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Selective oxidation of ethane over hydrothermally synthesized Mo–V–Al–Ti oxide catalyst

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Abstract

Mo–V-based oxide catalysts are known highly active for various hydrocarbon selective oxidations. Particularly those which are monophasic giving XRD diffraction at $d = 4$ Å are extremely active for alkane oxidations. We succeeded to synthesize this unique monophasic material by hydrothermal method and obtained $Mo_6V_2Al_1O_x$ mixed oxide catalysts which showed activities for gas-phase ethane oxidation to ethene and acetic acid. The addition of titanium to the $Mo_6V_2Al_1O_x$ oxide catalyst was found to result in a marked increase of the activity for the ethane selective oxidation, which was due to the morphological change of the catalyst particles and the increase of surface area by the addition of titanium. During the heat-treatment above 550°C under a nitrogen stream, the structural phase of the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst giving the XRD diffraction at $d = 4$ Å transferred to $(Mo_{0.93}V_{0.07})_5O_{14}$-like phase with drastic decreases of the oxidation activity and the surface area. On the basis of kinetic data and the fact that the lower reaction temperature and the existence of water vapor in the feed facilitated the formation of acetic acid, it is concluded that the breaking of C–H bond of ethane is the rate determining of the oxidation and acetic acid do not form through ethene. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxidation; Ethane; Ethene; Acetic acid; Molybdenum oxide; Vanadium oxide; Structure; Heteropoly acid

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1. Introduction

The selective oxidation of ethane has been paid much attention because ethane is a component of natural gas and a cheap raw material. The selective oxidation of ethane to ethene is not a highly difficult reaction because the reactivity of produced ethene is much lower than that of ethane. In fact, many metal oxides [1–6] have been reported as catalysts for the oxidative dehydrogenation of ethane. However, most of them required high reaction temperature more than 500°C. Only a few catalysts were found useful at low temperatures for the oxidative dehydrogenation and for the formation of acetic acid. The pioneer work in this field is one that was carried out by Thornsteinson et al. [1], who have found that molybdenum–vanadium-based oxide catalysts were highly active for ethane oxidation at temperatures as low as 300°C. They concluded that the addition of niobium stabilized the catalyst structure with the increases of both activity and selectivity, and suggested a correlation of the specific activity with the formation of phase having an XRD *d*-spacing at 4 Å. However, it is not easy to prepare this catalyst material by normal catalyst preparation method and therefore structural information on this phase is still not enough. About 15 years after the Thornsteinson's findings,

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Mitsubishi Chemicals claimed in their patents that Mo–V–Te–Nb–O oxide system showed extremely high activity for the ammoxidation of propane and high selectivity to acrylonitrile [7]. This catalyst material also has an XRD diffraction at 4 Å *d*-spacing. Again it is highly difficult to create this phase in the complicated Mo–V–Te–Nb–O oxide system by conventional oxide preparation method.

Recently, we have reported that this type of catalyst material can be easily synthesized using a hydrothermal synthetic method [8]. The procedure is simple, where Anderson-type heteropoly molybdates ($(NH_4)_3M^{III}Mo_6H_6O_{24}$) were reacted with $VOSO_4$ in water at 175°C using an autoclave, forming Mo–V–M–O oxides in rod-shape crystalline with characteristic XRD patterns; two sharp diffraction peaks at about 22° and 45° ascribable to (0 0 1) reflections. We assumed that the crystalline Mo–V–M–O oxide catalyst was formed by a self-organization between the Anderson-type heteropoly anions and vanadyl cations in a layer-type structure. We found that these catalysts showed activities for the partial oxidation of ethane and high selectivities for ethene and acetic acid at 340°C.

In this paper, we report the catalytic performance of hydrothermally synthesized Mo–V–Al–Ti oxide catalyst on the ethane oxidation since the addition of Ti to the Mo–V–Al oxide catalyst resulted in a pronounced increase of the activity without decreasing the selectivities of products.

