

PREPARATION AND EFFECT OF Mo-V-Cr-Bi-Si OXIDE CATALYSTS ON CONTROLLED OXIDATION OF METHANE TO METHANOL AND FORMALDEHYDE

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(Received 2 November 1997 • accepted 11 May 1998)

Abstract – Mo-Cr-V-Bi-Si multi-component oxide catalysts were synthesized by three different coprecipitation methods and used in the controlled oxidation of methane to methanol and formaldehyde. It was shown that Mo content in Mo-V-Cr-Bi-Si oxides and the performance of these catalysts were strongly influenced by different coprecipitation methods. The highest methanol and formaldehyde selectivity of 80.2% could be achieved at a methane conversion of 10% for the catalyst prepared by a particular method. The results of XRD indicated that the crystalline phase structures of catalysts were sensitive to Mo, V and Bi loadings. Bi(III) could combine with V(V) and Mo(VI) to form BiVO₄ and γ -Bi₂MoO₆, whereas Cr seemed to form a single Cr₂O₃ crystalline phase in the presence of Bi. The effects of Mo and Cr loading on controlled methane oxidation were also investigated. Mo(VI) oxide appears to favor the formation of partial oxidation products and Cr(III) oxide seems to enhance the conversion of methane.

Key words: Methane, Partial Oxidation, Metal Oxide Catalyst, Coprecipitation, XRD

INTRODUCTION

Direct conversion of methane to its partially oxidized products such as methanol and formaldehyde is a valuable objective in comparison with the energy intensive steam reforming process [Fox et al., 1990]. There have been a number of studies done during last two decades. Pitchai and Klier [1986] and Brown and Parkyns [1991] published review articles describing the catalytic partial oxidation of methane to methanol. Among three catalysts investigated, and it was shown that mixed metal oxides have been widely studied. Catalysts containing oxides of molybdenum, vanadium, chromium, iron and bismuth seem to be promising candidates for heterogeneous partial oxidation since several works have been reported to show high methanol selectivity with reasonable methane conversion [Iwamoto, 1983a,b]. However those excellent results have hardly been duplicated by other researchers [Foster, 1985; Chen et al., 1993]. This implies that the oxidation reaction might be structure sensitive. In order to predict what is required for a good catalyst, it is necessary to study the effect of preparation conditions on the structure and performance of the catalysts.

Recently, we reported that Mo-Cr-V-Bi-Si multi-component oxide catalysts showed relatively high activity for the oxidation of methane to methanol [Han et al., 1996]. In the present work, a series of catalysts with different loading of Mo, Cr, V, Bi and Si oxides were prepared by different coprecipita-

tion methods and were characterized to study the effect of different metal components on the structure of the catalysts. These catalysts showed somewhat different crystalline phase structures and different performance in a controlled methane oxidation reaction.

EXPERIMENTAL

1. Catalyst Preparation

Mo-V-Cr-Bi-Si oxide catalysts were prepared by coprecipitation. Stocks of mixed solutions were prepared by dissolving appropriate amounts of (NH₄)₆Mo₇O₂₄·4H₂O, Cr(NO₃)₃·9H₂O, NH₄VO₃ and Bi(NO₃)₃·5H₂O successively in distilled water which was acidified with nitric acid. Ammonia solution (25 wt%) was used as precipitating reagent. Three kinds of coprecipitation methods were carried out as follows: (1) A mixed solution with a certain amount of colloidal silica was dropped into a dilute ammonia solution. (2) A mixed solution with a certain amount of oxalic acid was added dropwise into the solution containing a certain amount of colloidal silica. The above two additions were adjusted to keep the pH constant at about 11. (3) A mixed metal salt solution with colloidal silica was poured into concentrated ammonia instead of being added dropwise into the dilute solution of ammonia; therefore, the pH value during the addition could not be kept constant. Precipitates produced by each method were dried and calcined under the same treatment conditions.

