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Crystalline structure of mixed metal oxide catalysts for propane selective oxidation to acrylic acid

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Abstract: The effects of the preparation procedure on the formation of crystal phases and catalytic performance of the MoVTeNbO mixed metal oxide catalysts in selective oxidation of propane to acrylic acid were investigated. The results show that the preferred drying method is the rotavapor method, which favors the formation of an effective crystal phase and suppresses the formation of impurity phases. The preferred calcination atmosphere is an Ar atmosphere. The MoVTeNb mixed metal oxide catalysts can be obtained by solution method after heat-treatment at 600 °C in an Ar atmosphere, via a rotavapor with a warm water bath at 60 °C, and a pH value of 4.0. The catalyst with a MoVTeNb molar ratio of 1.0:0.3:0.23:0.12 is the most effective and extremely active.

Key words: crystalline structure; propane oxidation; selective oxidation; acrylic acid; XRD

1 Introduction

Natural gas and petroleum refinery off-gases represent abundant resources of light alkanes. Recently, much effort has been undertaken to develop novel selective oxidation catalysts that convert these alkanes into more valuable petrochemicals [1]. Acrylic acid is useful as a starting material to produce various commercially important acrylates, which are important building blocks for many polymer materials, such as plastics, paints, adhesives, caulks, sealants and detergents. Furthermore, the direct utilization of propane in chemical productions can also provide additional energy and environmental benefits to the society. It has recently attracted great attention in both academia and industry [2]. Despite this interest, relatively few fundamental studies on the nature of the catalyst and, in particular, on the crystalline structure of catalyst were done.

Selective oxidation activity and selectivity of propane depend on the chemical nature of the composite catalyst, in particular, its chemical composition and phase, etc. In this work, the crystal structure of MoVTeNbO mixed metal oxide catalysts was characterized by XRD, the composition and catalyst preparation procedure on catalytic performance were studied, and the crystalline structure of catalysts and catalytic properties of the relationship was further discussed.

2 Experimental

2.1 Catalyst preparation

The oxides used as source chemicals for the precursor compounds are NH_4VO_3 (ammonium metavanadate) for V, $(NH_4)_6Mo_7O_{24}·4H_2O$ (ammonium heptamolybdate) for Mo, $Te(OH)_6$ (telluric acid) for Te, respectively and all of them were purchased from Aldrich. The precursor compound as the source for Nb was niobium oxalate, which was purchased from the Reference Metals Company. The desired amounts of ammonium metavanadate, ammonium heptamolybdate, and telluric acid were dissolved in deionized water and stirred at 80 °C for 1.0 h in a flask resulting in a uniform aqueous solution. The solution was cooled to 40 °C, and then an aqueous solution of niobium oxalate having the desired niobium concentration was mixed to result in slurry. The water of the slurry was removed via drying to obtain a dry powder precursor. The catalyst powder precursor was calcined at 400−750 °C for 4.0 h with a steady nitrogen stream in a covered tubular furnace so as to prevent the entry of air into the flask. The furnace had previously been heated to 200 °C at a rate of 2 °C/min and held at that temperature for 1.0 h, then ramped to 400−750 °C at a rate of 2 °C/min and held at

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Corresponding author: YU Zhen-xing; Tel: +86-459-4494766; Fax: +86-459-4494766; E-maill: yuzxing@sohu.com that temperature for 2.0 h. After being cooled to room temperature, the mixed metal oxide catalyst was obtained. Then the material was ground, pressed and sieved to 0.85−1.70 mm sized granules. The granules were directly used for the evaluation of vapor phase propane selective oxidation in a micro-reactor.

2.2 Catalyst evaluation

The catalytic performance of the mixed metal oxide catalysts was evaluated for the selective oxidation of propane to acrylic acid in a continuous flow fixed bed micro-reactor testing at atmospheric pressure. About 9.0 g of granules catalyst was packed into a quartz tube with 2 mm in diameter in a programmable oven and heated in a chamber over a temperature of 400 °C. A mixture of propane-oxygen-nitrogen-water vapor was fed in from the top of the reactor. The off-gas was condensed and separated from the liquid phase in several cold traps. The product streams were then analyzed by GC to determine the propane conversion and oxidation product distribution. The carbon balance was always above 95%. The performance of the catalyst is measured by propane conversion, yields of acrylic acid or other products, and specific selectivity. The selectivity, conversion and yield expressed in molar fraction form were calculated on a base of propane.