2. Experimental

2.1. Catalyst preparation

As reported in our previous paper [8], hydrothermal treatment at 175°C did not give any solid materials from mixed aqueous solution of $(NH_4)_6Mo_7O_{24}$ and either $VOSO_4$ or NH_4VO_3. We tried to add another metal cation to organize Mo and V. For this purpose, we selected Anderson-type heteropoly molybdate for the loading of the cations instead of $(NH_4)_6Mo_7O_{24}$. The Anderson-type heteropoly molybdate, $[(NH_4)_3AlMo_6H_6O_{24}\cdot 7H_2O]$, was prepared from the mixed aqueous solution of $(NH_4)_6Mo_7O_{24}$ and aluminum sulfate (or alum) at 80°C. The hydrothermal reaction between the Anderson-type heteropoly molybdates containing Al and $VOSO_4$ in aqueous solutions was carried out at 175°C for 48 h in an autoclave with an inner tube made of PTFE. Solid materials were hardly observed after 1–2 h reaction, but very small amount of black solid became observable on the wall of the autoclave after 3 h reaction. Then the amount of the solid increased with the hydrothermal reaction time. After 48 h, black or dark purple solids yielded both on the wall and at the bottom of the autoclave were separated from the solution, followed by washing with water and drying at 40°C overnight. The catalyst notation, $Mo_6V_2Al_1O_x$, is based on the preparative composition of the elements. For the synthesis of $Mo_6V_2Al_1Ti_{0.5}O_x$, desired amount of $(NH_4)_2TiO(C_2O_4)_2\cdot 2H_2O$ was added to the hydrothermal reaction mixture. The hydrothermal reaction conditions were the same as those for $Mo_6V_2Al_1O_x$.

2.2. Catalyst activity testing

Ethane oxidation was carried out at an atmospheric pressure in a conventional flow system with a fixed bed Pyrex tubular reactor (12 mm i.d.). Before the reaction, the catalysts were heat-treated in a nitrogen flow (50 ml min^{-1}) for 2 h at desired temperature. Unless otherwise indicated, 1 g of the catalysts was used in the reaction. The total flow rate was 50 ml min^{-1} with ethane:oxygen:water:nitrogen mole ratio of 15:5:10:20. The feed compositions were controlled by mass flow controller. Reaction temperature was normally 340°C. The reactants and products were analyzed with an on-line gas chromatograph operating with two sequential columns, a molecular sieve 13× (1 m) at room temperature for separation of O_2, N_2 and CO, and Porapak Q (4 m) at 60–140°C for hydrocarbons and CO_2. There was an ice cooling trap to collect other products like acids at the exit of the reactor, and the collected products were analyzed quantitatively with another gas chromatograph (TC-WAX 60 m capillary). Carbon balance was always more than 95% but the selectivity data were calculated on the basis of product sum since the conversions of ethane were small in many cases.

2.3. Catalyst characterization

Surface area was measured using nitrogen adsorption at −196°C by BET method. The samples were outgassed at 300°C for 1 h before adsorption. Powder XRD patterns were recorded on Rigaku Ras-Ivb diffractometer using Cu Kα radiation. SEM images were taken by using JEOL JSM-T100. IR spectra of the catalysts were measured with Paragon-1000 (Perkin Elmer) instrument by conventional KBr method. Temperature programmed desorption (TPD) of ammonia was carried out using a conventional apparatus. Helium was used as a carrier gas. A dry ice trap was used to remove the water in the carrier gas. The samples were pretreated in the He flow at 500°C for 1 h before ammonia was pulsed into the carrier gas. The programmed heating rate was $10°C\,min^{-1}$. Oxidation states of both molybdenum and vanadium of the samples were ascertained by XPS to be 6+ and 4+, respectively.

