Journal of Molecular Catalysis A: Chemical 394 (2014) 137–144

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Hydrogen-transfer dehydration between alcohols over V_2O_3 and MoO_2 catalysts for the formation of corresponding alkanes and aldehydes

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ARTICLE INFO

Article history:
Received 14 April 2014
Received in revised form 5 July 2014
Accepted 5 July 2014
Available online 14 July 2014

Keywords:
Alcohols
Alkanes
V_2O_3
MoO_2
Hydrogen-transfer dehydration

ABSTRACT

Conversion of alcohols in a gas phase under N_2 flow at 573 K was carried out using V_2O_3 and MoO_2 oxides with low valence oxidation states. It was found in the reaction of ethanol that equimolar amounts of ethane and acetaldehyde were catalytically formed as the main products over the oxides. Bi-products were small amounts of ethene and C4 compounds. Reactions of other alcohols (methanol, 1-propanol and 2-propanol) over the V_2O_3 and MoO_2 catalysts also led to the equimolar formation of corresponding alkanes and aldehydes or ketone. It was confirmed by XRD and XPS that the low valence states of V_2O_3 and MoO_2 were unchanged during the reactions and the oxides stably worked as the catalyst. Based on catalytic reaction results obtained under various reaction conditions (reaction temperature, contact time, introduction of H_2 and C_2H_4 into reaction stream) and on experiments of kinetic isotope effects on the ethanol reaction, a reaction scheme is proposed, in which hydrogen transfer reaction between two alcohol molecules adsorbed on metal–O^{2-}–metal sites on the surface of V_2O_3 and MoO_2 catalysts takes place *via* 6-membered transition state, followed by dehydration.

1. Introduction

Vanadium oxides and molybdenum oxides are one of the most frequently used catalytic materials in industrial chemical processes, such as partial oxidations of hydrocarbons and alcohols, dehydration of alcohols, de-NO_x reaction and so forth. In most of the cases of these catalytic reactions, the oxidation states of V and Mo under working conditions are either the highest or slightly reduced, but much reduced states like V^{3+} and Mo^{4+} are quite rare in any metal oxide forms under catalytically working states. Recently, we found that ethanol conversion can catalytically proceed over highly reduced vanadium oxides and molybdenum oxides, particularly over V_2O_3 and MoO_2 oxides and that the reaction selectively produces ethane and acetaldehyde in equimolar amounts [1]. This reaction itself and catalytic function of low valence V and Mo in metal oxides seem quite unique in catalysis and interesting in terms of reaction mechanism.

Formation of alkanes from aliphatic alcohols has been little studied in contrast to extensive studies of catalytic dehydration and dehydrogenation of alcohols. A few research results, however, have been reported for the formation so far. They showed that the formation of alkanes from corresponding alcohols mostly occurs *via* either direct hydrogenation of the alcohols or alkenes formed by dehydration of the alcohols with hydrogen that was formed by dehydrogenation of the alcohols [2–4]. Cd–Cr–O [2] and 12-molybdophosphate [3] catalysts were reported to form ethane from ethanol *via* hydrogenation of ethylene, on the basis of that the selectivity to ethane increased with decrease of the selectivity to ethylene. Lobo et al. also showed that propane could be formed *via* hydrogenation of 1-propanol over Pt supported catalysts (Pt/TiO_2, CeO_2, Al_2O_3) [4].

There seems other possible formation mechanisms of alkanes from alcohols. For example, Mohamed et al. reported that ethane and methane were formed as major products from ethanol over Fe ion-exchanged mordenite. They explained that the preferential formation of alkanes was due to the O-abstracting affinity of Fe^{3+} [5]. Ochoa et al. also reported that ethane, acetaldehyde and water were observed at low temperature on TPD profiles in the ethanol reaction over ferrite catalyst [6] They proposed that ethane was formed *via* disproportionation of ethanol or coupling of methyl species formed by dissociation of acetaldehyde. Jin et al. found that butane was formed from 1-, 2-butanols over Fe_2O_3, Fe_2O_3–ZrO_2 and Fe_2O_3–ZnO. On the basis of hydrogen effect over Fe_2O_3–ZrO_2, they concluded that formation of butane from butanol was *via*

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http://dx.doi.org/10.1016/j.molcata.2014.07.009
1381-1169/

nucleophilic substitution (S_N2) of hydroxyl group of alcohols by a hydride ion [7].

In the case of aromatic alcohol reaction like benzyl alcohol, there are several research reports on equimolar formation of toluene and benzyl aldehyde. Jayamani et al. and Ganesan et al. reported that toluene and benzaldehyde were produced in an equal amount from benzyl alcohol over alumina catalyst [8–10] and Ganesan et al. proposed that the disproportionation of di-benzyl ether is a pathway to form the toluene and benzaldehyde in a 1:1 ratio in addition to a direct disproportionation of benzyl alcohol. Moreover, they also proposed that the reaction mechanism is a hydride transfer reaction from one surface benzyloxy species to a neighboring one. Mathew et al. reported that the conversion of benzyl alcohol to toluene and benzaldehyde occurred over molybdenum supported $Al(OH)_3$ [11,12]. $ABB'O_3$ (A = Ba, B = Pb, Ce, Ti and B′ = Bi, Cu, Sb)-type perovskite oxides [13] and Au–Pd nanoparticle [14,15] are also found active for the reaction. In the case of the former, hydrogenation of benzyl alcohol to form toluene was proposed, while in the latter Hutching's group proposed a disproportionation of benzyl alcohol as a main pathway to form toluene and benzaldehyde since Au–Pd led to the equimolar formation of toluene and benzaldehyde in benzyl alcohol reaction under He.

