, as reported for CPOM over ZrO_2-based oxides previously [13]. Only traces of C_2-hydrocarbons were detected. Molecular oxygen was never detected in the effluent.

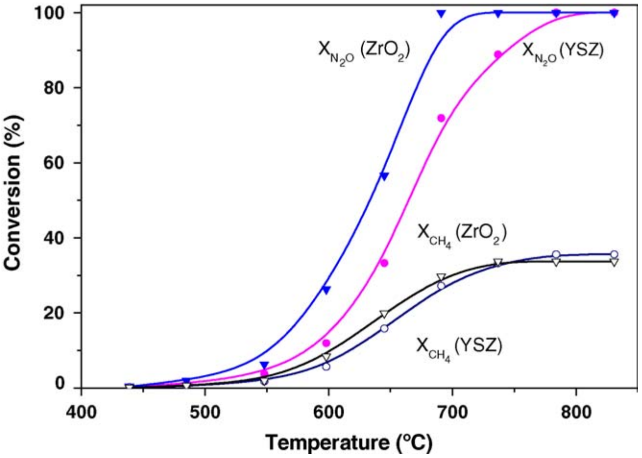

Fig. 1. Catalytic activity as a function of reaction temperature during CPOM over ZrO_2 and YSZ catalysts using N_2O as an oxidant. Catalyst, 0.3 g; mixture of reactants, N_2O:CH_4:He = 2:2:13 and total flow rate, 170 ml/min (STP).

3.2. Oxidation of CH_4 by O_2

Fig. 2 shows the conversions of methane and oxygen over ZrO_2 and YSZ conversions increase significantly with increasing reaction temperature below 700 °C. In contrast, only minor change is observed in methane conversion at temperatures above 700 °C due to oxygen exhaustion. Comparing with ZrO_2, YSZ is obviously much more active when O_2 is used as an oxidant, although they have comparable surface areas. CPOM over YSZ with O_2 instead of N_2O results in lower selectivity to CO and H_2. In contrast, over ZrO_2 almost identical product distributions are observed with both oxidants.

3.3. Activation of oxidant

Fig. 3 shows the influence of the addition of O_2 on both the decomposition rate of N_2O as well as conversions of N_2O and CH_4 during CPOM with N_2O over ZrO_2 and YSZ at 600 °C. ZrO_2 is always more active for N_2O conversion than YSZ, independent of the presence of methane. When methane is absent, N_2O conversion is not influenced by addition of O_2 for both ZrO_2 and YSZ (curves (b and d)). The presence of methane increases N_2O conversion when no oxygen was present in the reactant mixture (curves (a and c)). However, addition of O_2 results in that the N_2O conversion drops and eventually equals the N_2O decomposition in the absence of CH_4. In contrast, methane conversion increases significantly with increasing oxygen partial pressure.

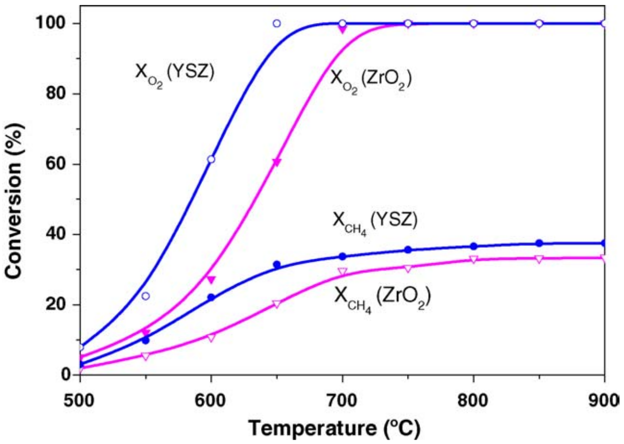

Fig. 2. Comparison of catalytic performance of ZrO_2 and YSZ during CPOM with O_2. Catalyst, 0.3 g; mixture of reactants, O_2:CH_4:He = 1:2:14 and total flow rate, 170 ml/min (STP).