3. Results and discussion

3.1. Addition effect of titanium on the $Mo_6V_2Al_1O_x$ catalyst

As reported previously [8], the hydrothermally synthesized $Mo_6V_2Al_1O_x$ catalyst was active for the selective oxidation of ethane to ethene and acetic acid at 340°C. However, the catalytic performance is still not satisfactory. We then tried to modify the catalyst by adding another metal element which does not have strong oxidation ability. We have tested the addition of titanium, tin, niobium, and tungsten on the $Mo_6V_2Al_1O_x$ catalyst and found that the addition of titanium or niobium had pronounced effect for enhancing the catalytic performance. Particularly, the titanium-added catalyst, $Mo_6V_2Al_1Ti_{0.5}O_x$, showed a high ethane conversion more than two times of that of the $Mo_6V_2Al_1O_x$ catalyst (from 3.9 to 9.1%) and also showed an increased selectivity to acetic acid of almost 12%. This pronounced effect of titanium can be seen in Fig. 1 by the activity comparison of the catalysts with and without Ti which were heat-treated at 410°C in N_2 stream.

We now concentrate the effect of titanium. We consider the effect in terms of structural phase change and surface area change. In Fig. 2, XRD patterns are compared for the catalysts with and without Ti which were heat-treated at 410°C in N_2 stream. Both samples have two sharp diffraction peaks at about 22° and 45° ascribable to (0 0 1) reflections in addition to the broad peaks at $2\theta = 9°$ and 27°. Obviously there is no difference of the structural phase between two samples, indicating that the addition effect is caused by other factors than the structural phase. However, one might see slightly broader peaks (half width, 0.246°) of (0 0 1) reflections of $Mo_6V_2Al_1Ti_{0.5}O_x$ than that (half width, 0.188°) of $Mo_6V_2Al_1O_x$ in Fig. 2, which suggest that the length of the rod-shape crystals is shorten by the addition of Ti. In fact, SEM images shown in Fig. 3 revealed that the specimen of the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst has a rod-shape with less than 0.5 μm length in average and 0.2 μm diameter, while the rod-shape specimen of the $Mo_6V_2Al_1O_x$ catalyst was much longer, more than 5 μm length in average but the diameter (0.2 μm) was similar. This result

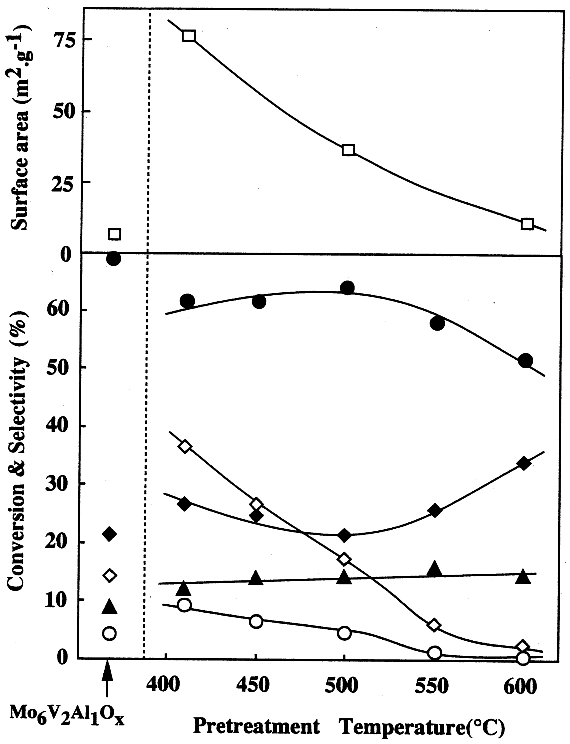


Fig. 1. Comparison of the surface area and catalytic activities of the $Mo_6V_2Al_1O_x$ catalyst and the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst along with the heat-treatment effect on the surface area and the activity of the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst in the selective oxidation of ethane at 340°C. Ethane conversion (○); oxygen conversion (◇); selectivity to ethene (●); selectivity to acetic acid (▲); selectivity to CO_x (◆); surface area (□).

