Synthesis of Acetic Acid by Catalytic Oxidation of Butenes (Part 1)*

Oxidation of *n*-Butenes and Isobutene to Acetic Acid over Binary Oxide Catalysts Containing Vanadium Pentoxide

by Takashi Yamashita**, Sadayoshi Ninagawa** and Tetsuya Kato**

Summary: The probability of acetic acid synthesis from *n*-butenes and isobutene was studied with V_2O_5 -binary catalysts. As a second component, following atoms were added to V_2O_5 in the form of oxide or metal; Rh, B, Cr, Nb, Zn, Pd, Ta, Zr, Si, Ni, Ge, Fe, Ca, Pt, W, Li, Cd, As, Co, Te, Mg, Mn, Mo, Cu, Ag, P, Ba, Ti, Sn, Al, and Sb.

In the presence of water, *n*-butenes and isobutene were oxidized to acetic acid with more than 40% selectivity based on the carbon atom at about 100% conversion of each butene with air containing 3% of butene over V-Cr(3/7), V-Rh(8/2), V-B(5/5) and V-Nb(5/5) catalysts at 270~310°C.

Acetaldehyde, acetone, formaldehyde, maleic acid, formic acid, propionic acid, acrylic acid and citraconic acid were obtained in low yields from *n*-butenes.

On the other hand, from isobutene methacrylic acid and isobutylic acid were formed in addition to above by-products in low yields.

As to the reaction path, acetic acid was considered to be formed via hydration of butenes to form an alcoholic intermediate¹⁾, followed by oxydehydrogenation on the catalyst which had some different active sites to induce other reactions at the same time.

1 Introduction

In the industrial production of acetic acid, some processes have been reported: the oxidation of acetaldehyde formed from ethylene with $PdCl_2$ - $CuCl_2$ type catalysts and the liquid phase oxidation of naphtha or butane and the carboxylation of methyl alcohol. In these processes, the last process seems to be most economical.

In 1966, Brockhaus found a new process of acetic acid synthesis with good yields by vapor phase catalytic oxidation of *n*-butenes with V_2O_5 -binary oxide catalysts such as V-Ti, V-Sn, V-Sb and V-Al²⁾. However, this process required separation of isobutene from *n*-butenes. However, it would be economical if mixed butenes after recovering butadiene from C_4 fraction could be used as the starting materials.

On the other hand, the synthesis of acetic acid in a yield of 20% from isobutene by catalytic gas phase oxidation over V_2O_5 catalyst is known

only by Bretton³⁾. Recently many catalysts have been mentioned in patents⁴⁾ to synthesize acetic acid from *n*-butenes and isobutene.

Accordingly, we investigated to find effective catalyst systems consisting of V_2O_5 and another element for the synthesis of acetic acid from *n*-butenes and isobutene. At the same time, the mechanism of acetic acid formation from butenes over these catalysts was elucidated.

2 Experimental

2.1 Apparatus and Procedure

n-Butenes and isobutene were supplied by Takachiho Chem. Ind. Co.. Air containing 3% olefin and water was introduced into a preheating tube made of Pyrex glass (25 mm i.d. and 20 cm length), which was electrically heated and maintained at ca. 200°C and was jointed with a reactor with a greaseless joint. This joint was convenient at the time the catalyst needed to be exchanged with another. The reactor was made of Pyrex glass (25 mm i.d. and 10 cm in length) and a thermometer well was located at the center of the reactor. The reaction temperature was controlled by heating the tube with an electric heater.

The effluent gas from the reactor was led

* Received June 8, 1976.

(This Paper was Presented in part at the 24th Annual Meeting of the Chemical Society of Japan at Osaka, April, 1971.)