3 Results and discussion

3.1 Effect of atomic ratio on composite catalysts

The MoVTeNbO mixed metal oxides catalysts contain multiple phases, but the best catalytic properties are associated with two active crystalline phases, orthorhombic, called the M1 phase TeMO$_n$ (M=V, Mo), and hexagonal, called the M2 phase TeMO$_x$ (M=V, Mo and Nb), the most effective phases for the reaction [3−6]. The relationship between these phases is believed to define the catalytic performance [7−9]. Much attention was focused on the study of the structure and chemical composition of the phases M1 and M2 and the oxidation states of their constituent elements [10−13]. The orthorhombic phase M1 has characteristic peaks with 2θ at 22.1° and 45.1°. The hexagonal phase M2 has characteristic peaks with 2θ at 28.3°, 36.4°, and 50.3°.

Figure 1 shows the XRD patterns of samples prepared with different atomic ratios of the catalyst system. There are MoO_3 and $(V_{0.07}Mo_{0.93})_5O_{14}$ phases in the $Mo_{1.0}V_{0.3}O_n$ sample, as shown in Fig. 1(a), in which MoO_3 is the major crystalline phase. It produces two new crystalline phase $TeMo_5O_{16}$ (and or α-$TeMo_4O_{13}$) and TeMO (M=V, Mo) after the introduction of tellurium in this system, as shown in Fig. 1(b). The sample without niobium shows the presence of MoO_3, $TeMo_5O_{16}$, $(V_{0.07}Mo_{0.93})_5O_{14}$ and TeMO (TeVMoO, M=Mo, V), as shown in Fig. 1(b).

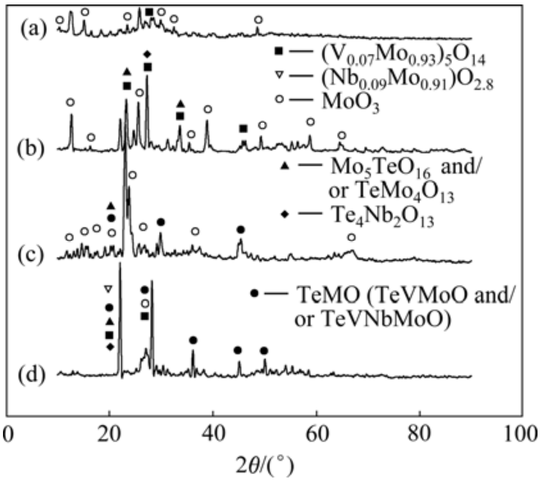

Fig. 1 XRD patterns of catalysts with different atomic proportion under same condition before catalytic testing: (a) $Mo_{1.0}V_{0.3}O_n$; (b) $Mo_{1.0}V_{0.3}Te_{0.23}O_n$; (c) $Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.6}O_n$; (d) $Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}O_n$

The incorporation of niobium proves the appearance of TeMO (TeVMoO or TeVNbMoO; M=Mo, V and Nb), $(V_{0.07}Mo_{0.93})_5O_{14}$, $TeMo_5O_{16}$ (and or $TeMo_4O_{13}$), $(Nb_{0.09}Mo_{0.91})O_{2.8}$, MoO_3 and $Te_4Nb_2O_{13}$, as shown in Fig. 1(d). Niobium atoms replace some V atoms of the TeMOn phase to form a new compound TeVNbMoO, which is pure M2 phase. In addition, the diffraction peaks of TeMO phase exit in Fig. 1(c), while the diffraction peaks of the other phases disappear, which means the five crystalline phases in the catalyst of $TeMo_5O_{16}$ (and or $TeMo_4O_{13}$), $(Nb_{0.09}Mo_{0.91})O_{2.8}$, MoO_3, $Te_4Nb_2O_{13}$ and $(V_{0.07}Mo_{0.93})_5O_{14}$ are in a highly dispersed state, or do not exist in the same system when the Mo/Nb ratio is equal to 0.6. When the niobium content increases to 0.12, it is attributable to that the peak intensity of MoO_3 catalysts greatly decreases, while the intensity of the molybdenum peak greatly increases. The five characteristic peaks with 2θ at 22.1°, 28.3°, 36.4°, 45.1° and 50.3° are present, indicating that the $Mo_{1.0}V_{0.3}Te_{0.23}$-$Nb_{0.12}O_n$ catalyst systems have good catalytic performance, as shown in Fig. 1(d). Vanadium is the key element in the activation of propane and the selective achievement of acrylic acid while V-and/or Nb-doped MoTe-containing crystalline phases are related to the selective transformation of propane to acrylic acid. The chemical composition of samples strongly depends on the amount of each element. It should be emphasized that the organization of catalyst elements and control of the circumstance of each element in particular structures are very important for achieving multi-step oxidation like propane oxidation selectively. Further works in this concern are underway and will be reported elsewhere. It explains the change of phase composition with the XRD data. This means that the adjustment of elemental composition is very effective. It is clearly seen that the optimum MoVTeNb molar ratio is achieved as 1.0:0.3:0.23:0.12.