2. Characterization and Activity-Selectivity Measurements

The BET method was used to measure the surface area of the prepared catalysts. X-ray diffraction (XRD) patterns for each

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sample were obtained using a SIEMENS-D500 Diffractometer with Cu K α radiation. The Mo, Cr, V, Bi contents were analyzed by X-ray fluorescence spectroscopy (XRF). The activity measurements were carried out at 3.0 MPa at a temperature of 425 °C in a fixed bed microreactor with a quartz-covered inner wall. The CH₄:O₂ molar ratio was adjusted to 5 while the feed space velocity was maintained at 7,000 hr⁻¹.

RESULTS AND DISCUSSION

1. Influence of Preparation Method on Metal Content and Structure

The metal contents of the bulk catalysts were quite different from those in the mixed solution (Fig. 1). As an exception, bismuth ions in the mixed solution could be precipitated completely since Bi(III) would be easily hydrolyzed even in acidic solution to produce hydrolysate BiONO₃ and could form BiVO₄ with vanadate. Both Cr and V contents of catalysts prepared by all three methods were found to be nearly constant although their relative amounts were less than those were in the mixed solution. This suggests that the V and Cr contents in the catalysts depended upon their own properties and concentrations in the mixed solution instead of the preparation methods. XRD data showed that Cr(III) could hardly react with vanadate to form CrVO₄ in the presence of Bi(III). Pure vanadium pentoxide is sparingly soluble in water, but dissolves in alkalis to form a wide range of vanadate ions and to form complexes of the VO₂⁺ ion in strong acids. The principal species in vanadium (V)-containing solutions depend on the concentration of hydrogen-ion; with a decrease in pH value they are VO₄³⁻, [VO₃(OH)]²⁻, V₃O₉³⁻, V₁₀O₂₈⁶⁻, V₂O₅ and VO₂⁺. Under the synthesis conditions, pH=11, VO₄³⁻ as main species of vanadate could not completely react with other metal cations to form precipitate, which resulted in exceedingly low V content. Unlike V and Cr, different methods led to different Mo content although the Mo concentration was the same in the mixed solution. This implies that the procedure of molybdenum precipitation might be controlled by deposition dynamics. Mo content in precursor was strongly influenced by aging time and washing condition as well as pH value during

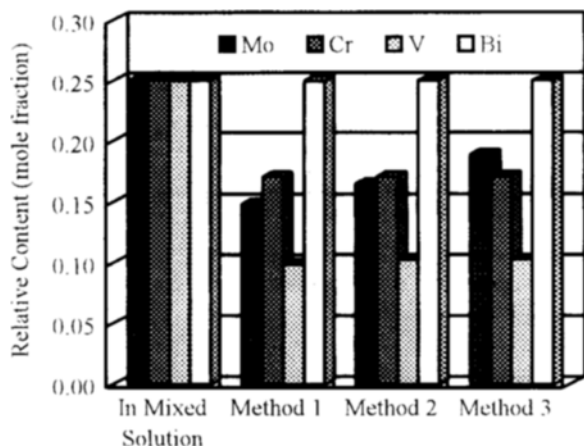


Fig. 1. Effect of preparation methods on metal contents in bulk catalysts.

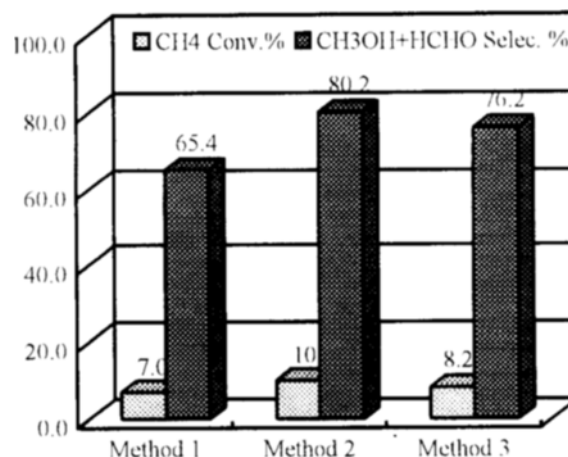


Fig. 2. Activities of catalysts prepared by different methods.

coprecipitation.

The results of BET analysis showed that the total surface area of the catalysts prepared by three methods was different: 96 m²/g for method 1, 66 m²/g for method 2 and 80 m²/g for method 3, respectively. This is probably due to the different dispersion of metal components on silica.