** Central Research Laboratories, Ajinomoto Co., Inc. (Suzuki-cho, Kawasaki-ku, Kawasaki, Kanagawa 210)

Table 1 Catalyst Preparation

X	A	B	C
Cr-1 Rh B Zn Si W Li Ag Pb Ba Cu Mo	NH ₃ VO ₃ /OA aq. V ₂ O ₅ /HCl aq. NH ₄ VO ₃ /aq. NH ₄ VO ₃ /aq. NH ₄ VO ₃ /OA aq. V ₂ O ₅ /EA aq. NH ₄ VO ₃ NH ₄ VO ₃ NH ₄ VO ₃ NH ₄ VO ₃ NH ₄ VO ₃ NH ₄ VO ₃ /OA aq.	CrO ₃ /OA aq. RhCl ₃ /aq. H ₃ BO ₃ aq. ZnCO ₃ aq. SiO ₂ gel WO ₃ /EA aq. LiCl/NH ₃ AgNO ₃ aq. Pb(NO ₃) ₂ aq. Ba(OH) ₂ aq. CuCO ₃ ·Cu(OH) ₂ (NH ₄) ₆ Mo ₇ O ₂₄ /OA aq.	Mix. of A and B was evaporated to dryness.
Cr-2 Nb Ta Zr Fe Ti Sb	V ₂ O ₅ /OA aq. V ₂ O ₅ /HCl aq. V ₂ O ₅ /HCl aq. V ₂ O ₅ /HCl aq. V ₂ O ₅ /HCl aq. V ₂ O ₅ /HCl aq. V ₂ O ₅ /HCl aq.	Ac ₂ Cr aq. Nb ₂ O ₅ /HCl aq. TaCl ₅ /HCl aq. ZrCl ₄ /HCl aq. FeCl ₃ /HCl aq. TiCl ₄ /HCl aq. SbCl ₃ /HCl aq.	Mix. of A and B was neutralized with NH ₃ and the precipitate was washed with water.
Ni Sn	V ₂ O ₅ /EA aq. V ₂ O ₅ /EA aq.	NiCl ₂ aq. SnCl ₂ aq.	Mix. of A and B was neutralized with EA or HCl and the precipitate was washed with water.
Pd Pt Bi Ge Mn Te	V ₂ O ₅ /HCl aq. V ₂ O ₅ /HCl aq. V ₂ O ₅ /HCl aq. V ₂ O ₅ /HCl aq. V ₂ O ₅ /HCl aq. V ₂ O ₅ /HCl aq.	FdCl ₂ /HCl aq. HPtCl ₆ /HCl aq. BiCl ₃ /HCl aq. GeCl ₄ /HCl aq. Ac ₂ Mn/aq. TeO ₂ /HCl aq.	Mix. of A and B was neutralized with NH ₃ aq. and the solution was evaporated to dryness.
Ca Mg Cd Co	V ₂ O ₅ /EA aq. V ₂ O ₅ /EA aq. V ₂ O ₅ /EA aq. V ₂ O ₅ /EA aq.	CaCl ₂ /aq. MgCl ₂ /aq. Ac ₂ Cd/aq. Co(NO ₃) ₂ /aq.	Mix. of A and B was neutralized with EA and the solution was evaporated to dryness.

EA; Ethanolamine, OA; Oxalic acid, Ac; CH₃COO

through a water condenser and then to a trap cooled with ice water. The condensed products and the water in the scrubber were made up to 100 ml for analysis as will be described later.

The outlet gas was analyzed as described elsewhere. The experimental data of a catalyst was obtained after air oxidation of *sec*-butyl alcohol (*sec*-BuOH) with water at 250~300°C under atmospheric pressure for 10~15 hr.

In the screening of a catalyst, its activity was measured at intervals of about 20°C and the critical temperature at which total acid was obtained in the maximum yield was taken. The reaction temperature was measured at the highest position of the catalyst bed.

When ethylene, propylene, butadiene and butene were oxidized, 1 vol% of *n*-butane was mixed to the reaction gas. Being stable to oxidation under the investigated conditions, *n*-butane was used as a standard gas for gaschromatographic analysis of olefins. In the oxidation of *sec*-BuOH, methyl ethyl ketone (MEK), diacetyl, isopropanol (*i*-PrOH), and acetaldehyde (AcH), 1.0 mol/l aqueous solution of these compounds

was fed with air at a constant rate.