3.2 Effect of preparation method on composite catalysts

Catalyst samples are obtained under different preparation methods (co-precipitation, hydrothermal synthesis and slurry method, solution method); the preparation method is the only variable factor. The four samples are labeled as A, B, C and D, respectively. Figure 2 shows the XRD patterns of the four samples. Recently, it was reported that the catalyst samples, which have a good catalytic properties, have the two major crystal phases (M1 and M2) in the reaction of selective oxidation of propane to acrylic acid [14−15]. It is proposed that phase M1 is active in propane activation but relatively unselective for the acrylic acid formation, while phase M2 is reasonably active for propane activation and fairly selective for acrylic acid formation.

The XRD patterns of the four fresh catalysts prepared by the solution method, slurry method, co-precipitation method and hydrothermal synthesis method are shown in Fig. 2. As shown in Fig. 2, the patterns of the four catalysts are obviously different. Samples A and C have only three diffraction peaks with 2θ at 22.1°, 28.2° and 45.2°, while the other two characteristic diffraction peaks with 2θ at 36.2° and 50.0° are missing, as shown in Figs. 2(a) and 2(c). Samples B and D have five characteristic diffraction peaks in Figs. 2(b) and 2(d). The diffraction peaks are observable and the basic crystal structure is the same. It is found that the $Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}O_n$ catalysts contain different crystalline structures, and the catalysts prepared by solution method have a better crystalline structure (the phases M1 and M2 with well-defined crystal morphologies) and larger surface area of about 28.65 m^2/g, while the surface areas of the catalysts prepared by co-precipitation, hydrothermal synthesis method and slurry method are 1.28, 15.1 and 6.51 m^2/g, respectively. As well known, larger surface areas of catalyst possesses better catalytic activity. The conclusions are consistent with Ref. [16]. It is proved that the MoVTeNb catalyst prepared by solution method has the best activity and selectivity for the selective oxidation of propane to acrylic acid. That solution method synthesized MoVTeNbO catalysts give higher activities and selectivity in the oxidation. The synthetic methods allow a better control of oxide structures.

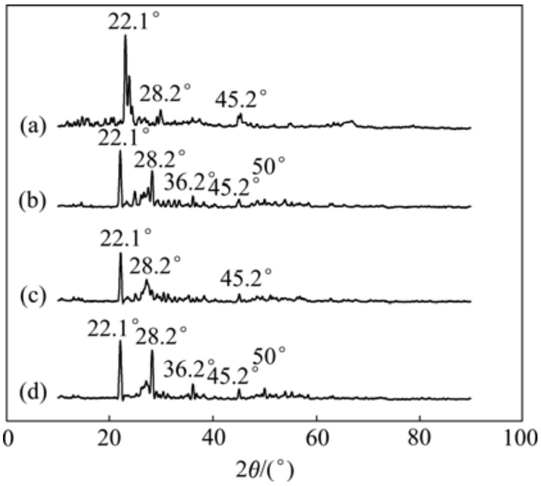

Fig. 2 XRD patterns of mixed catalyst with different preparation methods: (a) Co-precipitation method; (b) Hydrothermal method; (c) Slurry method; (d) Solution method

3.3 Effect of drying method on composite catalysts

Drying to remove the solvent from the precursor is the second step of the metal-oxide preparation. The main methods of drying were commonly spray drying, heating evaporation, freezing and rotary evaporation. The catalysts samples obtained from the rotary evaporation and heating evaporation (drying method is the only variable factor) are labeled as samples A and B, and their XRD patterns shown in Fig. 3.