Among the catalytic systems mentioned above, 12-molybdophosphate [3], Pt-supported catalysts [4] are the unique cases that simultaneously produced equivalent amounts of alkanes and aldehydes from aliphatic alcohols, although some other products were formed along with them and the proposed reaction mechanisms are still controversial. In addition, it seems have been considered that higher oxidation states of metal elements in the case of oxide catalysts favor the alkane formation. Meanwhile, our results reported recently using vanadium oxides and molybdenum oxides as catalysts for ethanol conversion evidently showed that equivalent amounts of alkanes and aldehydes were formed from corresponding alcohols as main products without H_2 formation and clarified that lower oxidation states of metal elements in these oxide catalysts are active for the equimolar formation [1]. Apparently vanadium oxides and molybdenum oxides in low valence states are now one of the representative catalysts for equimolar formation of alkanes and aldehydes from corresponding alcohols. In order to further confirm the simultaneous formation of equivalent amounts of alkanes and aldehydes and to elucidate a plausible reaction mechanism for the reaction, we conducted the reaction under different conditions and kinetic analysis. Here in this report, an intermolecular hydrogen-transfer dehydration of aliphatic alcohols will be described based on observed results.

2. Experimental

2.1. Catalyst preparation

V_2O_5 was prepared by the calcination of NH_4VO_3 (99% Wako Pure Chemical Industries) at 773 K for 2 h in air. V_2O_3 was then prepared by the reduction of the prepared V_2O_5 (0.3 g) in a tubular furnace under a H_2 stream (30 ml/min) at 773 K for 2 h. The reduced samples were then exposed to air when they cooled at room temperature before use for catalysis. MoO_3 was prepared by the calcination of $(NH_4)_6Mo_7O_{24}$ (99% Wako Pure Chemical Industries) at 773 K for 2 h in air. MoO_2 was obtained by the reduction of the obtained MoO_3 (0.3 g) in a tubular furnace under a H_2 stream (30 ml/min) at 773 K for 2 h. Subsequently, the reduced molybdenum oxide samples were exposed to air once after they cooled at room temperature. Then the samples were treated again in a tubular furnace under a 5%H_2/Ar (30 ml/min) stream at 773 K for 2 h. Finally the reduced sample was cooled to room temperature, followed by an exposure in air. Thus obtained MoO_2 was provided for catalysis.

2.2. Catalytic test

Catalytic reactions were carried out in a continuous flow fixed bed reactor (Pyrex). A similar volume mixture of the catalyst (0.03–1.5 g) and SiO_2 sands (1.3–2.6 g) as a diluent, which showed no catalytic activity in the alcohol reaction, was placed in the reactor and heated to a desired reaction temperature (533–633 K) under a N_2 flow (21.4 ml/min). Then, the catalytic reaction was started by the introduction of ethanol (99.5%, Wako Pure Chemical Industries) with N_2 carrier into the reactor. The total flow rate of the reactant gas was kept constant (21.4 ml/min) for all the reactions. Ethanol concentration was changed from 1.8–7.5 mol%. The concentrations of methanol (99.8%, Wako Pure Chemical Industries), 1-propanol (99.5%, Wako Pure Chemical Industries) and 2-propanol (99.7%, Wako Pure Chemical Industries) were 2.7, 1.7, and 4.3 mol%, respectively. For study on kinetic isotopic effect, two types of isotope-labeled ethanol, CH_3CH_2OD (99%, Wako Pure Chemical Industries) and CD_3CD_2OD (99%, Wako Pure Chemical Industries), were used as reactant.

The reaction products were analyzed by gas chromatography. Two gas chromatographs, Shimadzu GC-8A equipped with a thermal conductivity detector and a packed column Porapack-QS and GL Science GC-380 equipped with a thermal conductivity detector and a flame-ionization detector and two packed columns, Unicarbon and molecular sieve 5A, were used. N_2 gas was used as internal standard for quantitative GC analysis. Alcohol conversion, the product selectivity, and carbon balance were defined as the following Eqs. (1)–(3), respectively.

$$\text{Conversion}(\%) = \frac{X}{X_0} \times 100 \qquad (1)$$

$$\text{Selectivity}(\%) = \frac{A}{X} \times 100 \qquad (2)$$

$$\text{Carbon balance} = \text{Selectivity}_{\text{total}} \qquad (3)$$

where X_0, X, and A refer to the amount of alcohol feed, the amount of reacted, and amounts of products, respectively.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) measurements were performed with a RINT Ultima+ diffractometer (Rigaku) with Cu-$K\alpha$ radiation (λ = 0.1540 nm) and X-ray power of 40 kV/20 mA. Specific surface areas were measured by the BET method from N_2 adsorption at 77 K using a BELSORP MAX (BEL Japan Inc.). XPS measurements were performed using a JPS-9010 MC (JEOL). An Mg-$K\alpha$ radiation source (1253.3 eV) operated at a power of 100 W (10 kV, 10 mA) was employed. Vacuum in the analysis chamber was $<5 \times 10^{-6}$ during all measurements. Pass energy of 30 eV was used to acquire all survey scans. The binding energy (BE) was corrected for surface charging by taking the C1s peak of carbon as a reference at 248.7 eV. Data were analyzed using the SpecSurf including Shirley background subtraction and fitting procedure. Quantification of the components for the surface oxidation state of vanadium and molybdenum was made using the SpecSurf. The binding energies of 517.2, 516.0 and 515.2 eV were attributed to V^{5+}, V^{4+} and V^{3+}, respectively in the V_2O_3 [16,17], and Mo^{6+}, Mo^{5+} and Mo^{4+} oxidation states ($Mo3d_{3/2}$ and $Mo3d_{5/2}$) were identified at 235.8, 234.7 and 232.7 eV, and 232.2, 231.9 and 229.1 eV, respectively [18,19].

Table 1
Ethanol reaction in the presence of H_2 and C_2H_4 over V_2O_3 and MoO_2 catalysts.

Catalysts	S_{BET} (m^2/g_{cat})[a]	Condition	Conversion (%)	Selectivity (%)			
				C_2H_4	C_2H_6	CH_3CHO	Others[f]
V_2O_3	17	N_2[b]	13.4	2.0	42.7	43.6	11.7
		With H_2[c]	16.5	1.1	45.7	42.4	10.8
		With C_2H_4[d]	16.8	1.3[e]	45.8	41.5	11.4
MoO_2	6	N_2[b]	41.0	1.2	47.4	47.6	3.8
		With H_2[c]	38.0	1.1	44.4	45.9	8.6
		With C_2H_4[d]	36.8	4.3[e]	43.4	45.5	6.8

Reaction condition: reaction temperature 573 K, catalyst 0.15 g, 5 h time on stream.