2.2 Preparation of Catalysts

All chemicals were reagent grade and were used without further purification. **Table 1** shows the methods of preparation of the various catalysts. Solution A and solution B were treated with a preparation C. The resulting product was dried and calcinated to oxide or metal in air at 500~550°C for 5 hr. The catalysts thus obtained were used in sizes from 16 to 30 mesh. When the calcinated catalyst was a powder, it was pressed at 10~15 t/cm² and crashed to the size of from 16 to 30 mesh. V₂O₅ catalyst was prepared as follows. An aqueous solution of V₂O₅ in hot oxalic acid was concentrated and the resulting residue was calcinated in air at 500~550°C for 5 hr. V₂O₃ catalyst was prepared by reduction of the V₂O₅ catalyst with hydrogen at 500°C for 5 hr. A microspherical catalyst of V-Cr (3 : 7) was prepared as follows.

An aqueous solution of vanadyl oxalate and acetyl chromate was adjusted to pH 10 with conc. NH₄OH (28%) and then digested over-

night at room temperature. The resulting precipitate was filtered and washed. This gel was allowed to mix with an aluminium hydroxide gel free from chloride ion using a colloidal mill with water, and the resulting homogeneous gel was dried with a spray dryer to a dark-green microspherical powder, which was calcinated in air at 500~550°C for 5 hr.

2.3 Analysis

In the screening of a catalyst, gas products, total acid, AcH and acetic acid (AcOH) were quantitatively analyzed as follows. The difference between the total acid and AcOH was regarded as maleic acid (MA) in the oxidation of *n*-butene or *sec*-BuOH and as citraconic acid (CA) in the oxidation of isobutene. In order to analyze the reaction products rigorously the following methods were used.

Total acid; titrated with 0.1 N NaOH solution.

CO; gas chromatographed over molecular sieve column.

CO₂; gas chromatographed over silica gel column.

Olefins and *n*-butane; gas chromatographed over V. Z. 7.

Folmaldehyde; titrated with chromotropic acid⁵⁾.

AcH, acetone, *sec*-BuOH, MEK, diacetyl; gas chromatographed over 3% carbowax 20M on Porapak Q.

Formic acid; titrated with potassium permanganate after steam distillation⁶⁾.

AcOH, propionic acid, acrylic acid, MA, methacrylic acid (MAA), isobutyric acid and CA; gas chromatographed over 5% FFAP/Flusin T with glass column.

MA, MMA and CA; quantitatively analyzed UV spectrum at 212 nm. $\epsilon=4,400$ (MAA), 10,550 (MA), 7,500 (CA).

The reaction products were separated by gas chromatography and identified by IR, NMR and gas chromatography using another column. The yield and selectivity of each product were calculated based on the carbon atom. In the oxidation of *sec*-BuOH, conversion and selectivity were calculated based on the consumption of *n*-butenes formed from *sec*-BuOH, because *sec*-BuOH was completely dehydrated to *n*-butenes which was attained in equilibrium under the oxidation conditions.

3 Results and Discussion

3.1 Oxidation of *sec*-BuOH over V₂O₅-X Catalysts

To find a catalyst which has good selectivity to AcOH from *sec*-BuOH, many V₂O₅-binary catalysts systems which contained a second component up to 20% based on the metal were tested. In each case, *sec*-BuOH was completely dehydrated to *n*-butene isomers under the reaction conditions. Apparently the same results were obtained in the oxidation of either *sec*-BuOH or *n*-butenes.

Selectivity to products at 90% conversion of *n*-butenes with many catalysts are shown in Fig. 1~3. The second components which increased the selectivity to AcOH and AcH compared with V₂O₅ catalyst were in the order: Rh>Ta>Ca>W>Si, Nb, Cr>Pd, Li, B, V>

Cat.: 4 ml, Feed; *sec*-BuOH : air : H₂O = 1 : 41 : 58, SV=6, 200 hr⁻¹

●; *n*-Butene conversion was 90%

○; *n*-Butene conversion was 70%

() ; Atomic percentage of X in V/X catalyst except X=20%

Fig. 1 Selectivity to AcOH and AcH from *sec*-BuOH over V/X(8/2) Catalysts

Reaction conditions and notations as in Fig. 1

Fig. 2 Selectivity to AcOH+AcH and MA from *sec*-BuOH over V/X(8/2)

Reaction conditions and notation as in Fig. 1

Fig. 3 Relationship between the Selectivities to CO + CO₂ and AcOH + AcH + MA from *sec*-BuOH over V/X(8/2)

Co, Ge, Fe (**Fig. 1**). On the other hand, many second components which increased the selectivity to MA were in the order: Cu > Pb > Ni > K > Zn, Si, Cd, Fe, Co, Mn > P > Bi > Cr > Ge > B, Ag > V (**Fig. 2**). Complete combustion to CO and CO₂ was depressed in the case of Ba, P, Pb, Cr, Rh, Bi and B (**Fig. 3**).

