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Effect of surface OH groups on catalytic performance of yittrium-stabilized ZrO_2 in partial oxidation of CH_4 to syngas

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Abstract

The influence of water and surface hydroxyl groups on the catalytic performance of yittrium-stabilized ZrO_2 (YSZ) in the partial oxidation of methane to synthesis gas was investigated using FT-IR as well as steady state kinetic experiments. Besides physically adsorbed water, terminal OH groups, bi-bridging and tri-bridging OH groups exist on the surface of YSZ. Oxidation of formaldehyde to formate occurs on the low index planes rather than at the structural defects, *i.e.* corners, edges, kinks and steps. Adsorbed formaldehyde is attacked by neighboring lattice oxygen ions in low index surface planes to form surface formate. Neighboring hydroxyl groups and hydrogen-bonded molecular water on the surface of YSZ suppress this nucleophilic attack.

In short, the presence of water on the surface stabilizes adsorbed formaldehyde, decreasing the rate of oxidation to formate; this effect is responsible for the increase in selectivity to H_2 and CO when water is added during CPO.

Keywords: Partial oxidation of methane; Yittrium-stabilized ZrO_2; Surface hydroxyl groups; Formaldehyde

1. Introduction

Methane is a predominant component of natural gas, which is forecasted to outlast oil by a significant margin [1]. Transportation problem with methane and the increasing oil price have led to world-wide research in converting methane into easily transportable value-added products, such as ethylene, aromatics, oxygenates and liquid hydrocarbon fuels. Direct and indirect processes are known for methane utilization. Direct conversion of methane to more valuable and readily transportable products, *e.g.* methanol, formaldehyde, is not attractive because of the low yields obtained so far. Therefore, much attention has been paid to the indirect routes *via* synthesis gas (CO and H_2), which can be further converted to desired products. Catalytic partial oxidation of methane to synthesis gas (CPOM) is an attractive process for conversion of natural gas to synthesis gas, as an alternative to steam reforming of methane.

CPOM over hardly reducible oxides, for example, ZrO_2 and yittrium-stabilized ZrO_2 (YSZ), was reported in our previous work [2–6]. A Mars–van Krevelen mechanism was proposed for CPOM over ZrO_2 and YSZ, in which methane is oxidized by surface lattice oxygen ions. Gas-phase oxygen is dissociated and activated at surface defects that are formed by doping Y_2O_3 in ZrO_2. The consumed lattice oxygen in the surface is replenished *via* bulk diffusion [5]. Methane is activated and oxidized to reaction intermediates on the catalyst surface, *i.e.* adsorbed formaldehyde and formate. Formaldehyde decomposes to CO and H_2, while surface formate decomposes to either CO_2 and H_2 or CO and H_2O *via* dehydrogenation and dehydration, respectively [3]. In this work, transformation of formaldehyde to surface formate is investigated using *in situ* IR. Especially, the effects of surface hydroxyl species on the oxidation of formaldehyde to formate, and consequent effects on the selectivity in CPOM have been studied.

2. Experimental

2.1. Catalysts

Catalyst YSZ was prepared by calcining commercial powder of zirconia stabilized with 12 wt% Y_2O_3 (TOSOH, Japan) at 900 °C, which is identical to the catalyst YSZ12A described in our previous work [4]. After calcination in air for 15 h, the BET

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surface area was 15.4 m^2/g. More details about the characterization of the catalyst were presented previously [4].

2.2. Infrared spectroscopy

The catalyst powder was pressed into a self-supported wafer and analyzed *in situ* during adsorption by means of transmission FT-IR spectroscopy using a Bruker Vector 22 FT-IR spectrometer equipped with a MCT detector. A miniature cell equipped with CaF_2 transparent windows, which can be evacuated to pressure below 10^{-7} mbar, was used. The temperature can be varied from room temperature to 500 °C. Each spectrum consists of 32 scans taken at 4 cm^{-1} resolution. All FT-IR spectra are reported here in absorbance after background subtraction.

The catalyst sample was activated at 500 °C (heating rate 10 °C/min) for 7 h under 10^{-7} mbar, subsequently cooled to 50 °C for adsorption experiments. As demonstrated previously [6], this activation procedure does not affect the oxidation state at the surface of ZrO_2 and YSZ samples. After activation, formaldehyde was introduced into the IR cell until equilibrium was reached at 0.5 mbar.