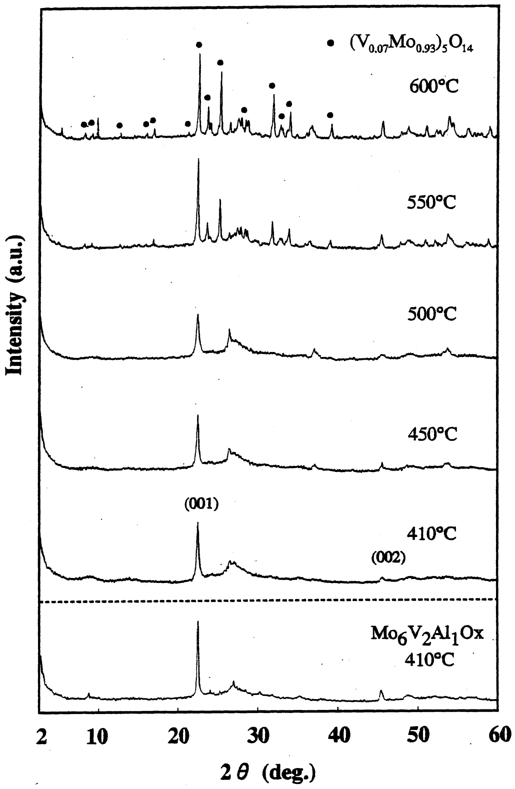


Fig. 2. XRD patterns (Cu Kα) of the $Mo_6V_2Al_1O_x$ catalyst and the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst heat-treated at different temperatures.

straightforwardly means that surface area changes by the addition of Ti.

Fig. 1 also shows the surface area change by the addition of Ti and by the heat-treatment at different temperature. The surface area of the $Mo_6V_2Al_1O_x$ catalyst was small with a value of 6.5 m^2/g. When titanium was added to this catalyst, the surface area greatly increased to 76.4 m^2/g. This result gives rise to a simple understanding that the promotion of the catalyst activity by the addition of titanium comes from the marked increase of the catalyst surface area. Before concluding in such a way, however, it is should be taken into account that the surface area increase was about 10 times while the activity increase was about twice. Since such the big difference cannot be explained simply by often observable surface area decreases after the use for the catalytic reaction, the difference should be considered on the basis of that the catalytic oxidation of ethane is surface-structure dependent.

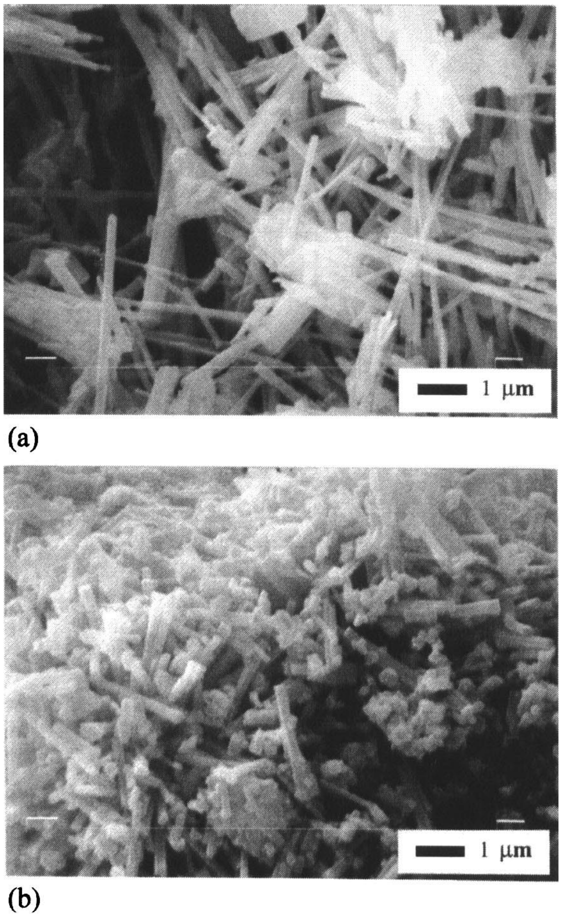


Fig. 3. SEM images of the $Mo_6V_2Al_1O_x$ catalyst and the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst.