Although some higher selective catalysts than V₂O₅ catalyst were found to form AcOH and AcH from *n*-butenes, the maximum selectivity to AcOH was only 39% with V-Rh (8 : 2) catalyst. Economically, this level of selectivity is unsatisfactory.

As selectivity to some useful products from olefin generally changes with the composition of a catalyst, all above binary catalysts containing a wider range of second elements were tested. With almost all of the catalysts, *sec*-BuOH was dehydrated to *n*-butenes and MEK was not detected. With V-Co and V-Rh catalysts, MEK was exceptionally found in the product when the second component exceeded over 30~40% of the metal atom. In these cases, different results were obtained in the oxidation of *sec*-BuOH and *n*-butenes, about which the authors will report in a subsequent paper.

Figure 4 shows the optimal compositions of the various binary catalysts over which *sec*-BuOH formed AcOH with the maximum selectivity at 80~100% conversion of *n*-butenes formed from *sec*-BuOH. The selectivity to MA is shown in the same Fig.. AcOH was formed in good yields from *sec*-BuOH with the following catalysts: V-Rh (5 : 5), V-Cr (3 : 7), V-Ti (4 : 6),

() ; Atomic percentage of a second component in V/X Catalyst, Cat.; 4 ml, Feed; *sec*-BuOH : air : H₂O = 1 : 41 : 58, SV = 6, 200 hr⁻¹

Fig. 4 Optimal Composition of Each Binary Catalyst giving AcOH with the Maximum Selectivity from *sec*-BuOH

V-B (5 : 5), V-Pd (98.3 : 1.7) and V-Zn (95 : 5). With V-Cr (3 : 7) catalyst *n*-butenes and *sec*-BuOH gave AcOH with the maximum selectivity of 47% at 98% conversion of *n*-butenes. These results indicate that MA was obtained in small quantities over these catalysts, the active site for allylic type oxidation of olefin still remained on the catalysts.

The relationship between the composition of V-Cr catalysts and the selectivity of products is shown in **Fig. 5**. The temperatures in the Fig. are the optimal values at which *n*-butenes gave the maximum yields of total acid. The V-B catalyst was very hard before use, but it gradually became porous and fragile after several hours of reaction. Almost all of the B₂O₃ in the catalyst had evaporated with steam, and the content of boron was only 100~150 ppm at the time the activity of the catalyst was measured. In spite of the loss of B₂O₃ from the V-B catalyst, the selectivity to AcOH increased to 54% over the V-B (1 : 1) catalyst from 25% over V₂O₅ catalyst. Whether the role of boric acid is mechanical effect such as increasing surface area or essential for the appearance of the active site was not investigated, but the result obtained seems to be of interest in the search of more effective catalysts.