[a] Specific surface area of the catalysts measured by N_2 adsorption -196 °C.

[b] N_2 21 ml/min, ethanol 0.39 ml/min.

[c] N_2 20 ml/min, C_2H_5OH 0.39 ml/min, H_2 1.0 ml/min.

[d] N_2 20 ml/min, C_2H_5OH 0.39 ml/min, C_2H_4 1.0 ml/min.

[e] Obtained by subtraction of the concentration of ethylene introduced into the feed from the concentration of ethylene in the products.

[f] Others are attributed to C4 compounds mainly.

3. Results and discussion

3.1. Catalytic activity of V_2O_3 and MoO_2 in ethanol reaction

Over the V_2O_3 catalyst and the MoO_2 catalyst, we observed the formation of ethane and acetaldehyde as the main products in the conversion of ethanol. Main by-product detected was ethylene and trace amounts of C4 compounds such as ethyl acetate, *n*-butanol, crotonaldehyde and 2-butanone were also detected. We also observed heavy products in the outlet of the reactor, so that the carbon balances were around 90% in the ethanol reaction. The product selectivity of these products including C4 compounds was calculated on the basis of the carbon balances and is listed as others in Tables 1 and 3. No formations of diethyl ether and H_2 were observed. Ethylene can be simply formed by dehydration and the C4 by-products can be formed *via* condensation reaction of ethanol.

Fig. 1 shows the conversion of ethanol and the selectivity to products as a function of time on stream on the V_2O_3 and MoO_2 catalysts. The conversion of ethanol on the V_2O_3 catalyst, as can be seen in Fig. 1(a), was 24% at the beginning of the time on stream and decreased sharply to 15% with the increase of the time on stream. The reason for the sharp decrease is unclear, but possibly due to a change of oxidation state of V on the surface during the reaction as observed in our previous paper [1]. Nevertheless, the conversion then kept unchanged after 2 h time on stream. On the other hand, the ethane selectivity of 38% and the acetaldehyde selectivity of 43% were observed at the beginning of the reaction and the ethane selectivity gradually increased, giving 43% selectivity to ethane with 44% selectivity to acetaldehyde at 5 h time on stream (Table 1).

Compared to the above V_2O_3 catalyst, the MoO_2 catalyst showed more stable and better performance for the conversion of ethanol to ethane and acetaldehyde, as can be seen in Fig. 1(b) and Table 1. The conversion was about three times higher than that of the V_2O_3 catalyst and only slightly decreased from 47% to 41% at 2 h time on stream and then was stabilized. Obviously, intrinsic activity the MoO_2 catalyst for the ethanol reaction seems higher than that of the V_2O_3 catalyst, since the surface area of the V_2O_3 (17 m^2/g shown in Table 1) is higher than that of MoO_2 (5 m^2/g). In addition, the MoO_2 catalyst clearly revealed the high selectivity performance for the equimolar product formation in which 47% ethane selectivity and 48% acetaldehyde selectivity were achieved from the beginning of the ethanol reaction and continued to 9 h time on stream without appreciable changes in the selectivities.

For both the V_2O_3 and MoO_2 catalysts, the equimolar formation of ethane and acetaldehyde from ethanol is now apparent and active sites on the catalysts are stable during the ethanol reaction. Interesting thing is that very small amount of ethylene and no formation of diethyl ether were observed for both the V_2O_3 and MoO_2 catalysts. This fact indicates that no acid sites, which can promote dehydration of ethanol to ethylene and diethyl ether, exist on the surface of the low valence V_2O_3 and MoO_2. This result suggests at the same time that the reaction is not a simple acid-catalyzed reaction.

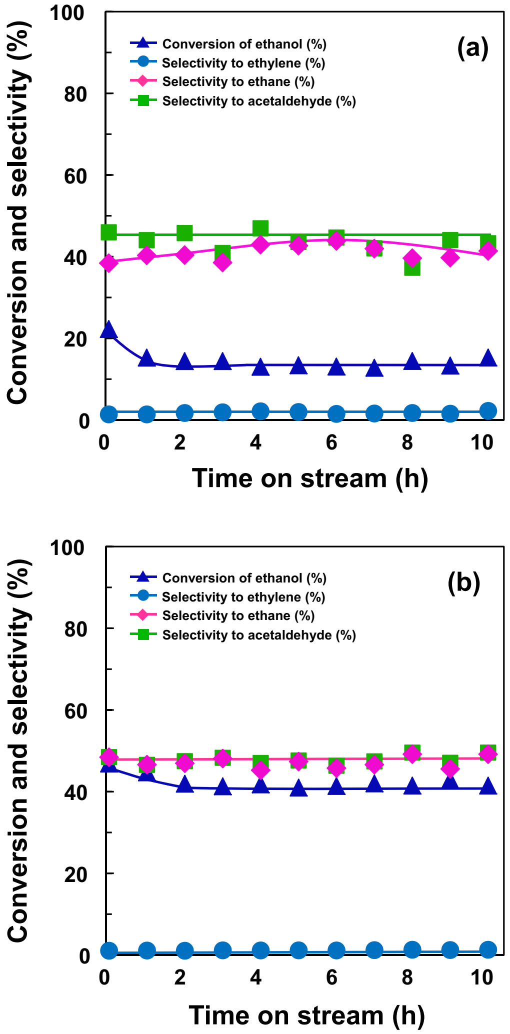


Fig. 1. Ethanol conversion to ethane and acetaldehyde as the function of time on stream over V_2O_3 (a) and MoO_2 (b) catalysts at 573 K. Reaction condition: cat. 0.15 g, flow rate N_2 21 ml/min, ethanol 0.39 ml/min.