For better understanding of the above result, we conducted TPD experiments of NH_3 for two samples. There were two ammonium desorption peaks at 180 and 300°C in both the catalysts, revealing that two acidic sites exit on the surface. The total amount of ammonia desorption per surface area were 8.70×10^{-4} and 7.57×10^{-4} mol m^2 for the $Mo_6V_2Al_1O_x$ catalyst (heat-treated in N_2 at 500°C) and the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst (heat-treated in N_2 at 500°C), respectively. The ratio of the amount of desorbed ammonia at 180–300°C was about $\frac{5}{4}$ and was not clearly affected by the addition of titanium. Apparently titanium has a weak influence on the surface acidic property.

As mentioned above, titanium induces the shortening of the rod-shape crystalline. However, it can be shown easily by simple calculation that the surface area of rod-shape materials do not increase so much by the shortening like observed in the SEM measurement (Fig. 3). Therefore, the increase of the surface area must be caused mainly by a separation of the rod-shape crystalline from rod-aggregates. By further analysis of the SEM images of low magnification, many of the rod-aggregates were observed for the sample of the $Mo_6V_2Al_1O_x$ catalyst while a little was found in the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst. In addition, it is reasonable that the acidic property remains unchanged if the surface area increases by the above way. In other words, the appearance of cross-section by the splitting of the rods only contributes weakly to the over-all properties like surface area and amount of surface acid sites but may do strongly to the catalytic oxidation. As a consequence, we speculate that the part of cross-section of the rod crystalline constructs a structure active for ethane selective oxidation and the side part of the rods has no contribution to the catalysis.

3.2. Effect of heat treatment

Fig. 1 shows the variations in the activity and selectivity of the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst as a function of heat-pretreatment temperatures. The catalysts were heated in a nitrogen flow at each temperature for 2 h. The conversions of ethane and oxygen decreased with the heat temperatures. When the heat temperature was above 550°C, the catalyst became almost inactive. When heat-treated at 500°C, total selectivities of ethene and acetic acid achieved a maximum and the selectivity of CO_x achieved its lowest value. Ethene selectivity slightly increased with the heat temperatures in the range 410–500°C, then decreased above 500°C. The CO_x selectivity showed the opposite change with respect to ethene. The selectivity to acetic acid increased slowly with the heat temperatures. Fig. 1 also shows the surface area which was monotonously decreased as increasing the treatment temperature.

Fig. 2 shows the XRD patterns of the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalysts after the heat treatment at different temperatures. The sample heated at 410°C showed the characteristic XRD pattern which has been described in Section 1: two sharp diffraction peaks were observed at about 22° and 45° ascribable to (0 0 1) reflections. There were not much changes in the XRD patterns as the heat-treatment temperatures increased up to 500°C. But the intensity of the reflection peak at $2\theta = 22.2°$ showed a small weakening and the reflection peaks at about 27°, 37°, 52° grew up slowly. As the heat-treatment temperature exceeds 500°C, a large number of new reflection peaks appeared and developed much after the treatment at 600°C. Most of these peaks are attributed to $(Mo_{0.93}V_{0.07})_5O_{14}$-like phase.

Obviously, the decrease of the catalytic activity with the increase of the heat-pretreatment temperature is mainly due to the decrease of surface area. However, it should be noted that the abrupt changes above 550°C were observed both in the structural phase and the catalytic activity, as can be seen in Figs. 1 and 2. The decrease of the catalytic activity, therefore, must be caused by the decrease of active phase having a d-spacing at 4 Å as well as by the decrease of surface area.

3.3. Effect of reaction variables and reaction mechanism

At the beginning of the reaction, the ethane conversion was somehow low and increased with the reaction time, and then 2 h after, the conversion reached a constant. The selectivities of the products were stable with the reaction time. We could also confirm structure stability of this catalyst by XRD measurement before and after the reaction. In the FT-IR spectra, the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst showed absorption bands at 590, 700, 810, 860, 920 cm^{-1} which are attributed to the absorption bands of Mo–O–Mo. No absorption peaks of Mo=O band were observed in this catalyst. Besides these peaks, a peak at 1400 cm^{-1} was also observed. The peak was ascribed to the absorption of ammonium ion. The absorption peak of ammonium ion was completely disappeared after the heat treatment under nitrogen flow at 410°C, indicating that the desorption of ammonia takes place during the heat treatment with leaving an acidic catalyst and then makes the catalyst active.