3.2 Oxidation of Isobutene

A number of catalysts have been proposed

Table 2 Oxidation of Isobutene

Cat.	Temp. (°C)	SV (hr ⁻¹)	Conv. (%)	Selectivity		
				AcOH (%)	CA (%)	CO+CO ₂ (%)
V-Cr (5 : 5) ^{a)}	275	3, 100	98.8	47.7	7.6	36.5
	299	6, 200	97.7	37.7	5.4	48.5
V-B (5 : 5)	306	3, 100	99.3	43.7	5.3	46.5
V-Rh (8 : 2)	305	3, 100	97.5	43.0	3.8	50.7
V-Nb (5 : 5)	275	3, 100	96.2	42.3	2.6	42.8
V-Zr (5 : 5)	285	3, 100	96.2	39.7	2.4	56
	298	3, 100	99.0	31.1	5.8	61
V-Zn (95 : 5)	268	3, 100	99.5	38.8	3.6	57
V-Ni (5 : 5)	305	3, 100	99.2	35.5	3.0	61
V-Fe (9 : 1)	290	3, 100	96.2	37.3	8.0	45.9
V-Ti (5 : 5)	265	3, 100	98.0	32.0	3.2	58
V-Sn (6 : 4)	300	3, 100	97.0	33.0	11.2	
V-Bi (9 : 1)	322	3, 100	98.0	34.7	5.4	38.8
V-Pd (98.3 : 1.7)	285	3, 100	98.9	31.9	1.6	48.5
V-Li (9 : 1)	335	3, 100	97.8	33.4	4.5	61
V-Pt (97.2 : 2.8)	290	3, 100	100	23.1	7.3	48.2

a) Prepared as Cr-1 in Table 1.

Feed; Isobutene : air : H₂O = 1.1 : 41 : 58

Cat.: 4 ml, preparation as Cr-2, Feed; Butene: air : H₂O = 1.33 : 44 : 55, SV = 5,600
 ◇; Optimal reaction temp., O; Butene conversion, □; AcOH, ▲; AcH, ●; MA, △; CO+CO₂, ○; CA, ○; Acetone, —; *n*-Butene, ---; Isobutene

Fig. 5 Effect of Atomic Ratio of V/Cr Catalyst on *n*-Butene and Isobutene Oxidation

for the synthesis of methacrolein from isobutene through the allylic type intermediate by vapor phase catalytic oxidation.

Interestingly, Bretton found that AcOH in a yield of 20% was obtained from isobutene over

V₂O₅ catalyst²⁾. Furthermore, Kaneko et al.⁷⁾ recently found that isobutene gave AcOH with selectivity of 15~17% over V-Sn-W (1 : 1 : 0.5) catalyst at a low conversion level. From these facts V₂O₅ itself has the active site to form AcOH from isobutene.

With many V₂O₅-binary catalysts the oxidation of isobutene was carried out and found that isobutene formed AcOH in good yields over some catalysts better than V₂O₅ catalyst. Acetone and CA were the main by-products and methacrolein was little found.

Table 2 shows the results of oxidation of isobutene with some catalysts over which *n*-butenes formed AcOH in good yields. Over V-Cr (5 : 5) catalyst isobutene gave AcOH with the maximum selectivity of 47%. The plot of the selectivity for AcOH from isobutene and that from *n*-butenes gave nearly a linear relationship except V-Pt catalyst. This result suggests that both butenes give AcOH on the same active site and with a similar mechanism. The optimum temperature giving AcOH in the maximum yield from isobutene was higher by about 10~20°C than that from *n*-butene.

The relationship between the catalyst component and the selectivity of products is shown in **Fig. 5** for V-Cr catalyst. The optimal molar ratio of V-Cr catalyst to obtain AcOH with maximum selectivity from *n*-butenes and isobutene respectively was the same composition at the molar ratio V-Cr (3 : 7).

Table 3 Products from Butenes

Cat.	V/Cr(3/7)		V/Cr(3/7)/20% Al ₂ O ₃		
Raw Mate.	<i>n</i> -	<i>i</i> -	<i>n</i> -/ <i>i</i> -(1/1)	mix. b. ^{c)}	
Reactor	Fixed Bed			Fluid. Bed	
Cat. (ml)	4	4	4	60	60
Air (l/hr)	10 ^{a)}	10 ^{a)}	10 ^{a)}	30 ^{a)}	30 ^{b)}
H ₂ O/But. (-)	50	50	50	13	13
Temp. (°C)	267	268	296	242	240
Conv. (%)	99.0	99.5	97.5	99.4	100
1/4 CO + CO ₂	21.0	37.9	31.3	45.0	45.0
1/4 HCOOH	1.03	1.15	1.74	0.93	0.85
1/4 HCHO	1.02	0.90	0.90	—	—
1/2 AcOH	45.4	39.7	35.1	37.5	38.8
1/2 AcH	1.97	0.17	2.11	0.94	0.97
3/4 C ₂ H ₅ COOH	0.10	0.017	0.013	tr.	tr.
3/4 C ₃ H ₇ COOH	0.36	0.011	0.29	0.0005	0.0004
3/4 CH ₃ COCH ₃	0.36	1.91	1.39	1.10	1.36
<i>i</i> -C ₃ H ₇ COOH	tr.	0.012	tr.	tr.	tr.
<i>i</i> -C ₃ H ₇ COOH	tr.	0.036	0.014	0.0004	0.0003
MA	3.90	tr.	6.86	0.68	1.19
5/4 CA	0.30	0.77	0.10	1.37	1.47