XRD results of the catalysts prepared by three methods showed similar patterns. Crystalline phases of BiVO₄ and Cr₂O₃ were detected on these catalysts, while the silica was amorphous. However, the catalytic behavior of three kinds of catalysts was different under the same reaction conditions. The catalysts prepared by method 2 showed the highest activity with methanol selectivity up to 80.2 % and methane conversion of 10 % (Fig. 2). Due to the addition of oxalic acid during the preparation, the precursor of the catalysts might have somewhat different structure compared with other precursors. The surface structure of the catalysts should be further analyzed in order to explain their differences in catalytic activities.

2. Influence of Metal Content on Structure of Catalysts

Figs. 3-5 show XRD patterns of three series of Mo-V-Cr-Bi-Si oxide catalysts with variable Bi, Cr loading and Mo/V atomic ratio, respectively. When the Bi(III) loading was low, crystalline phases of Cr₂O₃, BiVO₄ and CrVO_{4-x} were observed in catalyst. With increased Bi loading, the amount of BiVO₄ phase increased, while the CrVO_{4-x} phase gradually disappeared (Fig. 3).

Fig. 4 shows that almost no changes of crystalline phases could be found with Cr loading increasing except that the amount of Cr₂O₃ phase increased; however, BiVO₄ was always the main crystalline phase in the catalyst.

The effect of Mo and V loading on the crystallite structure of catalyst is shown in Fig. 5. When the Mo/V atomic ratio was 3.23, the main crystalline phase in catalyst was γ -Bi₂MoO₆. When the Mo/V ratio equaled to 0.65, the main crystalline phase became BiVO₄ with the disappearance of γ -Bi₂MoO₆. A new phase V_xO_y, which was similar to V₆O₁₃, appeared when the Mo/V ratio further decreased to 0.13. The valence of vanadium in V_xO_y was between +4 and +5. Among the three preparation methods mentioned above, it was found that the catalyst prepared by method 2, by which oxalic acid was introduced during the synthesis procedure, contained more of the

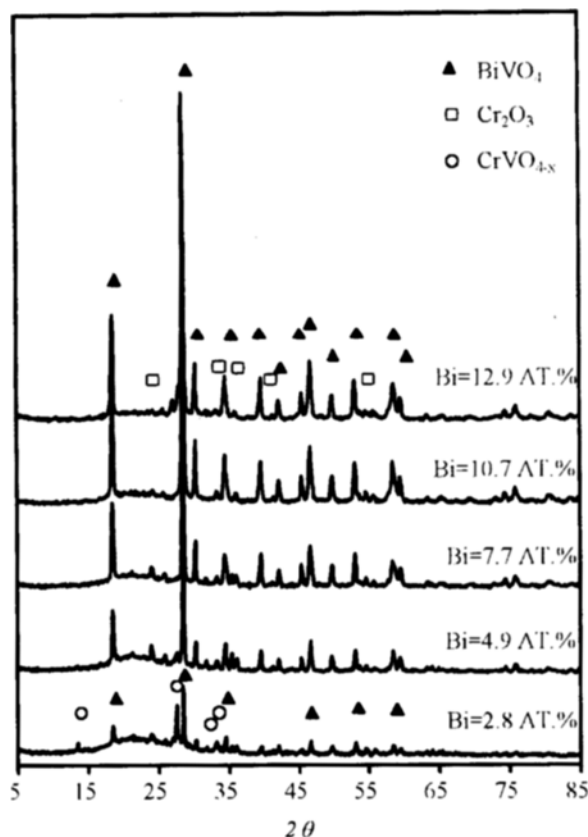


Fig. 3. XRD patterns of Mo-V-Cr-Bi-Si oxide catalysts with different Bi loading.