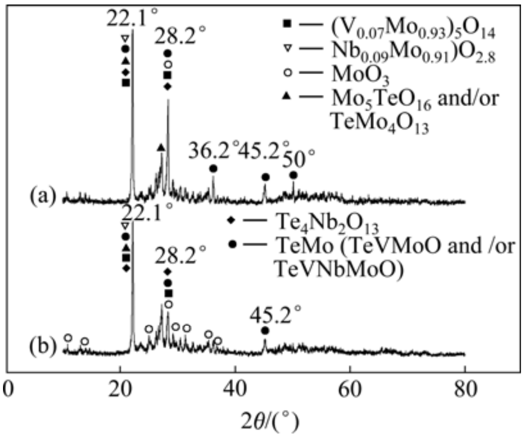

Fig. 3 XRD patterns of mixed catalysts from precursors obtained via different drying methods: (a) Rotary evaporation; (b) Heat evaporation

As shown in Fig. 3, after drying, a mixture of phases is obtained in samples A and B. It shows that the two catalysts have completely different crystalline structure, which means that drying method significantly affects the crystal structure in the preparation of the catalyst. Sample A has five characteristic diffraction peaks with 2θ values of 22.1°, 28.2°, 36.2°, 45.2° and

50.0°, as shown in Fig. 3 (a). The main phases in sample B are MoO_3 and $(V_{0.07}Mo_{0.93})_5O_{14}$, as shown in Fig. 3(b). It shows that sample B does not fully comply with the five characteristic diffraction peaks, only the three characteristic diffraction peaks are with 2θ at 22.1°, 28.2° and 45.2°, and the relative intensity of diffraction peaks is weaker than that of sample A. The heating evaporation leads to the formation of significant amounts of MoO_3 in MoVTeNb oxides, as shown in Fig. 3(b). Some authors pointed out that the existence of MoO_3 and V_2O_5 makes the deep oxidation of propane [17]; so the presence of MoO_3 phase should be avoided. This shows that different drying methods of the $Mo_{1.0}V_{0.3}Te_{0.23}$-$Nb_{0.12}O_n$ catalyst can change the peak size, composition and properties of the crystalline phase. The rotary evaporator catalyst increases the activity of catalyst for the purpose of improving the selectivity of acrylic products. From what said above and previous research [18−19], a conclusion can be drawn that the drying process on the catalyst structure plays an important role in the formation of the crystalline structure of catalysts. Thus, the rotavapor drying method seems to favor the formation of specific M1 and M2 crystal phases, which are related to their catalytic performances.

3.4 Effect of calcination on composite catalysts

Calcination is typically the last step for the preparation of the catalysts, where the composition and in particular, the bulk and surface structures of the oxides are finally settled, which ultimately determine the performance of the catalysts. The synthesized catalyst samples A and B before and after the heat treatment at 600 °C in argon were characterized by XRD.

Figure 4 shows the XRD patterns of the solution method synthesized catalysts before and after the heat treatment at 600 °C in an Ar atmosphere. As shown in Fig. 4, the XRD patterns of the two fresh catalysts are quite different. Sample A has strong and sharp characteristic diffraction peaks with 2θ at 22.1°, 28.2°, 36.2°, 45.2° and 50.0°, showing a strong crystalline structure. The two major crystal phases of the catalyst are the M1 and M2, as shown in Fig. 4(a). However, it is obvious in Fig. 4(b) that there is a very broad XRD peak around 28°, so that the powder seems to be poorly crystallized in the direction of the *c*-axis (this peak can be indexed to 001) and amorphous in the other axes. It can be seen that sample B without calcination shows the non-crystalline structure throughout the scan range. No obvious diffraction lines owing to M1 and M2 phases are detected, suggesting that the phase of catalyst before calcination does not basically exist. Phase differences between the catalysts lead to the main reason for the different catalytic properties. From the results of XRD patterns, it is confirmed that the calcination process plays an important role in the course of catalyst preparation, which determines the catalyst structures, such as the formation of the active phases or sites.