The oxidation activities and selectivities of the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst at different reaction temperatures are summarized in Table 1. Below 280°C, ethane was not oxidized. As the reaction temperature increased from 280 to 380°C, the conversions of

Table 1
Influence of reaction temperature on the ethane oxidation over $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst

Temperature (°C)	Conversion (%)		Selectivity (%)		
	C_2H_6	O_2	C_2H_4	CH_3COOH	CO_x
280	1.3	3.6	73.3	22.8	3.8
300	3.4	10.2	72.4	17.0	10.6
320	5.7	19.1	69.0	14.3	16.6
340	9.1	36.3	61.5	11.9	26.6
360	17.4	81.5	54.6	7.5	38.0
380	19.8	93.8	54.0	6.5	39.5

ethane and oxygen increased while the selectivities of ethene and acetic acid decreased. The complete oxidation became main at higher reaction temperatures. When the reaction temperature was over 360°C, carbon oxides shared almost 40% of the products. Apparently the lower reaction temperature is preferable for the formation of acetic acid, the selectivity of acetic acid reached 23% at 280°C.

The dependence of the ethane conversion and the selectivities on the contact time is shown in Fig. 4. The ethane conversion increased with the contact time while the selectivity to ethene decreased and the selectivity to CO_x increased conversely. Interestingly the selectivity to acetic acid was unchanged during these changes. It is apparent that as the contact time increased, formed ethene converted into carbon oxides subsequently, but the formation rate of acetic acid was not influenced by the partial pressure of ethene. Ruth et al. [9] also reported similar results over Mo–V–Nb–O catalyst. These facts indicate that acetic acid did not form through the formation of ethene over the Mo–V–Al–Ti oxide catalyst and suggest that acetic acid forms through an intermediate species from ethane. In the work on the Ti/VPO catalyst which is an active catalyst for the selective oxidation of ethane to acetic acid, Tessier et al. [10] pointed out that ethene is not a major intermediate for the formation of acetic acid and acetic acid, once formed, does not transform to carbon oxides in the catalytic conditions. Our results is consistent on this point.

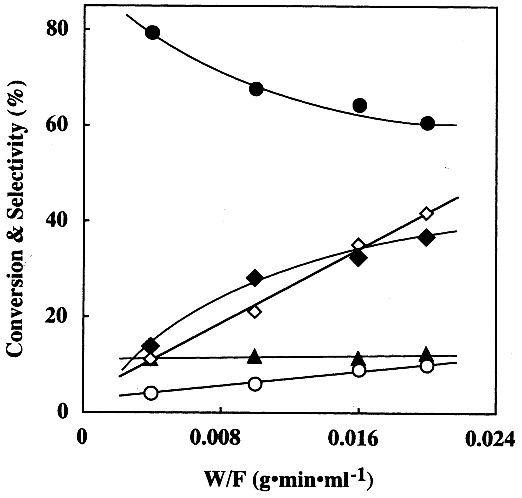


Fig. 4. Effect of contact time on the ethane oxidation over the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst at 340°C. The figure symbols were the same as those in Fig. 1.

We determined the reaction orders with respect to the partial pressures of ethane and oxygen. The results are shown in Fig. 5. Even though the ethane partial pressure increased with a constant oxygen pressure, ethane conversion remained unchanged and a little changes were observed in the selectivities of ethene, acetic acid and carbon oxides. In other words, the reaction rate of ethane and the formation rates of products increased linearly with the ethane partial pressure. The reaction orders with the respect of ethane pressure for the formation of ethene, acetic acid, carbon monoxide and carbon dioxide were calculated to be 1.0, 1.0, 0.8, 0.8, respectively. On the other hand, the formation rates of the products were not very sensitive to the oxygen partial pressure. The calculated orders with respect to oxygen partial pressure for the formation of ethene, acetic acid, carbon monoxide and carbon dioxide were 0.1, 0.05, 0.4, 0.4, respectively. These kinetic data simply mean that the selective oxidation of ethane is approximately first order with respect to ethane and almost independent of oxygen. The similar results were already reported in the literature [9,11,12].