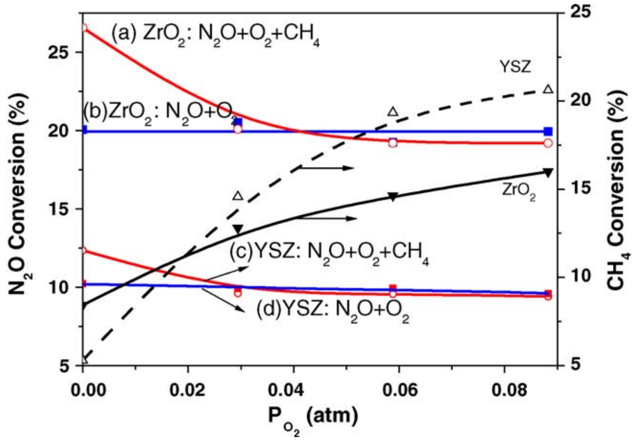

Fig. 3. Influence of partial pressure of O_2 on N_2O conversion over ZrO_2 and YSZ at 600 °C. (a) and (c) In the presence of CH_4 during CPOM ($N_2O:O_2:CH_4:He = 3:(0–1.5):2:14$); (b) and (d) in the absence of CH_4 during N_2O decomposition ($N_2O:O_2:He = 3:(0–1.5):14$). Total flow rate 170 ml/min.

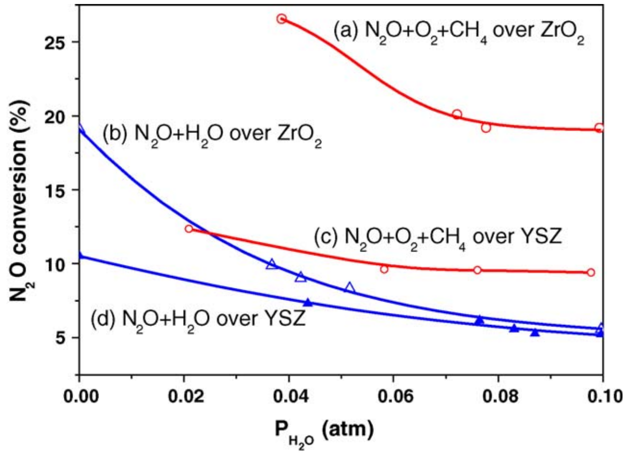

Fig. 4. N_2O conversion over ZrO_2 and YSZ at 600 °C as a function of partial pressure of H_2O, which is (a) and (c) produced by oxidation of CH_4; (b) and (d) added to the feed. Total flow rate 170 ml/min.

N_2O conversion over ZrO_2 and YSZ as a function of the concentration of H_2O in the reactor is shown in Fig. 4. As shown by curves (b) and (d), N_2O conversion decreases significantly with increasing concentration of H_2O added to the reaction mixture. Curves (a) and (c) correlate N_2O conversion with the concentration of H_2O in the exit of the reactor. For both ZrO_2 and YSZ, N_2O conversion decreases when more water is produced during CPOM. The effect of water on ZrO_2 is much more pronounced as compared to YSZ.

4. Discussion

Fig. 2 shows that YSZ is much more active than ZrO_2 for CPOM when O_2 is used as oxidant. It is well known that oxygen vacancies are created in ZrO_2 by doping Y_2O_3. Improvement of catalytic performance has been related to the presence of vacancies in many oxidation processes over mixed oxides, e.g. the oxidation of propane over YSZ [18] and oxidative coupling of methane over Y_2O_3-CaO [19]. It was proposed previously that CPOM over ZrO_2 and YSZ proceeds via a Mars–van Krevelen mechanism [16]. Methane is oxidized by surface lattice oxygen ions in the surface of ZrO_2 and YSZ. The positive effect of doping Y_2O_3 in ZrO_2 was attributed to an increase in concentration of oxygen vacancies, inducing rapid replenishment of the extracted oxygen ions via fast activation of molecular oxygen at Y-induced oxygen vacancies on the surface and via rapid bulk-diffusion of oxygen ions.