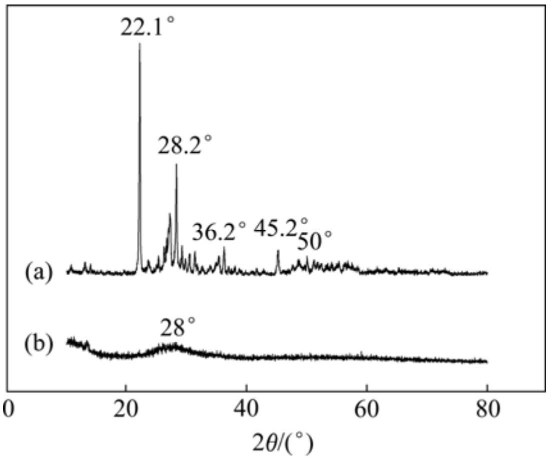

Fig. 4 XRD patterns of metal oxides catalysts after (a) and before (b) calcination

3.5 Effect of calcination temperature on composite catalysts

In order to understand the effect of calcination temperature on the bulk structure of the catalyst, the catalysts calcined at different temperatures were characterized by XRD. The roasting process is carried out at high temperatures. A wide variety of reactions can occur, such as the thermal decomposition, solid state reaction, formation of solid solution and phase transition reactions, so the calcination temperature must be strictly controlled in order to get good crystalline phase, pore structure, surface area and so on. The catalyst samples A, B, C and D were calcined at 500, 550, 600 and 650 °C, respectively (the calcination temperature is the only variable).

Sample A has an amorphous structure and poor crystal form, indicating high dispersion of these species, as shown in Fig. 5(a). Sample B has several diffraction peaks, but the relative intensities of the diffraction peaks are very small, as shown in Fig. 5(b). Together with these diffraction peaks at lower angle region, many XRD peaks also appear in higher angle regions. Sample C has principal diffraction peaks with 2θ at 22.1°, 28.2°, 36.2°, 45.2° and 50.0°, as shown in Fig. 5(c). The sample prepared in the present work is obviously oriented or crystallized better than those reported previously. It is confirmed that the changes of calcination temperature result in the different crystalline structures of the catalysts and lead to different catalytic properties. It can be seen in Fig. 5 that the XRD patterns change depending on the calcination temperature of the catalysts.

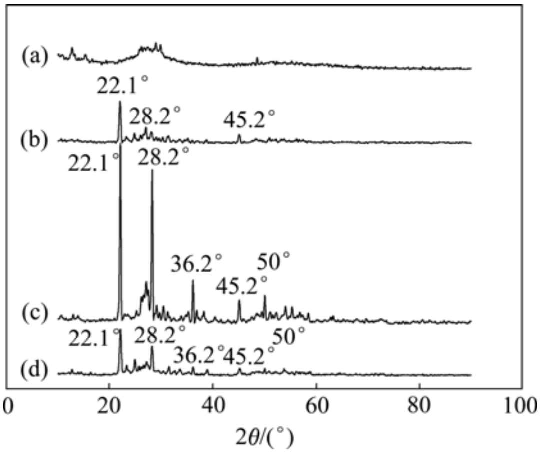

Fig. 5 XRD patterns of mixed catalysts at different calcination temperatures: (a) 500 °C; (b) 550 °C; (c) 600 °C; (d) 650 °C

3.6 Effect of drying temperatures on composite catalysts

Under different drying temperatures, the precursors of composite oxide catalyst have different pore structures, and affect the structure of the catalyst. The three catalyst samples A, B and C dried at 50, 60 and 70 °C, respectively (drying temperature is the only variable) were characterized by XRD, as shown in Fig. 6.