a) Contained 3% *n*- or isobutene in air

b) Contained 3.48% mixed butene in air (3% as butenes)

c) *n*-Butene (41.3%), Isobutene (44.9%), Butadiene (0.49%)

3.3 Oxidation of *n*-Butenes, Isobutene and Mixed Butenes and By-products from These Olefins

Normal butenes, isobutene, mixed butenes (*n* : *i* = 1 : 1) and spent butene were oxidized over V-Cr catalyst in fixed bed and by fluidization. The results are shown in Table 3. Not only the main products, but also by-products obtained only in small quantities were quantitatively analyzed.

With regard to the by-products from *n*-butenes and isobutene, the following characteristics were observed. Formic acid and formaldehyde were obtained from *n*-butenes and isobutene with the same selectivity. AcOH, propionic acid, acrylic acid and MA were obtained with higher selectivity from *n*-butenes than from isobutene. Acetone, isobutyric acid, MAA and CA were obtained with higher selectivity from isobutene than from *n*-butenes.

Comparing the results of the fixed bed and fluidized, by-products were obtained with lower selectivity for the latter than the former, and reverse results were observed for overoxidation to CO and CO₂. In the fixed bed experiments, by-products may be stable to overoxidation because of the presence of sufficient quantities of water.

The relationship between the amount of water and selectivity to the products is discussed in another section.

Spent butene and mixed butenes gave AcOH and by-products with the same selectivity. From the results of oxidation of mixed butenes with these catalysts, spent butene gave AcOH and by-products in the following weight ratios: AcOH (100), MA (2—3), CA (0.2—3), AcH (1—3), acetone (0.7—1.3), formic acid (2—3), formaldehyde (1—2) and other C₃ and C₄ acid (0.5).

3.4 Reaction Path of AcOH Formation

With regard to the reaction path of AcOH formation from *n*-butenes and isobutene, an alcoholic intermediate that formed *via* the hydration of butenes is the most plausible path based on the oxidation products of butenes and the similarity of the results of oxidation of olefins and alcohols by Moro-Oka¹⁰⁾ or by Kaneko⁷⁾ with Co-Mo or V-W-X catalysts as shown in Scheme 1 and 2.

Normal butenes may give *sec*-BuOH by hydration, which may result in MEK *via* oxydehydrogenation, and the MEK may be further oxidized to diacetyl. Unstable diacetyl may be hydrated to AcOH and AcH.

The latter may be easily oxidized to AcOH (Scheme 1). In the same way, isobutene may give AcOH *via* *t*-BuOH and acetone (Scheme 2).

In order to form AcOH from butenes in good yields, a catalyst must have several different active sites for each hydration step and for each oxidation step. Whether *n*-butene can be oxi-

Scheme 1

Scheme 2

Table 4 Isomerization of 1-Butene

	N ₂ (l/hr)	Air (l/hr)	H ₂ O ^{b)} (ml/hr)	Temp. (°C)	Distri. of Butene (%)		
					1-bu.	t-2-bu.	c-2-but.
V ₂ O ₃ ^{a)}	50			300	87	5	8
	50		50	300	87	5	8
V ₂ O ₅ ^{a)}		50	50	300	21	49	30
	50		50	275	94.9	0	5.1
	50		50	275	87.4	0	12.6

a) Cat. 4 ml

b) As liquid

dized to AcOH over V₂O₅ and V₂O₅-binary catalysts as expected by the above-mentioned schemes was studied.