2.3. Catalytic measurements

The CPOM was performed with a fixed-bed reactor made of an alumina tube (i.d. 4 mm). A mixture of 0.2 g YSZ and 0.2 g α-Al_2O_3 particles with the same particle size was held by quartz wool in the isothermal zone of the reactor. In order to minimize the contribution from the gas-phase reaction, two thin alumina sleeves (o.d. 3 mm) were put above and below the catalyst bed in the reactor, which were also used as thermocouple well. A gas mixture of 10% CH_4, 5% O_2 and balance helium was used as reaction feed. Total flow rate was 170 ml/min (STP). To introduce water to the reaction system, a water saturator was mounted to the catalytic setup, which was connected to the catalytic reactor. The partial pressure of water in the feed was controlled by temperature of the saturator. On-line gas chromatography equipped 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. Conversions (X) and yields (Y) were calculated according to:

$$X_{CH_4} = \frac{CH_4^{in} - CH_4^{out}}{CH_4^{in}}; \quad X_{O_2} = \frac{O_2^{in} - O_2^{out}}{O_2^{in}}; \quad Y_{CO} = \frac{CO^{out}}{CH_4^{in}};$$

$$Y_{CO_2} = \frac{CO_2^{out}}{CH_4^{in}}; \quad Y_{H_2} = \frac{H_2^{out}}{2CH_4^{in}};$$

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

3. Results and discussion

3.1. Effect of the presence of water

Fig. 1 shows the selectivity of YSZ in CPOM at 600 °C as a function of partial pressure of water added to the reaction mixture (CH_4, O_2, H_2O and He). Addition of water increased the selectivity to CO and H_2 at the expense of CO_2 and H_2O. Methane conversion (typically 7.5%) was hardly influenced by addition of water. Increase of both CO and H_2 selectivity clearly excludes the possibility that the change in the selectivity is caused by (reverse) water-gas shift ($CO_2 + H_2 \leftrightarrow CO + H_2O$). To clarify these effects of water addition, the role of surface hydroxyl species on the oxidation of formaldehyde to surface formate was investigated, as discussed in the following sections.

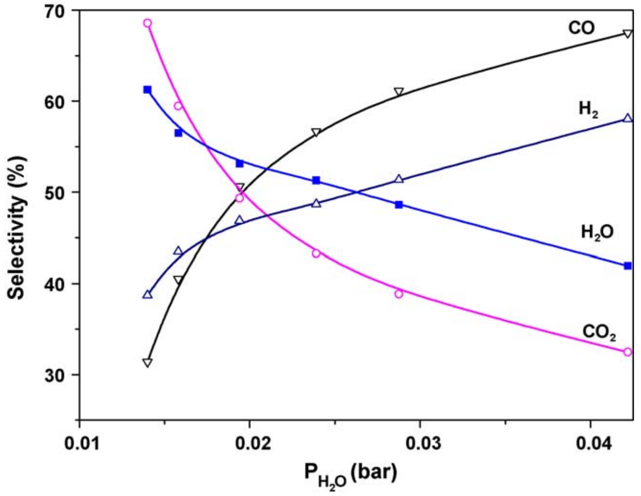

Fig. 1. Selectivities as a function of partial pressure of H_2O added to the reaction of CPOM: catalyst, 0.2 g YSZ; T, 600 °C; F_{total}, 200 ml/min; P_{CH_4}, 0.1 bar; P_{O_2}, 0.05 bar; P_{H_2O}, 0.014–0.042 bar; He balance. CH_4 conversions X_{CH_4}, 7.5 ± 0.2%.

3.2. Hydroxyl groups on YSZ surface

Infrared spectra of the OH stretching region for YSZ samples with different degrees of dehydration are shown in Fig. 2. The spectra were referenced to the empty cell. On the fresh YSZ sample (spectrum a), five adsorption peaks are observed in the region from 3400 to 3600 cm^{-1}. A very broad band with the lowest frequency at 3455 cm^{-1} is attributed to adsorbed molecular water. Three isolated hydroxyl groups are observed on the dehydrated sample (spectrum b). Compared with two bands at high frequencies (3778 and 3733 cm^{-1}), the adsorption peak at 3686 cm^{-1} is significantly large.

