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Applied Catalysis A: General 309 (2006) 187–191
APPLIED CATALYSIS A: GENERAL
www.elsevier.com/locate/apcata

Active state of tungsten oxides on WO_3/ZrO_2 catalyst for steam reforming of dimethyl ether combined with CuO/CeO_2

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Received 1 February 2006; received in revised form 27 April 2006; accepted 1 May 2006
Available online 19 June 2006

Abstract

Steam reforming of dimethyl ether (DME) was carried out over WO_3/ZrO_2–CuO/CeO_2 catalysts. The effect of the method of preparation of WO_3/ZrO_2 on its activity was investigated. Three kinds of WO_3/ZrO_2 were prepared by impregnating ammonium paratungstate (APT), ammonium metatungstate (AMT), and tungsten hexachloride (WCl). Although these WO_3/ZrO_2 catalysts had different activities, no difference was observed in their acidic property. The TG-DTA analysis clarified that the different kinds of W precursors affected the crystallization process of zirconia differently. The interaction with zirconia during calcination gave specific properties to the surface W species that are different from those of the single component WO_3. The XPS study on the surface W species showed that H_2 production rate depended on the surface WO_3 amount and on the W(V)/[W(VI) + W(V)] ratio. Excess WO_3 loading brought about the decrease in H_2 production due to the formation of inactive bulk WO_3. The active surface tungsten species were originated from W(V) components interacting with ZrO_2. The APT gave the highest W(V)/[W(VI) + W(V)] ratio and, thus, was the best W precursor among the three.

Keywords: WO_3/ZrO_2; Steam reforming; Dimethyl ether; Valence state of W; XPS; Hydrogen; TG-DTA

1. Introduction

Recently, fuel cells attract much attention as a promising energy production device which does not produce harmful by-products such as SO_x and NO_x. This process needs hydrogen and oxygen as fuel sources, but transportation of pure hydrogen is difficult due to its explosive nature and storage problems. Therefore, on-spot hydrogen production is preferable. One method is the steam reforming of hydrogen containing substances. These substances include methanol, gasoline, and natural gas. Although the infrastructures for gasoline and natural gas are well established, their steam reforming needs high temperatures (above 600 °C for natural gas and above 800 °C for gasoline), requiring much energy, refractory reactors, and stable catalysts. Reforming of methanol proceeds at lower temperatures (150–300 °C); however, methanol is relatively expensive. Moreover, it is biologically toxic and is not desirable for household use. Previously, we focused our attention on dimethyl ether (DME) as a hydrogen source [1,2]. Dimethyl ether has various advantages; it is harmless and does not cause ozone layer destruction, it is easy to handle like LPG, and its steam reforming proceeds at low temperatures (200–300 °C). Steam reforming of DME (Eq. (1)) is the combination of two consecutive reactions: hydration of DME to produce methanol over acid catalysts (Eq. (2)) and steam reforming of methanol to produce hydrogen and carbon dioxide (Eq. (3)) [3,4].

$$CH_3OCH_3 + 3H_2O \rightarrow 6H_2 + 2CO_2 \quad (1)$$

$$CH_3OCH_3 + H_2O \rightarrow 2CH_3OH \quad (2)$$

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad (3)$$

The CuO-based catalysts are effective for steam reforming of methanol [5,6]. Therefore, the overall process needs solid acid + CuO-based catalysts. Hydration of DME (Eq. (2)) is an endothermic reaction and proceeds efficiently at high temperatures. However, much CO, which is poisonous to Pt electrode of

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0926-860X/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.apcata.2006.05.002

the fuel cells, is produced at high temperatures due to the reverse water gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$). Therefore, the reforming at low temperatures is desirable. Our previous study showed that solid acid catalysts with high acid strength ($H_0 \leq -3.0$) are effective for hydration of methanol [1]. The combination of H-mordenite and CuO/CeO_2 had the highest efficiency; however, the durability of this combined catalyst was low. Some subsequent research revealed that WO_3/ZrO_2 could be an alternative [2]. Although the activity of WO_3/ZrO_2 was lower than that of H-mordenite, it had higher durability and produced less CO.

The catalytic property of WO_3/ZrO_2 has been well investigated. The discussion was made from the point of surface W density on zirconia [7–15] and its reduction behavior [16–20]. However, the relationship between the catalytic activity and the valence state of surface W has not been clarified.

This paper deals with the activity of the combined DME steam reforming catalyst ($WO_3/ZrO_2 + CuO/CeO_2$) in relation to the valence state of surface W in WO_3/ZrO_2. The WO_3/ZrO_2 catalyst was prepared by impregnation, and ammonium paratungstate, ammonium metatungstate, and tungsten hexachloride were employed as the W precursors.

2. Experimental

2.1. Preparation of the catalysts

2.1.1. CuO/CeO_2 catalysts

A series of CuO/CeO_2 catalysts were prepared by coprecipitation [5,6]. An aqueous solution containing $Cu(NO_3)_2$ and $Ce(NO_3)_3$ was stirred at 80 °C and 3N NaOH was then added until the pH of the solution was 11. The precipitate was filtered and washed with deionized water three times, followed by drying at 80 °C overnight and calcination at 300 °C for 3 h. The amount of CuO in the CuO/CeO_2 catalyst was 40 wt%.