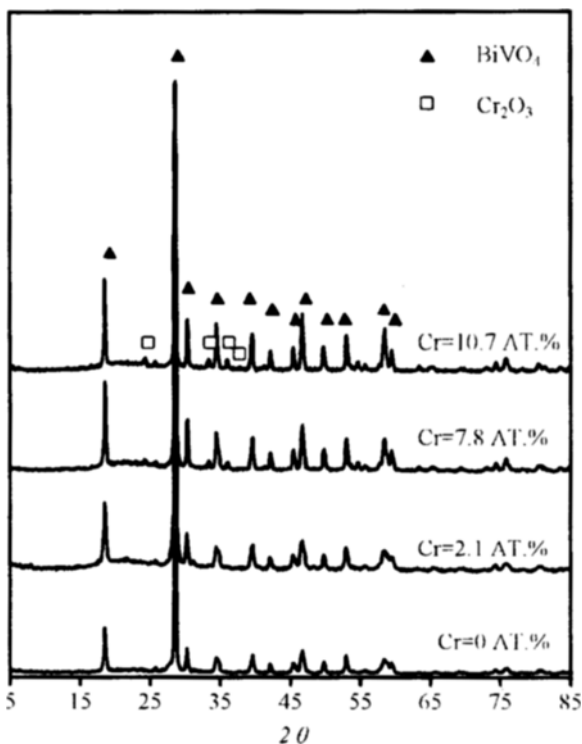


Fig. 4. XRD patterns of Mo-V-Cr-Bi-Si oxide catalysts with different Cr loading.

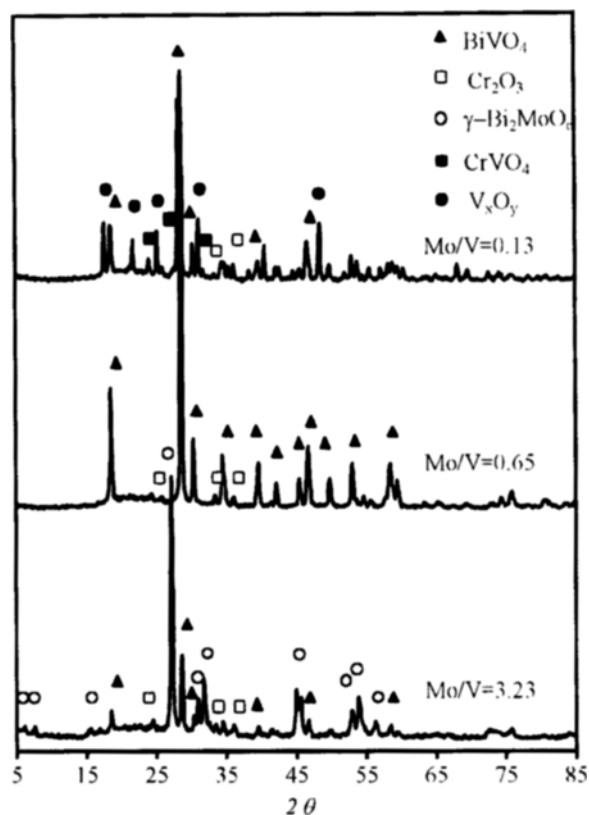


Fig. 5. XRD patterns of Mo-V-Cr-Bi-Si oxide catalysts with different Mo/V mole ratio.

V_xO_y phase than those produced by the other two methods. This indicated that some amount of vanadate could be reduced from V(V) to V(IV) or V(III) by oxalic acid.

In all multicomponent metal oxide catalysts prepared by coprecipitation, no single metal oxide crystallite (such as MoO_3 , V_2O_5 , Bi_2O_3) except Cr_2O_3 was observed in a wide range of each metal's content. This was quite different from the catalyst prepared by impregnation method [Faraldos et al., 1996].

In conclusion, the results of XRD indicated that the structure of multicomponent oxide catalysts was sensitive to metal loading, especially to Bi(III) content. The XRD analysis also showed that the peak intensity of some crystalline phases that contained Bi(III), such as $BiVO_4$, decreased after the oxidation reaction of methane. This suggests that the crystalline phases might participate in the process of the reaction.