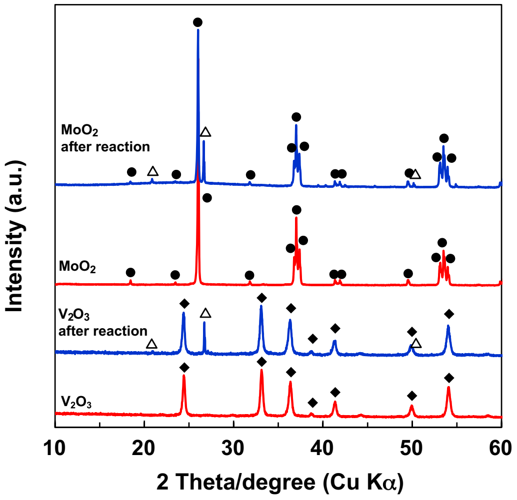


Fig. 2. XRD patterns of the V_2O_3, MoO_2 before and after ethanol reaction. Reaction condition: cat. 0.15 g, reaction temperature 573 K, 9 h time on stream, flow rate N_2 21 ml/min, ethanol 0.39 ml/min. (◆) V_2O_3, (●) MoO_2, (△) SiO_2 (diluent).

3.2. *Oxidation state of the catalysts after the reaction*

XRD measurements were carried out for the V_2O_3 and MoO_2 catalysts before and after the ethanol reaction. Results are shown in Fig. 2. A typical XRD pattern of V_2O_3 was observed without any other crystal phases both before and after the ethanol reaction. MoO_2 phase was also confirmed by XRD and the XRD after the ethanol reaction showed no additional peaks of any impurities such as H_xMoO_3 [20] and other molybdenum oxides. These results evidently reveal that the reduced state of V and Mo in each oxide can be maintained under the reaction conditions and no decomposition of the oxide catalysts takes place during the reaction. To obtain further insight into the stability of the oxidation state of the catalysts, surface oxidation states of V and Mo before and after the ethanol reaction were examined by XPS. Since the measurements were unable to be conducted on the samples without exposure to air, note that obtained XPS results are not for actual surface under the reaction. Nevertheless, the results summarized in Table S1 showed that the surfaces kept highly reduced states and consisted of V^{3+} and Mo^{4+} species mainly and these reduced states were almost the same before and after the reaction. This result is apparently consistent with the XRD result. As a consequence, it is reasonable to conclude that the crystal phases and the surface oxidation states of the V_2O_3 and MoO_2 catalysts are stable under the ethanol reaction.

3.3. *Addition of H_2 and C_2H_4 into the reaction stream*

Hydrogenation of ethanol or of ethylene formed by dehydration of ethanol with formed hydrogen molecules during the reaction was thought to be a likely pathway for the formation of ethane [2,3,13]. Direct hydrogenation of ethylene with ethanol as a source of hydrogen molecules is also a possible pathway to form ethane. To investigate whether reactions on these pathways actually occur or not, the ethanol reaction was carried out in the presence of H_2 and/or C_2H_4 into the reaction stream. H_2 (1.0 ml/min) or C_2H_4 (1.0 ml/min) was added into the reaction stream and the total flow rate was maintained at 21.4 ml/min. Ethanol conversion and products distribution in the presence of H_2 or C_2H_4 in the reaction stream over the V_2O_3 catalyst and the MoO_2 catalyst are listed in Table 1. For both the V_2O_3 and MoO_2 catalysts, the conversion of ethanol and the selectivities to all kind of the products did not change in the presence of H_2 in the reaction stream. Therefore, it can be concluded that hydrogen molecule is not involved in the formation of ethane from ethanol. Similarly, the addition of C_2H_4 had also no effect on the conversion of ethanol and the selectivities to the products. These results suggest that the pathway of the hydrogenation of ethylene is not responsible for the formation of the equivalent amount of ethane and acetaldehyde from ethanol over V_2O_3 and MoO_2.

Coupling reaction of methylene group formed by decomposition of diethyl ether [2] or dissociation of acetaldehyde [6] are also a possible reaction mechanism as proposed for the formation of ethane from ethanol. However, we could observe no formation of formaldehyde and no diethyl ether conversion over the both catalysts under the same reaction conditions for ethanol conversion, so that these two reaction pathways can be excluded.

3.4. *Effect of reaction condition*

Effects of the reaction temperature on the selectivities to ethane and acetaldehyde were examined over V_2O_3 and MoO_2 in the temperature range from 533 K to 653 K. Results are shown in Fig. 3. V_2O_3 showed the selectivities to ethane and acetaldehyde of 43.4% and 45.3%, respectively, at low reaction temperature (573 K). The selectivity to these products did not change even when the