Hydroxyl species on the surface of ZrO_2 are commonly assigned based on the number of coordinating Zr cations. Generally, three types of hydroxyl groups are observed with bands in the ranges of 3780–3750, 3750–3720 and 3660–3680 cm^{-1}, which were ascribed to terminal, bi-bridged and tri-bridged hydroxyl groups, respectively [7–12]. Surface hydration of YSZ has been studied by Morterra et al. [13], who observed OH bands very similar to those reported in the present work. Therefore, the high-frequency band at 3778 cm^{-1} is assigned to OH groups bounding directly to a single cation at edges, kinks and/or corners of the oxide particles. Adsorption band at 3733 and 3686 cm^{-1} are attributed to bi-bridged and tri-bridged hydroxyl groups coordinated to surface lattice cations

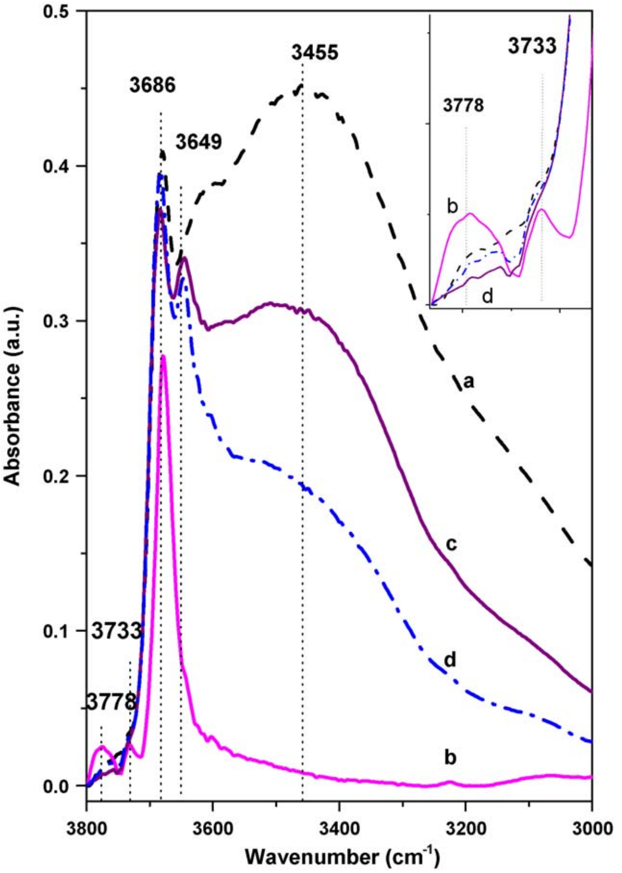

Fig. 2. FT-IR spectra of (a) fresh YSZ, (b) dehydrated at 500 °C for 7 h, (c) dehydrated sample b exposed to water vapor at 50 °C for 30 min and (d) sample c evacuated at 50 °C for 30 min.

on low index surface planes [9,12]. A new OH band at a relatively low frequency 3649 cm^{-1} appears after exposure to water vapor (spectrum c), which is assigned to hydrogen-bonded hydroxyl groups [14]. The band assigned to tri-bridging OH groups at 3686 cm^{-1} increase after exposure to the water vapor, whereas the bands at high frequencies (3778 and 3733 cm^{-1}) are getting weaker. In good agreement with Agron et al. [9], this can be tentatively assigned to hydrogen bonding of molecular water to linear and bi-bridged OH groups, causing the absorption to shift to lower frequency. In contrast, tri-bridged OH groups are positioned at lattice oxygen sites on low index planes. Thus, the oxygen atoms of these OH groups are less capable of hydrogen bonding to a hydrogen atom of a donor water molecule because of steric constraints. Finally, evacuation at 50 °C exclusively results in partial desorption of physically adsorbed water (spectrum d).

The intensities of the IR peaks of terminal and bi-/tri-bridging surface hydroxyls are reported to be similar on monoclinic ZrO_2 [9,12]. In the present study, the intensity of the tri-bridging OH groups on YSZ is significantly higher than terminal OH. This can be attributed to partially replacement of Zr^{4+} by Y^{3+} at edges, kinks, steps and corners when doping Y_2O_3 in ZrO_2, as demonstrated in our previous work [6].

3.3. Adsorption of CHOH

Fig. 3 shows similar FT-IR spectra collected after adsorption of formaldehyde at 50 °C on both dehydrated and hydrated YSZ samples, corresponding to samples b and d in Fig. 2. Significant difference between these two samples is the formation of two new bands at 1650 and 1452 cm^{-1} on hydrated YSZ, which are assigned to coordinated formaldehyde species on the surface [10]. Formate is a major surface species observed on both samples as characterized by bands at 1584 ($\nu_{(as)OCO}$), 1396