2.1.2. WO_3/ZrO_2 catalysts

A series of WO_3/ZrO_2 catalysts were prepared by impregnation. Ammonium paratungstate hydrate $5(NH_4)_2O\cdot 12WO_3\cdot 5H_2O$ (abbreviated as APT) (Nacalai tesque), Ammonium metatungstate hydrate $(NH_4)_6H_2W_{12}O_{40}\cdot nH_2O$ (AMT) (Aldrich), and tungsten hexachloride (WCl) (Nacalai tesque) were employed as the W precursors. The W precursor was dissolved in 200 ml of a solvent (water for APT and AMT, and ethanol for WCl). Zirconium(IV) hydroxide (High Purity Chemicals Co.) was added and the mixed solution was stirred for 30 min. The solvent was evaporated and the residue was dried at 80 °C overnight, followed by calcination at 750 °C for 3 h. The amounts of WO_3 loaded were 5–25 wt% as WO_3. The catalyst with x wt% of WO_3 prepared from the W precursor, y, was designated as xWZ y; for example, 15 wt% WO_3/ZrO_2 prepared from APT is designed as 15WZ APT.

2.1.3. DME steam reforming catalysts

Dimethyl ether steam reforming catalysts were composed of a mixture of 40 wt% CuO/CeO_2 and a series of WO_3/ZrO_2. The 40 wt% CuO/CeO_2 and WO_3/ZrO_2 (0.1:0.25 weight ratio) were mechanically mixed and molded into a disk. Each disk was cut and sieved into 14–28 mesh size.

2.2. Apparatus and procedure for steam reforming of DME

Steam reforming of DME was carried out with a fixed bed flow reactor under atmospheric pressure using 0.35 g of the catalyst. The catalyst was pretreated with 10 vol.% H_2/Ar (100 ml/min) at 300 °C for 1 h. Dimethyl ether, water, and 7.1 vol.% N_2/He were supplied to the catalyst bed at feed rates of 2.3, 8.1, and 16.0 ml/min, respectively. The feed gas was induced to the reaction bed when it was cooled down to 200 °C. Then the temperature was increased at 5 °C/min, maintained for 30 min at 25 °C temperature increase interval points up to 300 °C, and the analysis was carried out at these interval point temperatures. The reaction temperature range was set to 200–300 °C. The products were analyzed with a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector at 150 °C (column: Porapack T, 3 m) and with a Shimadzu 3BT gas chromatograph equipped with a thermal conductivity detector (column: Unibeads C, 2 m).

2.3. Characterization of WO_3/ZrO_2

A series of Hammett indicators were used for the measurement of the acid strength. Acidity of the catalysts was measured by the titration with n-butyl amine using dicinnamalacetone ($H_0 = -3.0$) as an indicator. The TG-DTA diagrams were obtained with a Rigaku Thermo Plus TG8120 TG-DTA analyzer. The XPS spectra of O (1s), Zr (3d), W (4f), and Zr (4p) regions of WO_3/ZrO_2 were measured with a JEOL JPS-9010MX X-ray photoelectron spectrophotometer using Mg Kα radiation. The binding energy of the spectra was determined based on the Zr ($3d_{5/2}$) peak at 182.5 eV. The W (4f) and Zr (4p) spectra are superimposed and a part of W exists in the valence state of 5+ [13,17]. Then these spectra in the region of 26–40 eV were deconvolved using the parameters shown in Table 1 with Gaussian curves and were separated into six peaks [2]. Each peak was integrated and the intensity ratios of W(V)/W(total) and W(total)/Zr were estimated to see the relationship with the catalytic activity, where W(total) is the sum of W(V), and W(VI). The intensities of Zr, W(V), and W(VI) are the sum of peaks (1) and (2), that of peaks (3) and (4), and that of peaks (5) and (6), respectively.

Table 1
Peak fitting parameters for W (4f) and Zr (4p) regions (B.E. = 26–40 eV)

Peak no.	Component	Peak position (eV)	FWHM[a] (eV)	Intensity ratio
1	Zr ($4p_{3/2}$)	30.5 ± 0.3	2.65–2.70	
2	Zr ($4p_{1/2}$)	32.3 ± 0.3	2.65–2.70	(2)/(1) = 0.5
3	$W^{5+}(4f_{7/2})$	34.5 ± 0.3	1.60–2.00	
4	W^{5+} ($4f_{5/2}$)	36.6 ± 0.3	1.60–2.00	(4)/(3) = 0.75
5	W^{6+} ($4f_{7/2}$)	35.6 ± 0.3	1.60–2.00	
6	W^{6+} ($4f_{5/2}$)	37.7 ± 0.3	1.60–2.00	(5)/(6) = 0.75

[a] Full width at half maximum.