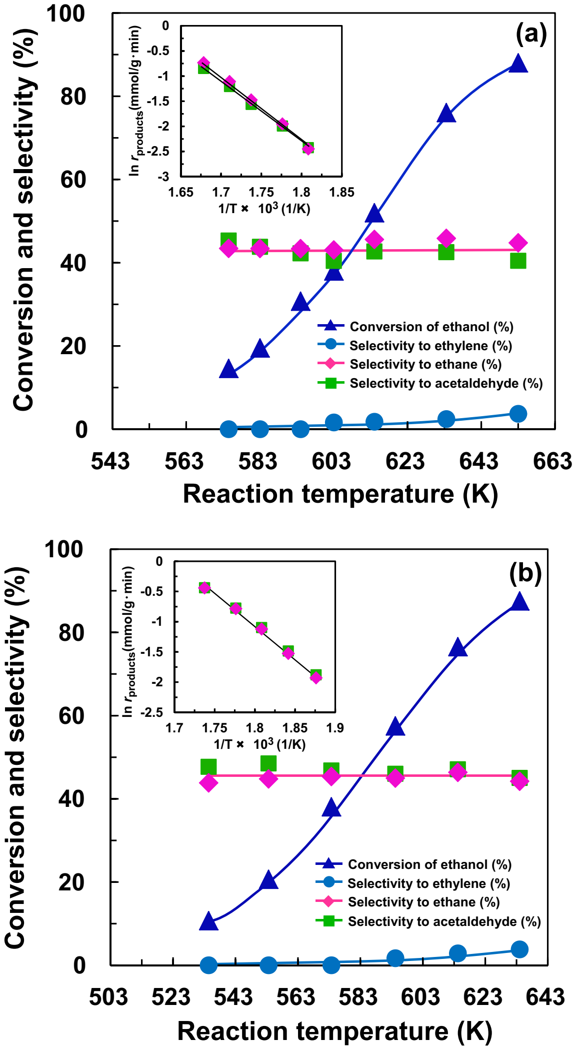


Fig. 3. Ethanol reaction over V_2O_3 (a) and MoO_2 (b) catalysts at different reaction temperature from 533 K to 653 K. Reaction condition: cat. 0.15 g, flow rate N_2 21 ml/min, ethanol 0.39 ml/min. The inset shows Arrhenius plots using the rate of formation of ethane and acetaldehyde.

Table 2
Kinetic parameters of ethanol reaction over V_2O_3 and MoO_2 catalysts.

Catalysts	Reaction order	E_{app} (kJ/mol) for the formation of	
		C_2H_6	CH_3CHO
V_2O_3	0.35	106	100
MoO_2	0.40	90	87

reaction temperature was increased until 653 K, although the some amounts of ethylene with the selectivity 1.3% was appreciably produced at 603 K and increased to 3.7% at 653 K. MoO_2 also showed no temperature effect on the selectivities to ethane and acetaldehyde. The selectivities to ethane and acetaldehyde in all reaction temperatures were within the range of 44–46% and 45–48%, respectively. The insets of Fig. 3 show Arrhenius plots for the formation of ethane and acetaldehyde over V_2O_3 and MoO_2. Apparent activation energies ($E_{a,app}$) of ethane and acetaldehyde formation were calculated to be 106 kJ/mol and 100 kJ/mol, respectively, for V_2O_3 and 96 kJ/mol and 90 kJ/mol for MoO_2 as listed in Table 2. The $E_{a,app}$ values for ethane and acetaldehyde formation were similar both over V_2O_3 and MoO_2, but the values over V_2O_3 were slightly higher than those of MoO_2. In the oxidative dehydrogenation of ethanol to acetaldehyde $VO_x/TiO_2/SiO_2$ catalyst [21] and MO_x/Al_2O_3 (M=V, Mo, W) catalysts [22] have been reported to give apparent activation energies of 46 kJ/mol and 17–23 kJ/mol, respectively. These values are obviously much lower than those observed in the ethanol reaction over V_2O_3 and MoO_2 which is a non-oxidative reaction. This comparison may suggest that the equimolar formation of ethane and acetaldehyde from ethanol takes place without accompanying a reduction–oxidation process of the V_2O_3 and MoO_2 catalysts.

Effects of contact time on the selectivities ethane and acetaldehyde were shown in Fig. 4. Ethane and acetaldehyde were formed with an equal amount over V_2O_3 under the W/F conditions of lower that 0.023 g ml/min. However, the selectivity to acetaldehyde constantly decreased with increase of the contact time and reached to 34.9% under the W/F of 0.07 g ml/min, while the selectivity to ethane kept unchanged in all contact time range tested. MoO_2 also revealed a similar selectivity change, that is, the selectivity to acetaldehyde slightly decreased from 50.9% at 0.03 g ml/min to 39.4% at 0.07 g ml/min and on the other hand the selectivity to ethane did not change in this contact time range. The observed decrease of the selectivity to acetaldehyde seems due to a consecutive condensation reaction of formed acetaldehyde when concentration of acetaldehyde increased under longer contact times. By summarizing all the data collected under the different reaction conditions, it is evident that the product selectivities are practically independent of the reaction temperature and the conversion of ethanol. This clearly indicates that ethane and acetaldehyde are not formed by consecutive reactions but in a single step from common intermediate.

3.5. Reaction of various alcohols over V_2O_3 and MoO_2 catalysts

In order to further study the equimolar formation of alkanes and aldehydes, catalytic reactions using methanol, 1-propanol, 2-propanol were carried out over V_2O_3 and MoO_2 oxide catalysts. Results are summarized in Table 3. Like as ethanol, almost the same selectivities to alkanes and corresponding aldehydes or ketones were observed in all kind of tested alcohols over both V_2O_3 and MoO_2 oxide catalysts, except for the 2-propanol reaction in which much amounts of propylene were simultaneously formed by the dehydration of 2-propanol and also the selectivity to acetone in the reaction over MoO_2 was slightly higher than that of propane probably due to a occurrence of simple dehydrogenation of 2-propanol to acetone. It is now evident from the data that the equimolar formation of alkanes and aldehydes or ketones occurs regardless of alcohols. Moreover, it is noteworthy that methane was obtained from methanol with reasonably high selectivity. This result strongly confirms that the equimolar formation of alkanes and aldehydes from alcohols is not *via* the formation of olefin.

Formation rates of the products of each alcohol were calculated by using the data summarized in Table 3 and the values are listed in Table 4. The order of the product formation rates of the different alcohols over V_2O_3 was as follows: 2-propanol ≫ ethanol > 1-propanol > methanol. In the case of MoO_2, the order was as follows: 2-propanol ≫ methanol > ethanol > 1-propanol. There are difference in the order between the catalysts but the order among normal alcohols seem to have less meanings, since the rates of these alcohols are more or less similar. More prominent is that much higher production rates were obtained in the reaction of 2-propanol for both the V_2O_3 and the MoO_2 catalysts than those of the other alcohols. This interesting result of the high reaction rate of 2-propanol could be related to reactivity of α-hydrogen of 2-propanol, namely easy elimination of α-hydrogen in 2-propanol compared with the other alcohols. Then a hydrogen transfer reaction at α-position of alcohols is suggested involved in the rate-determining step for the equimolar formation of alkanes and aldehydes from alcohols.