3.4.1 Isomerization of *n*-Butene with V₂O₃ and V₂O₅ Catalyst

The isomerization of 1-butene over V₂O₃ catalyst began at 260°C either in the presence or absence of water in a nitrogen stream. After the oxidation of V₂O₃ with air at 350°C for 1 hr, the isomerization of 1-butene increased from 5.1% to 12.6% in the presence of water under nitrogen at 250°C. In the presence of water and air, it increased to 79% and the distribution of *n*-butene isomers attained equilibrium (Table 4).

These results suggest that acidity of V₂O₅ is greater than that of V₂O₃ and that, only with V₂O₅ catalyst, water participates in the appearance of acidity, but oxygen plays an important role in the appearance of acidity of the catalyst, that is, the oxidation-reduction system of the

catalyst may relate to the appearance of acidity of the catalyst.

3.4.2 Effect of Water on the Selectivity to AcOH

Generally in a catalytic oxidation of olefins, water effectively depresses the oxidation of the intermediate. In this oxidation reaction, water may be a reagent in the Schemes 1 and 2 and may participate in the appearance of acidity of the catalyst. The object of this study was to determine the minimum amount of water needed to form AcOH from *n*-butene and isobutene in the maximum yield. The experiment to prove participation of water in the hydration of butenes with V-Cr catalyst was not performed by the tracer technique as had been done in the oxidation of propylene over SnO₂-MoO₃ catalyst by Moro-oka¹⁾. Figure 6 shows the relationship between the amount of water and the selectivity of products with V-Cr (3 : 7) catalyst.

Cat.; V/Cr(3/7) 4 ml, preparation as Cr-2, Feed; 10 l/hr air containing 3% butene, Notations as in Fig. 5, —; *n*-Butene, ---; Isobutene

Fig. 6 Effect of Steam Addition on *n*-Butene and Isobutene Oxidation

When the molar ratio of H_2O /butene was over 10, both *n*-butene and isobutene gave AcOH with good selectivity, and deep-oxidation to CO and CO_2 was depressed. The selectivity to MA from *n*-butenes and to CA from isobutene gradually increased from 1.5% to about 4%.

3.4.3 *n*-Butene Conversion and Products Selectivity

Figure 7 shows the relationship between the conversion of *n*-butene and the selectivity of products over V_2O_5 and V-Cr (5 : 5) catalyst. The following characteristics were observed. (i) *n*-Butenes were oxidizable at lower temperatures over V-Cr (5 : 5) than over V_2O_5 catalyst by 40~50°C. (ii) The selectivity to MA was constant over V_2O_5 catalyst, but over V-Cr (5 : 5) catalyst it decreased with the increase in conversion of *n*-butenes. These results show that MA is more easily oxidized to CO and CO_2 over V-Cr than over V_2O_5 catalyst. (iii) The selectivity to AcH increased from 10% (V_2O_5) to 16% (V-Cr 5 : 5) at 88% conversion of *n*-butenes, and it slowly decreased to 5~6% at 100% conversion of *n*-butenes. (iv) The selectivity to AcOH increased with increasing

Reaction conditions and notations as in Fig. 5
—; V/Cr(5/5) preparation as Cr-1, ---; V_2O_5

Fig. 7 Relation between Conversion of *n*-Butene and Selectivity of Products over V/Cr and V_2O_5

conversion of temperature although in the oxidation of 1-butene over V-Sn-W (1 : 1 : 0.5), Kaneko⁷⁾ found a different result, that is, the selectivity to AcOH only depended on the reaction temperature and not on the conversion of 1-butene and contact time. The increased selectivity was not explicable from the decrease in the selectivity of AcH with conversion. There may be other intermediates giving AcOH beside AcH, for example, MEK, biacetyl, acetone and etc. Which were produced with lower selectivity than that of AcOH as shown in Table 3.

Because of low selectivity of these intermediates they were not analyzed.