3. Influence of Metal Content on Activity of Catalysts

The activities were also investigated over a series of Mo-V-Cr-Bi-Si oxide catalysts prepared by the method 1 with a variety of loading of Mo, Cr, V and Bi, respectively. Fig. 6 shows that the total selectivity of $CH_3OH + HCHO$ increased with molybdenum loading and then leveled off at intermediate loading, but the yield ratio of $HCHO/CH_3OH$ decreased rapidly with the increase of Mo loading. In other words, at low Mo content, the main product of controlled oxidation of methane was HCHO, while CH_3OH was almost the only partial oxidation product at higher Mo loading. This implies that molybdate might strongly influence the mechanism of

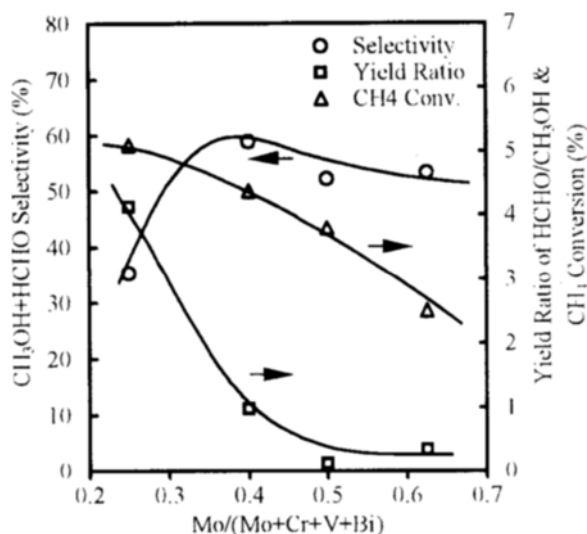


Fig. 6. Activities of Mo-V-Cr-Bi-Si oxide catalysts with different Mo loading.

catalytic controlled oxidation of methane and favor the formation of CH₃OH.

Our studies also show that the conversion of methane increased from 12 % to 26 % as the molar fraction of chromium (Cr/Mo+Cr+V+Bi) in catalysts went up from 0.22 to 0.5; meanwhile the conversion of O₂ also increased from 26 % to 100 %. But the addition of Cr₂O₃ induced a negative effect on the selectivity of CH₃OH. Significant oxygen desorption from Cr₂O₃ was also observed at 450 °C by O₂-TPD technique [Iwamoto et al., 1978]. These results suggest that the addition of Cr₂O₃ could enhance the molecular oxygen transfer to adsorption oxygen (O'_a), which is the intermediate species between O₂(g) and lattice oxygen. It is believed that the surface adsorptive oxygen species (O'_a) over the catalyst were the most likely to cause complete oxidation of methane as well as to activate C-H bond of methane, while lattice oxygen species (O²⁻) would cause methanol and formaldehyde formation [Barboux et al., 1988]. Quick deep reduction of molecular oxygen O₂(g) to lattice oxygen (O²⁻) was crucial to good selectivity. If the intermediate species (O'_a) have a long lifetime, the selectivity of desirable product will decrease even though the conversion of methane can be maintained at a high level.

The effect of vanadium and bismuth oxide loading has been investigated in our previous research [Han et al., 1996]. V and Bi promoters might play an important role in the homogeneous-heterogeneous combining reactions. Not only might they enhance the migration rate of lattice oxygen on the surface of multi-metal oxides, but also inhibit the complete oxidation of methane in the gas phase.

CONCLUSION

The combined results of XRF and XRD show that Mo content in Mo-V-Cr-Bi-Si oxide catalysts is strongly influenced

by different coprecipitation methods as well as by the concentration of molybdate in stock solution. The V, Cr and Bi contents in catalysts only depend on their own concentrations in the stock mixed solution. Bi content has an effect on the formation of most crystalline phases since Bi can easily combine with V(V) and Mo(VI) to form BiVO₄ and γ-Bi₂MoO₆. Cr seems rarely to react with Mo, and only forms a single Cr₂O₃ crystalline phase in the presence of Bi. According to the results of the kinetic experiment, appropriate Mo loading in catalyst is critical in its functioning for the controlled oxidation of methane to methanol or formaldehyde. The activities of catalysts prepared by different coprecipitation methods were also somewhat different and the highest methanol formaldehyde selectivity of 80.2 % could be achieved at methane conversion of 10 % by operating at suitable reaction conditions.

ACKNOWLEDGEMENT

The financial support for this work by National Nature Science Foundation of China, and the partial support from City University of Hong Kong Foundation are gratefully acknowledged.

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