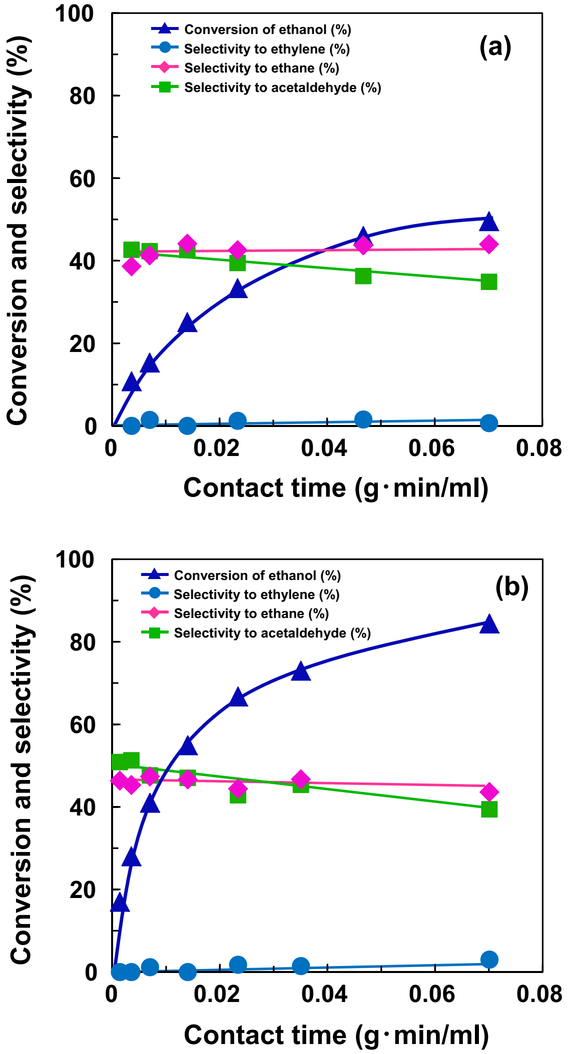


Fig. 4. Ethanol reaction at different contact time over V_2O_3 (a) and MoO_2 (b) catalysts at 573 K. Reaction condition: cat. 0.03–1.50 g, flow rate N_2 21 ml/min, ethanol 0.39 ml/min.

Table 3
Reaction of various alcohols over V_2O_3 and MoO_2 catalysts[a].

Catalysts	Reactants	Conv. (%)[b]	Selectivity to products (%)[c]									
			MA	EE	EA	PE	PA	FA	ACA	ACT	PPA	Others[d]
V_2O_3	CH_3OH	10.8	40.7	–	–	–	–	47.1	–	–	–	12.2
	C_2H_5OH	14.6	–	2.0	42.7	–	–	–	43.6	–	–	11.7
	C_3H_7OH	11.4	–	–	–	<1	47.6	–	–	–	47.2	4.8
	$CH_3CH(OH)CH_3$	72.1	–	–	–	17.9	39.1	–	–	42.5	–	0.5
MoO_2	CH_3OH	19.8	47.8	–	–	–	–	43.1	–	–	–	9.1
	C_2H_5OH	41.0	–	1.2	47.4	–	–	–	47.6	–	–	3.8
	C_3H_7OH	29.5	–	–	–	4.3	44.9	–	–	–	44.8	6.0
	$CH_3CH(OH)CH_3$	100.0	–	–	–	41.4	26.2	–	–	32.0	–	0.4

[a] Reaction condition: cat. 0.15 g, reaction temperature 573 K, time on stream 5 h, flow rate: N_2 21 ml/min, CH_3OH 0.59 ml/min, C_2H_5OH 0.39 ml/min, C_3H_7OH 0.36 ml/min, $CH_3CH(OH)CH_3$ 0.93 ml/min.
[b] Conversion of the reactants.
[c] Selectivity to product, MA: methane, EE: ethylene, EA: ethane, PE: propylene, PA: propane, FA: formaldehyde, ACA: acetaldehyde, ACT: acetone, PPA: propionaldehyde.
[d] Others are attributed to condensation products.

3.6. *Kinetic investigation for the formation of ethane and acetaldehyde*

Study on H–D kinetic isotope effects (KIE) was conducted to reveal the reaction mechanism. KIE was measured using CH_3CH_2OD and CD_3CD_2OD with respect to CH_3CH_2OH. The results are shown in Table 5. The KIE values in the conversion of C_2H_5OD (KIE; $\nu_{C_2H_5OH}/\nu_{C_2H_5OD}$) were 1.09 for V_2O_3 and 1.12 for MoO_2 catalysts. On the other hand, slightly high KIE value for MoO_2 (KIE; $\nu_{C_2H_5OH}/\nu_{C_2H_5OD}$ is 1.32) was observed when C_2D_5OD was used as the reactant. Very differently, V_2O_3 showed an inverse isotope effect (KIE; $\nu_{C_2H_5OH}/\nu_{C_2H_5OD}$ is 0.84). This will be discussed in the following section.

We estimated KIE value as primary isotope effect for ν_{-CH}/ν_{-CD} at 573 K for C—H cleavage (α-H elimination) to be 2.8, which is obviously higher than that of the experimental values (entry 1, 2 in Table 5) of 0.80 and 1.32 for V_2O_3 and MoO_2, respectively. The experimental KIE values ($\nu_{C_2H_5OH}/\nu_{C_2H_5OD}$ = 4.9, entry 3 in Table 5) in the case of oxidative cleavage of C—H bond of alcohols have been reported very close to the estimated KIE value as primary isotope effect (KIE = 5.0), indicating that C—H bond in methylene group is completely dissociated [23]. Ru/carbon catalyst (entry 4) showed KIE values for both O—H and C—H which are lower than those of estimated value, suggesting that α-hydrogen elimination is not a rate-determining step [24]. Hydroxyapatite [25], Al-complex [26] and Zr-complex [27], which have been reported as catalysts for hydrogen transfer reaction, showed also small KIE values as primary isotope effect for the cleavage of C—H bond. All of these reports (entry 5–7) indicate that C—H and O—H bonds are not completely dissociated in the transition states and hydride transfer favorably occurred *via* a concerted mechanism [25–27]. The experimental KIE values ($\nu_{-CH/CD}$) for the V_2O_3 and MoO_2 are similar to that of these reports, so that a hydrogen transfer-type reaction could occur as a rate-determining step for the equivalent formation of ethane and acetaldehyde from ethanol over V_2O_3 and MoO_2.