No additional peaks are detected beside those of the orthorhombic structure, as shown in Fig. 6(b). The relative intensity of diffraction peak of sample B is ten times as that of sample A. These three oxides with quite different catalytic performances have reasonably similar XRD characteristics, except that the peak of sample B at 28.2° has a higher intensity and a few minor peaks of samples A and C are observed in the region of 25°−28°. It is clear that these mixed oxides are composed of several phases and that a synergetic effect exists between $MMoO_x$, $TeMO_n$ (M=V, Mo), and $TeMO_x$ (M=V, Mo and Nb) mixed oxides, as shown in Fig. 6(b). Obviously, these results suggest that the drying temperature of the catalyst affects the formation of the catalyst structure, which further affects the performance of the catalyst. The catalytic performances of the catalysts are closely related to both their components and the preparation methods. It is found that the preferred drying temperatures of MoVTeNbO mixed metal oxides catalyst is 60 °C via a rotavapor with a warm water bath.

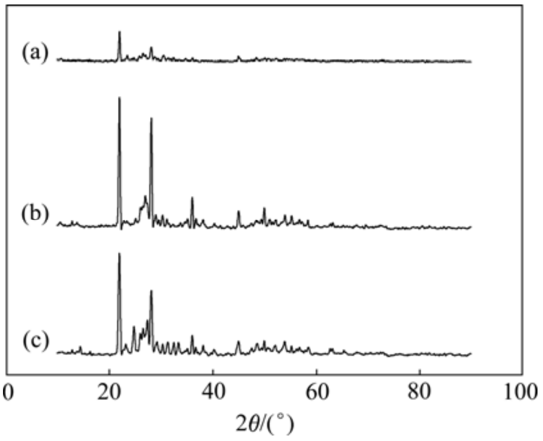

Fig. 6 XRD patterns of mixed catalysts with different drying temperature: (a) 50 °C; (b) 60 °C; (c) 70 °C

3.7 Effect of protective gas on composite catalysts

In order to understand the effect of protective atmosphere on the microstructure of $Mo_{1.0}V_{0.3}Te_{0.23}$-$Nb_{0.12}O_n$ catalyst during calcination process two catalyst samples A and B are prepared in the atmosphere of Ar and N_2 (calcination atmosphere is the only variable factor). The samples were characterized by XRD, as shown in Fig. 7.

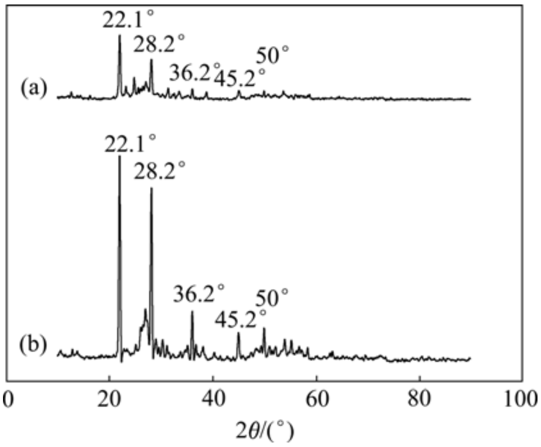

Fig. 7 XRD patterns of mixed catalyst with different protection gases: (a) Calcined in nitrogen gas; (b) Calcined in argon

The XRD patterns shown in Fig. 7 indicate that the phases of samples calcined under nitrogen or argon gas are slightly different. Apparently, all the five characteristic peaks exit in the patterns, indicating that an effective catalyst is formed. Although both samples contain the same several phases, having the major diffraction peaks with 2θ at 22.1°, 28.2°, 36.2°, 45.2° and 50.0°, the relative intensities of the diffraction peaks are very different. It is recently discovered that $Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}O_n$ system containing the M1 and M2 phases is highly selective in propane oxidation to acrylic acid [20]. More details will be reported elsewhere. The latter sample contains more M1 and M2 phases, indicating that the diffraction peaks of the sample calcined in argon gas has stronger relative intensities than those in nitrogen gas. The phases M1 and M2 are attributable to the characteristic peaks of the two samples. This indicates that different calcination atmospheres can change the relative intensities of diffraction peaks of each phase significantly. From the present study, the precursor of the mixed oxide calcined in argon gas gives better catalytic activity and selectivity to acrylic acid compared with those calcined in nitrogen gas. It further confirms that the calcination processes and protective gas have great influence over the multicomponent MoVTeNbO oxide catalysts. It is possible to assume that the particular calcination conditions crucially influence on the catalysts in phase composition and reduction degree of metal ions.