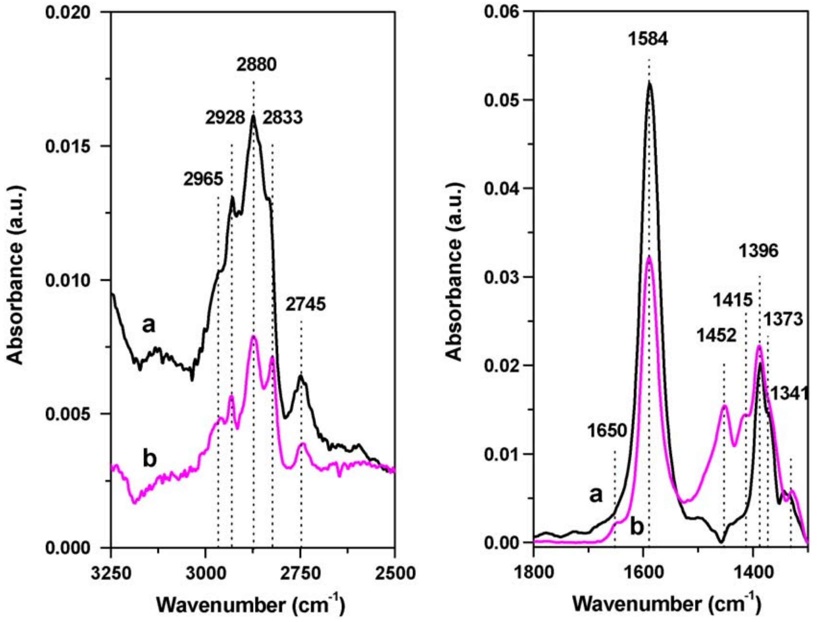

Fig. 3. FT-IR spectra of HCHO adsorbed on (a) dehydrated and (b) hydrated YSZ samples, corresponding to samples b and d in Fig. 2, respectively.

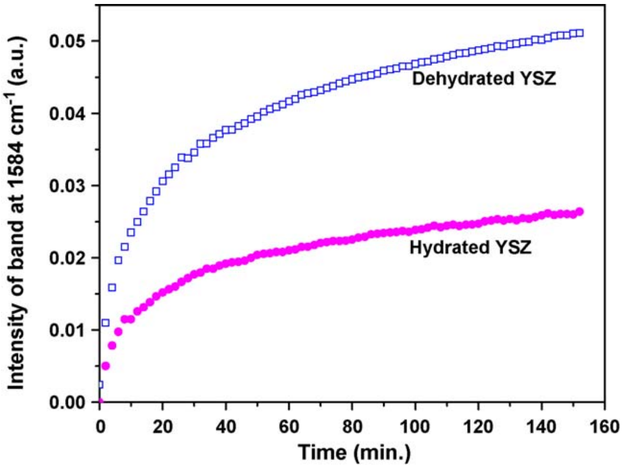

Fig. 4. Intensity of the formate band as a function of adsorption time.

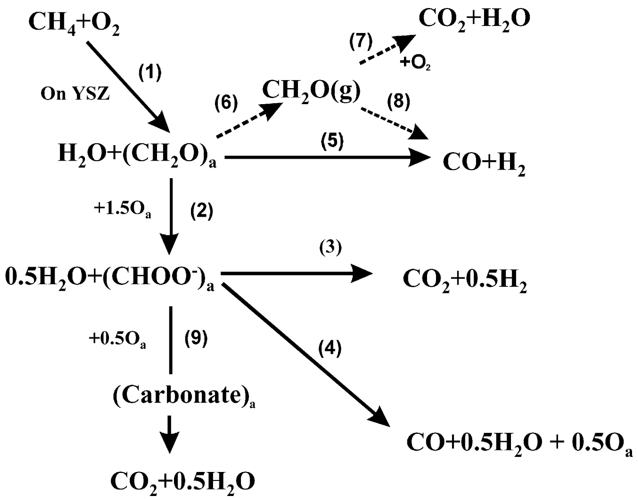

Fig. 6. The reaction scheme for CPOM over YSZ [3].

(δ_{CH}), 1373 ($\nu_{(s)OCO}$), 2880 (ν_{CH}) and 2965 ($\nu_{(a)OCO} + \delta_{CH}$) cm^{-1} [10,15]. Thus, formaldehyde is oxidized by lattice oxygen ions on the surface of YSZ. Oxidation of formaldehyde to formate on ZrO$_2$ at room temperature was also reported by Busca et al. [10]. Bands at 2745 and 1415 cm^{-1} in Fig. 3 are assigned to dioxymethylene, while bands at 2928 and 2833 cm^{-1} indicate presence of methoxy species on the surface [10].