Table 4
Rate of product formation in the various alcohol reactions on V_2O_3 and MoO_2 catalysts[a].

Catalysts	Reactant	Rate of product formation (μmol/g min)		
		Alkene	Alkane	Aldehyde
V_2O_3	CH_3OH	–	7.6	8.4
	C_2H_5OH	0.6	6.9	7.4
	C_3H_7OH	0.2	5.3	5.2
	$CH_3CH(OH)CH_3$	33.2	74.6	80.4[b]
MoO_2	CH_3OH	–	12.9	11.6
	C_2H_5OH	0.6	23.8	24.1
	C_3H_7OH	1.5	14.7	14.5
	$CH_3CH(OH)CH_3$	106.9	62.3	70.4[b]

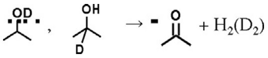
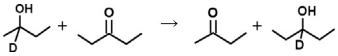
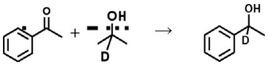
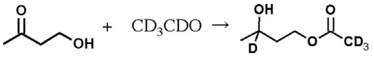
[a] Reaction condition: cat. 0.15 g, reaction temperature 573 K, 5 h time on stream, flow rate N_2 21 ml/min, CH_3OH 0.59 ml/min, C_2H_5OH 0.39 ml/min, C_3H_7OH 0.36 ml/min, $CH_3CH(OH)CH_3$ 0.93 ml/min.
[b] Acetone.

3.7. *Co-formation of ethane and acetaldehyde from ethanol over V_2O_3 and MoO_2*

For better discussion, we made adsorbed state models of ethanol on (0 1 2) plane of V_2O_3 and (−1 1 1) plane of MoO_2. The models are illustrated in Fig. 5. A chosen hexagonal crystal structure of the V_2O_3 catalyst grows in the direction to (0 1 2) plane [28], and the preferential orientation is reported along (1 1 *l*) directions for normal MoO_2 [29]. Almost the same distance of H_a–O_b was able to set for both V_2O_3 (2.30 Å) and MoO_2 (2.37 Å) catalyst surface. However, a much longer distance of H_b–C_b was necessary for V_2O_3 catalyst (2.21 Å) while a short distance (1.61 Å) was realized on MoO_2 catalyst (1.61 Å). The model can help to reasonably explain the observed various kinetic results by assuming that simultaneous formation of ethane and acetaldehyde proceeds *via* the hydrogen transfer dehydration through a 6-membered cyclic intermediate, which is a concerted process where two ethanol molecules are adsorbed at V–O and Mo–O sites on the surface of the catalysts.

First, the apparent activation energy for the formation of ethane and acetaldehyde over V_2O_3 (106 kJ/mol and 100 kJ/mol, respectively, in Table 2) was higher than that of MoO_2 (90 kJ/mol and 86 kJ/mol, respectively, in Table 2). The higher activation energy seems caused by the longer distance between H_b and C_b over V_2O_3 than MoO_2, *i.e.*, the interaction of H_b in methylene group and adjacent C_b in methylene group is more difficult over V_2O_3 compared with MoO_2. The KIE values when C_2H_5OD was reacted were almost the same for V_2O_3 ($\nu_{C_2H_5OH}/\nu_{C_2H_5OD}$ = 1.09 in Table 4) and MoO_2 ($\nu_{C_2H_5OH}/\nu_{C_2H_5OD}$ = 1.12 in Table 4), and the KIE values when C_2D_5OD was used were, on the other hand, very different between V_2O_3 ($\nu_{C_2H_5OH}/\nu_{C_2H_5OD}$ = 0.84 in Table 4) and MoO_2 ($\nu_{C_2H_5OH}/\nu_{C_2H_5OD}$ = 1.32 in Table 4). The observed KIE values when C_2H_5OD was reacted clearly indicate that the OH interaction of alcohol with oxide surface is not a rate-limiting step. Although the observed KIE over MoO_2 was rather small, the KIE values for $\nu_{C_2H_5OH}/\nu_{C_2H_5OD}$ more than unity is not discrepant with the assumption that α-hydrogen is eliminated by a concerted mechanism and hydrogen transfer as the rate-determining step takes place *via* formation of the 6-membered cyclic (nonlinear) intermediate, followed by dehydration to form the products. In fact, KIE values in hydrogen transfer reaction are more than 6 when the reaction takes place in

Table 5
KIE in alcohol reactions over several catalytic systems.

Entry	Catalysts	Reactions	Temp. (K)	KIE values		Ref.
				$\nu_{-OH/-OD}$ ()[a]	$\nu_{-CH/-CD}$ ()[a]	
1	V_2O_3	C_2H_5OD, C_2D_5OD → ethane, acetaldehyde, H_2O	573	1.09 (3.1)	0.84 (2.8)	This work
2	MoO_2	C_2H_5OD, C_2D_5OD → ethane, acetaldehyde, H_2O	573	1.12 (3.1)	1.32 (2.8)	This work
3	VO_x/Al_2O_3	C_2H_5OD, $C_2D_5OD \xrightarrow{O_2}$ acetaldehyde, H_2O	473	1.02 (3.9)	4.90 (5.0)	[23]
4	Ru/carbon		373	1.57 (5.6)	1.69 (4.6)	[24]
5	Hydroxyapatite		573		1.80 (2.8)	[25]
6	Al-complex[b]		310		2.33 (6.5)	[26]
7	Zr-complex[c]		353		1.80 (4.1)	[27]

[a] Estimated values for KIE as primary isotope effect are shown in parenthesis.
[b] BINOLate/Al/^{i}PrOH system, BINOL (2,2′-dihydroxy-1,1′-binaphthyl).
[c] Zirconocene complex, Cp_2ZrH_2.