Effect of water addition in the feed is rather interesting since it is well known that the water vapor often benefits the formation of carbon acid. Effect of water vapor on the ethane oxidation over the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst is given in Fig. 6. When the addition of water was stopped after the reaction for 4 h, the selectivity to acetic acid clearly decreased and in place of that the selectivity to ethene increased. The conversion of ethane decreased a little. The selectivity to carbon oxides also decreased slightly. After the

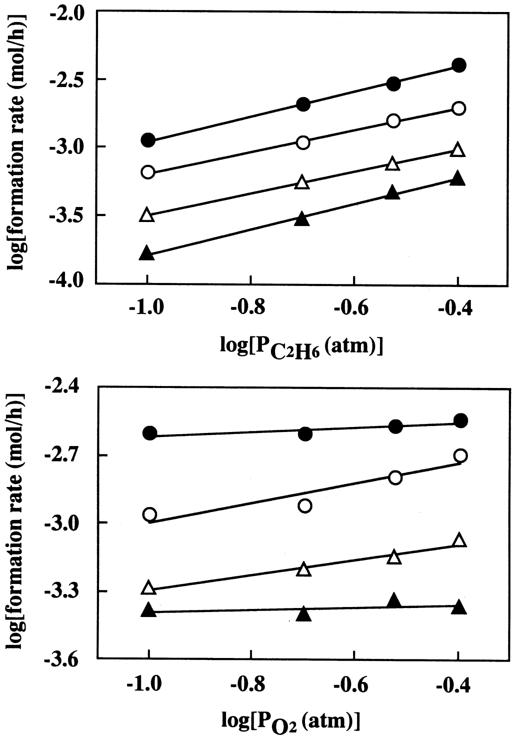


Fig. 5. Partial pressure dependencies of the ethane oxidation over the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst at 340°C. Ethane partial pressure was changed in the range of 10–40 kPa with the constant oxygen pressure of 10 kPa in the upper figure and oxygen partial pressure was changed in the range of 10–40 kPa with the constant ethane pressure of 30 kPa in the lower figure. The figure symbols were the same as those in Fig. 1.

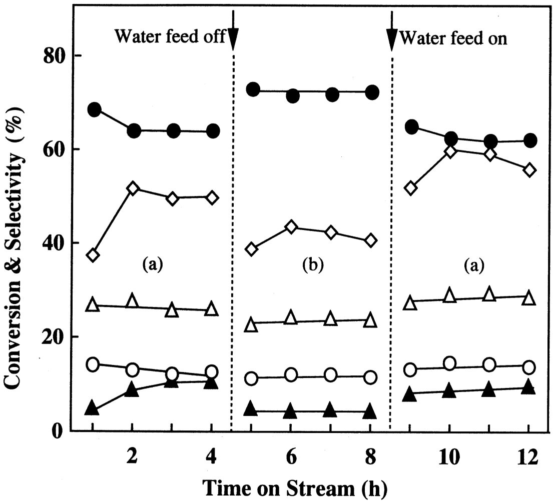
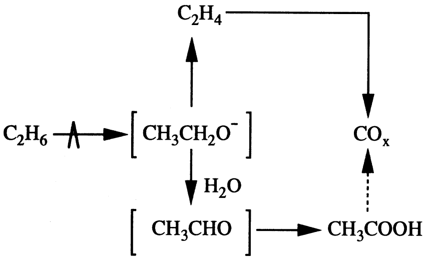


Fig. 6. Effect of water feed on the ethane oxidation over the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst at 340°C. The figure symbols were the same as those in Fig. 1.

re-addition of water, the conversion of ethane gained the initial level and both the selectivities to ethene and acetic acid recovered the values before the water was stopped, and the selectivity of carbon oxides followed the same trend. Apparently, the existence of water vapor facilitates the formation of acetic acid.