Fig. 4 shows that dehydrated YSZ is more active than hydrated YSZ for the conversion of formaldehyde to formate, based on the increase in intensity of the main formate peak at 1584 cm^{-1}. This is in agreement with the observation in Fig. 3 that adsorbed formaldehyde is observed on hydrated sample exclusively. It seems that surface hydroxyl groups and molecular water adsorbed at the YSZ surface partially block the active sites for oxidation of formaldehyde, *i.e.* lattice oxygen ions in YSZ surface.

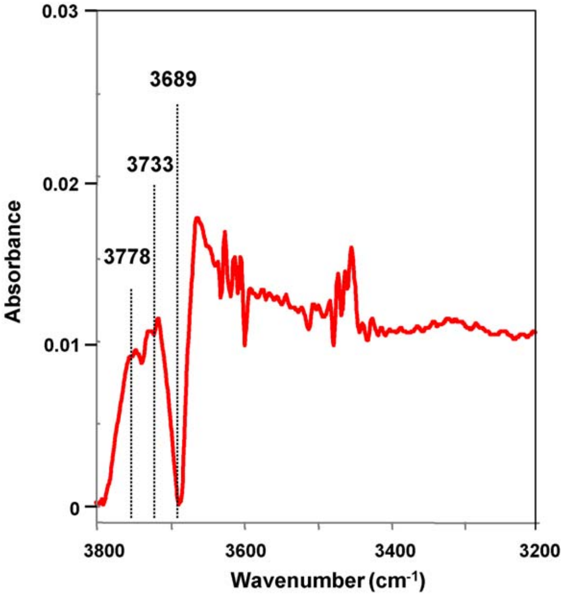

Fig. 5. IR spectra of the hydroxyl group stretching region after adsorption of HCHO on the dehydrated YSZ.

Fig. 5 shows the IR spectrum of the hydroxyl group after adsorption of formaldehyde on the dehydrated YSZ sample. The spectrum was subtracted with spectrum of the sample before adsorption of formaldehyde. Negative peak at 3686 cm^{-1} indicates that tri-bridging OH groups have disappeared after exposure of the sample to formaldehyde. At the same time, the intensity of terminal and bi-bridging hydroxyls increase. This indicates that reaction of formaldehyde with lattice oxygen in low index planes induces relocation of tri-bridging hydroxyls that are originally located on the low index planes to structural defective sites, *e.g.* corners, edges, kinks and steps. However, it is also possible that additional OH groups on defect sites are formed from hydrogen atoms of formaldehyde when it is converted to formate.

The observation of dioxymethylene and methoxy in Fig. 3 is in agreement with literature data on surface species on the surface of many oxides including ZrO$_2$, as reported by Busca et al. [10] and Frusteri et al. [16]. Formaldehyde, first coordinates with the Lewis sites (Zr^{4+} on the surface), consequently interacts with neighboring nucleophilic sites (surface lattice O^{2-} ions) to form dioxymethylene, which either is further oxidized to formate or converted to formate and methoxyl *via* a Cannizzaro type of reaction.

In our previous work [3], a reaction scheme including all significant reaction pathways (Fig. 6) was proposed for CPOM over YSZ. The selectivity to CO and H$_2$ could be significantly improved by preventing further oxidation of formaldehyde to formate on YSZ surface. As discussed above, surface hydroxyls and/or physically adsorbed water partially protect adsorbed formaldehyde against attack by neighboring lattice oxygen ions, which corresponds to reaction 2 in the scheme. The significance of decomposition of adsorbed formaldehyde to CO and H$_2$ (reaction 5 in Fig. 6) thus increases. Consequently, the selectivity to synthesis gas increases when significant water is present in the reaction as shown in Fig. 1.

4. Conclusions

The influence of surface hydroxyl groups and water on the catalytic performance of YSZ in the partial oxidation of methane to synthesis gas was investigated using FT-IR and steady state kinetic experiments. Besides physically adsorbed water, terminal OH groups, bi-bridging and tri-bridging OH groups exist on the surface of YSZ. Oxidation of formaldehyde to formate occurs on the low index planes rather than at the structural defects, *i.e.* corners, edges, kinks and steps. Apart from directly decomposing to CO and H_2, adsorbed formaldehyde is attacked by neighboring lattice oxygen ions to form surface formate. Neighboring hydroxyl groups and hydrogen-bonded molecular water on the surface of YSZ suppresses this nucleophilic attack.

In short, the presence of water on the surface stabilizes adsorbed formaldehyde and this effect is responsible for the increase in selectivity to H_2 and CO when water is added during CPOM.

Acknowledgements

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