However, ZrO_2 appears to be more active than YSZ in the oxidation of methane with N_2O (Fig. 1) as well as in N_2O decomposition (Fig. 3). Moreover, as shown in Fig. 3, increasing concentration of oxygen in the feed did not affect the N_2O decomposition rate over both YSZ (curve (d)) and ZrO_2 (curve (b)). These results indicate that O_2 and N_2O are activated at different active sites. This agrees well with our previous work [17], proving that structural defects, i.e. oxygen co-ordinatively unsaturated Zr cations (Zr-CUS) located at corners, edges, steps and kinks, are active sites for N_2O decomposition. In contrast, oxygen vacancies are active for O_2 activation. The effect of doping ZrO_2 with Y_2O_3 is attributed to a decrease in the number of the Zr-CUS (active sites for N_2O activation) due to replacement of Zr cations by Y cations at corners, steps, kinks and edges of the crystallites.

During oxidation of methane with N_2O, addition of O_2 in the mixture of reactants results in a decrease in N_2O conversion (Fig. 3). A similar phenomenon was observed in oxidative coupling of methane over SrO and Li/Bi_2O_3 by Anshits et al. [20] and was interpreted in terms of competitive activation of N_2O and O_2 at identical active sites. This, however, disagrees with our conclusion above. The effect of water produced during the reaction was neglected, however, and may be responsible for the disagreement, as will be discussed next.

Fig. 4(b and d) demonstrates a significant effect of H_2O on the rate of decomposition of N_2O. As discussed above, Zr-CUS are active sites for N_2O activation, which are also able to dissociate molecular H_2O, forming surface OH group [21]. Curves (a) and (c) in Fig. 4 demonstrate that water formed by the CPOM reaction may well be responsible for decreasing N_2O conversion. The effects are even significantly smaller as compared to addition of water, which may be due to obvious difference in the water concentration profile through the reactor when water is added or formed, respectively.

On the other hand, according to the reaction mechanism the intrinsic oxygen vacancies ($Zr'_{Zr} - V_O^{\bullet\bullet} - Zr'_{Zr}$) are formed on low index planes via extracting surface lattice oxygen ions by methane during CPOM [16]. It was also demonstrated previously [17] that these formed oxygen vacancies can be eliminated also by exposing to N_2O at temperatures above 300 °C, indicating that these oxygen vacancies are active sites for N_2O decomposition as well. The fact that no competition was observed between N_2O and O_2 indicates that the contribution of N_2O decomposition via methane-induced oxygen vacancies is negligible.

Addition of oxygen strongly increases the conversion of methane as shown in Fig. 3, especially on YSZ. Furthermore, comparison of Figs. 1 and 2 demonstrates that CPOM with O_2

gives much higher rates than with N_2O. Moreover, it is remarkable that no molecular oxygen remains in the effluent of methane oxidation with N_2O at temperatures from 500 to 850 °C (Fig. 1), although the level of N_2O decomposition is significant (Fig. 4(b and d)). These observations indicate that O_2 is easier to be activated than N_2O over both ZrO_2 and YSZ. This finding is remarkable, given the fact that N_2O is thermodynamically unstable.

5. Conclusion

Different active sites are operative for N_2O and O_2 activation, respectively, on ZrO_2 and YSZ. Molecular oxygen can be dissociatively activated at Y-induced oxygen vacancies in YSZ. In contrast, Zr-CUS located at corners, edges, steps and kinks are responsible for N_2O activation, whereas they are not active for O_2 activation. YSZ is more active than ZrO_2 in oxidation of methane with O_2, surprisingly the opposite is true when N_2O is used as an oxidant. Replacement of Zr cations by Y cations at corners, steps, edges and kinks, is responsible for the decrease in reactivity of N_2O when Y_2O_3 is added in ZrO_2. The presence of H_2O in the system decreases N_2O conversion via competitive adsorption with N_2O at the active sites, i.e. edges and corners. Moreover, O_2 reacts faster than N_2O over YSZ and ZrO_2 during catalytic partial oxidation of methane.

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