3.8 Effect of pH value on composite catalysts

The $Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}O_n$ mixed oxide catalysts, prepared by a solution method at various pH values (in the range of 2−6), were tested in the partial propane oxidation to acrylic acid. The pH value was adjusted in the range of 2−6 by NH_4OH or HNO_3. The XRD patterns of the mixed oxide catalysts prepared at different pH values are shown in Fig. 8.

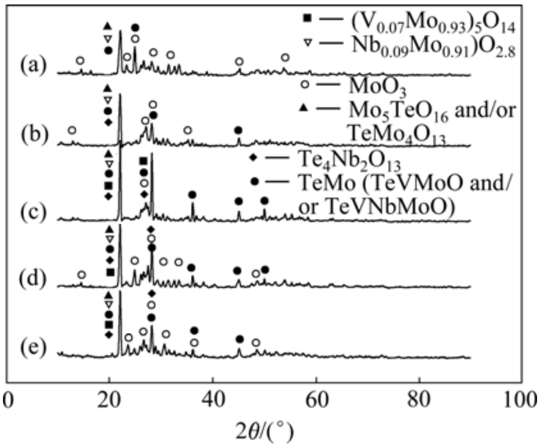

Fig. 8 XRD patterns of mixed catalysts prepared at different pH values: (a) pH=6.0; (b) pH=5.0; (c) pH=4.0; (d) pH=3.0; (d) pH=2.0

The catalyst prepared at pH 4.0 (sample M-4) presents the obvious characteristic diffraction peaks with respect to the rest of the catalysts, the relative intensity of each peak of sample M-4 is the largest, and the content of MoO_3 is the lowest. The relative intensities of diffraction peaks increase with decreasing the pH value at which the catalyst is prepared, reaching a maximum for sample M-4 and a minimum for the sample prepared at pH 2.0.

The main crystalline phase of samples M-5 and M-6 is MoO_3, which is known to be inactive in propane oxidation [20]. When the pH value varies from 5.0 to 6.0, samples M-5 and M-6 generate the nanocrystalline precursors of the phases, as shown in Figs. 8(a) and 8(b). When the pH value is reduced to 3.0−2.0, the MoO_3 phase content of samples M-3 and M-2 are gradually increased, that is to say, the Mo^{6+} content increase, resulting in the catalytic activity decreasing, as shown in Figs. 8(d) and 8(e). The catalytic performances of the catalysts prepared at pH 4.0 are the best, as shown in Fig. 8(c). Based on these results, the pH value is a critical factor controlling the phase composition and morphology of the resultant phases.

4 Conclusions

1) The active and selective multicomponent MoVTeNbO mixed metal oxides catalysts can be obtained by solution method after heat-treatment at 600 °C in an Ar atmosphere, via a rotavapor with a warm water bath at 60 °C, and a pH value of 4.0. And the optimum molar ratio is found to be $n(Mo):n(V):n(Te):n(Nb)=1.0:0.3:0.23:0.12$.

2) The catalyst preparation procedures are closely connected with the phases M1 and M2. The fine crystalline structure of the catalysts improves the catalytic performances by enhancing the formation of phases M1 and M2 (the diffraction peaks with 2θ at 22.1°, 28.2°, 36.2°, 45.2° and 50.0°).

3) By optimizing the preparation parameters of the catalyst, a further improvement in crystal structures and catalytic performance was obtained.

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丙烷选择氧化制丙烯酸复合金属氧化物催化剂晶体结构的研究

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摘　要：研究制备过程对丙烷选择氧化制丙烯酸所用 MoVTeNbO 复合金属氧化物催化剂晶相的形成及其催化性能的影响。最优的干燥方法是用旋转蒸发仪进行干燥，该方法有利于有效晶相的形成和杂质相的抑制。最佳的催化剂焙烧气氛是氩气。X 射线衍射分析结果表明，在采用溶液法制备、旋转蒸发干燥温度为 60 ℃、pH 值为 4.0、氩气为保护气、煅烧温度为 600 ℃等条件下，可获得 MoVTeNb 复合金属氧化物催化剂。当该催化剂的 MoVTeNb 摩尔比为 1.0:0.3:0.23:0.12 时具有最高的催化活性。

关键词：晶体结构；丙烷氧化；选择性氧化；丙烯酸

(Edited by HE Xue-feng)