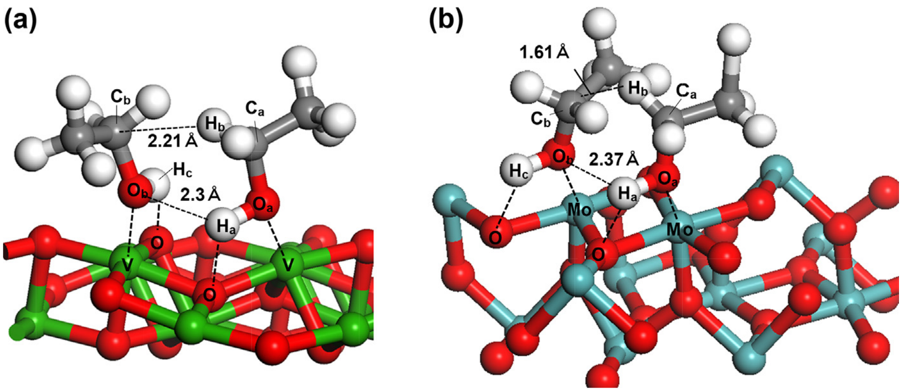
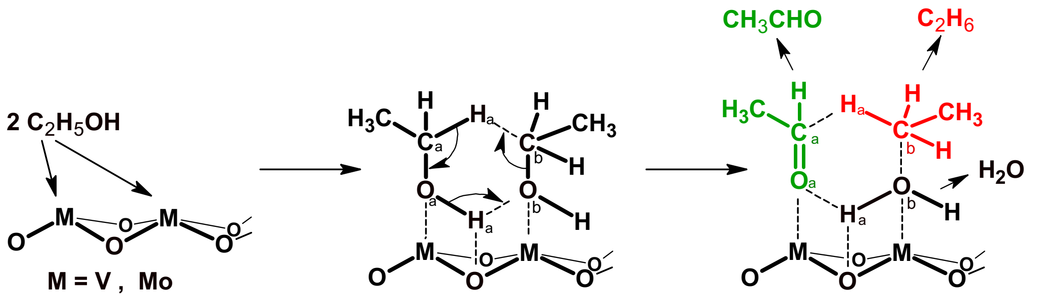


Fig. 5. Model of adsorbed ethanol on (0 1 2) planes of V_2O_3 (a) and (−1 1 1) plane of MoO_2 (b) surface. Green, blue, red, grey and white balls correspond to V, Mo, O, C and H, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

linear transition structure [30], and nonlinear transition structure shows decreased KIE values as low as $2^{1/2}$ [31]. On the other hand, an inverse kinetic isotope effect was observed on V_2O_3. It appears that the inverse kinetic isotope effect should be related to conformation of the 6-membered cyclic intermediate over the oxide surface. The intermediate with C_2H_5OD cannot stably form due to the long distance of H_b–C_b over V_2O_3. However, when C_2D_5OD is reacted, an adsorbed state of C_2D_5OD may alter the conformation of the 6-membered cyclic intermediate to facilitate easier hydrogen transfer.

Based on these results, we proposed a plausible reaction scheme for the co-formation of ethane and acetaldehyde from ethanol on V_2O_3 and MoO_2 as shown in Scheme 1. In the first step, the 6-membered cyclic intermediate is formed by a interaction between two adjacently adsorbed ethanol over coordinatively unsaturated V–O and Mo–O sites than can be created when the metal elements are in a low valence state. The H atoms of the hydroxyl groups of alcohol may be stabilized by hydrogen bonding with lattice oxygen atoms of V_2O_3 and MoO_2 catalysts. H_a adsorbed on lattice oxygen simultaneously interacts with the O_bH of adjacent adsorbed alcohol and H_b in methylene group also interact with C_b in adjacent methylene group. Then 6-membered cyclic intermediate as a transition state is formed [32,33]. Subsequently, H_a in hydroxyl group adsorbed on lattice oxygen completely



Scheme 1. A reaction mechanism for the equivalent formation of ethane and acetaldehyde from ethanol over V_2O_3 and MoO_2 catalysts.

transfers as proton to the hydroxyl group adsorbed at adjacent site ($-O_bH$), forming water. Concertedly H_b in the methylene group also transfers as hydride ion to the C_b in methylene group of another ethanol adsorbed on the adjacent site accompanied by the cleavage of $C_b—O_b$ bond. Thus, ethane and acetaldehyde are simultaneously formed.

4. Conclusion

Equimolar amounts of ethane and acetaldehyde were formed from ethanol over V_2O_3 and MoO_2 catalysts. The selectivity to ethane and acetaldehyde were almost independent of the reaction temperature in the range of 533–653 K and contact time in the range 0.0014–0.07 g/ml/min, confirming the equimolar formation scheme. Both over the V_2O_3 and MoO_2 catalysts, the reactions of methanol, 1-propanol and 2-propanol also produced the equivalent amount of corresponding alkanes and aldehydes. The reaction over the V_2O_3 and MoO_2 catalysts is generally applicable for aliphatic alcohols. The formation of methane strongly supports that olefin is not an intermediate in the co-formation of alkanes from aliphatic alcohols. Kinetic isotope effects for C_2H_5OD and C_2D_5OD respect to C_2H_5OH were rather small for both the V_2O_3 and MoO_2 catalysts. It is concluded that plausible reaction mechanism for the co-formation of ethane and acetaldehyde from ethanol is a hydrogen transfer reaction between two ethanol molecules adsorbed on metal–O^{2-}–metal sites of V_2O_3 and MoO_2 catalysts surface *via* formation of six-membered transition states. This reaction itself and catalytic function of low valence V and Mo in metal oxide form seem quite unique in catalysis field and interesting for further application.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.07.009.

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