On the basis of the above data on the reaction variables, we discuss a reaction mechanism for ethane selective oxidation to ethene and acetic acid as follows. That the reaction order with respect to ethane is approximately first order is consistent with a mechanism in which the breaking of a C–H bond is rate determining. The reaction was almost independent of the oxygen, suggesting that activation of molecular oxygen is rapid process. The result, however, gives no suggestion about active oxygen species which might be formed on the catalyst surface by the interaction of the catalyst with adsorbed molecular oxygen and which might be involved in the breaking of a C–H bond of an adsorbed ethane. In spite of that reoxidation of reduced Mo- or V-based oxide catalysts is normally very slow at temperatures where the $Mo_6V_2Al_1Ti_{0.5}O_x$ catalyst worked effectively and selectively for the ethane oxidation, it was observed that the selective oxidation of ethane is almost independent of oxygen partial pressure. This suggests that the reaction takes place via a redox mechanism and oxygen species formed in reoxidation process of reduced catalysts are of very weakly bound lattice oxygens in the vicinity of the catalyst surface. In this case, the active surface oxygen can be formed rapidly and then reacts with the C–H bond of the adsorbed ethane to form a surface ethoxide intermediate as the rate-determining process.

The reaction of the surface ethoxide intermediate now seems to control the selectivity; if the ethoxide intermediate is dehydrated by the catalysis of surface acid sites, ethene can be formed, and on the other hand if the ethoxide intermediate is dehydrogenated oxidatively over the catalysis, acetaldehyde can be formed, which will be readily oxidized to acetic acid. Carbon oxides are mainly generated from ethene, since the ethane conversion increased with the contact time while the selectivity to ethene decreased and the



Scheme 1. Possible reaction pathways for the formation of ethene and acetic acid.

selectivity to CO_x increased conversely, in addition to that the selectivity of acetic acid remained constant with the contact time. According to the above discussion we depicted a reaction scheme (Scheme 1). An interesting point that should be discussed is the effect of water addition. The effect can be generally discussed either by a backward reaction of ethene with water to form the ethoxide intermediate or by an involvement of water as reactant of the reaction of the ethoxide intermediate to acetic acid. The former decreases the formation rate of ethene and the latter increases the formation rate of acetic acid. However the former may not work because, as can be seen in Fig. 4, the selectivity to acetic acid is almost constant in spite of that the partial pressure of ethene changes with the contact time (or ethane conversion). As a consequence, water is directly involved in the course of acetic acid formation from the ethoxide intermediate. At present stage, however, whether acetaldehyde is an intermediate for the formation of acetic acid or not is uncertain.

4. Conclusions

We found that Mo–V–M–O catalyst materials which can be easily synthesized using the hydrothermal synthetic method are rod-shape crystalline with characteristic XRD patterns; two sharp diffraction peaks at about 22° and 45° ascribable to (0 0 1) reflections. This phase is active for the selective oxidation of ethane but changes into other inactive phase after the heat-treatment above 550°C in a nitrogen stream. The addition of titanium to $Mo_6V_2Al_1O_x$ catalyst synthesized by hydrothermal reaction brought out the increase of the ethane oxidation activity without changing the product selectivities to ethene and acetic acid. Although the increase of the catalytic activity is mainly due to the increase of surface area, it was concluded on the basis of the particle structure analysis that the part of cross-section of the rod crystalline constructs a structure active for ethane selective oxidation and the side part of the rods has no contribution to the catalysis. The selective oxidation of ethane is approximately first order with respect to ethane and almost independent of oxygen pressure. The results of contact time suggested that acetic acid was not formed through the formation of ethene. The addition of water vapor showed an increase of acetic acid and a decrease of ethene. On the basis these reaction data we concluded that water is directly involved in the course of acetic acid formation from the ethoxide intermediate. Water may also contribute to construct surface active structure active and selective for the formation of acetic acid. More work is undertaken now on this point.

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