The material balance of the main products, which were CO, CO_2 , AcH, AcOH and other acid, was only 73~90% for V-Cr (5 : 5) and 64~99% for V_2O_5 . The deviation of the material balance from 100% was large at low conversion levels. This finding indicates the existence of small quantities of various intermediates giving AcOH or other products. Figure 8 shows the relationship between conversion of *n*-butenes and selectivity of products over V-Ti (4 : 6) catalyst over which AcOH was obtained from *n*-butenes with good selectivity that was next

Cat.; 14 ml, Feed; *n*-Butene : air : H₂O = 1.1 : 36 : 63, —; SV = 1,700 hr⁻¹, ---; SV = 420 hr⁻¹, Notations as in Fig. 5

Fig. 8 Relation between Conversion of *n*-Butene and Selectivity of Products over V/Ti(4/6)

to that over V-Cr catalyst (Fig. 4). The oxidation of *n*-butenes was carried out under more moderate conditions than these of above. The maximum selectivity to AcOH was obtained before the complete conversion of *n*-butenes differing from that over V-Cr catalyst, that is, the maximum selectivity to AcOH was 72% at 84% conversion of *n*-butenes. The deviation of the material balance from 100% was observed at low conversions of *n*-butenes as in the case of V-Cr catalyst, and the deviation diminished with increasing conversion of *n*-butenes.

In the oxidation of 1-butene over V-X, V-Su-X and V-Sn-W catalysts⁷⁾, the deviation of material balance was similarly observed.

3.4.4 Oxidation of MEK and Diacetyl

The reactivity of MEK and diacetyl over V₂O₅ catalyst was studied to compare with the reactivity of *n*-butenes or *sec*-BuOH, because MEK and diacetyl were supposed to be the plausible intermediates to form AcOH from *n*-butenes. At low temperatures where *sec*-BuOH could not be dehydrated, only a trace of MEK was detected by gas chromatography. At high temperatures, MEK could not be detected by gas chromatography and *sec*-BuOH was completely dehydrated to *n*-butenes. These facts

Table 5 Oxidation Over V₂O₅ Catalyst

	Temp. (°C)	Conv. (%)	Selectivity (%)			
			AcOH	MA	CO+CO ₂	AcH
C = C - C - C ^{a)}	345	47.2	7.2	22.4	35	10
C - C = C - C ^{a)}						
$\begin{array}{c} \text{OH} \\ \\ \text{C} - \text{C} - \text{C} - \text{C}^{\text{a)}} \end{array}$						
$\begin{array}{c} \text{O} \\ \\ \text{C} - \text{C} - \text{C} - \text{C}^{\text{b)}} \end{array}$	285	96.0	26.9		35	0
	220	95.0	65.6		12	0
$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{C} - \text{C} - \text{C} - \text{C}^{\text{b)}} \end{array}$	285	89.0	70.5		15	0
	265	86.5	70.0		8	0

a) Cat.; 4 ml, *sec*-BuOH (Butene) : air : H₂O = 1.1 : 44 : 55, SV = 27,000 hr⁻¹

b) Cat.; 4 ml, MEK (diacetyl) : air : H₂O = 1.2 : 40 : 59, SV = 5,800 hr⁻¹

suggest that *sec*-BuOH is not present in the vapor phase and even if it is present, most of it will be strongly adsorbed on the surface of the catalyst.

Table 5 shows the results of oxidation of *n*-butene, MEK and diacetyl. The oxidation of MEK proceeded under more moderate conditions than those of *sec*-BuOH or *n*-butene. At 285°C, the conversion of MEK was 96% and the selectivity to AcOH was 26.9%. Under moderate conditions the selectivity to AcOH increased to 66% at 95% conversion of MEK. Only a trace of diacetyl was detected by gas chromatography. On the other hand, diacetyl was more easily oxidized than MEK to give AcOH with selectivity of 70% at 86.5% conversion. This finding was in accord with the fact that *sec*-BuOH, MEK and diacetyl were not detected in the oxidation of *n*-butenes.

3.4.5 Oxidation of Ethylene, Propylene and Butadiene

In previous papers, AcOH was produced from ethylene⁸⁾ and propylene⁹⁾ via catalytic oxidation with air over solid acid catalysts containing molybdic acid or tungstic acid. Ozaki et al.¹⁰⁾ found that olefins and alcohols were oxidized to ketone with good selectivity over Mo-Sn and Mo-Co catalysts coproducing AcOH and AcH in low yields.

With regard to V₂O₅-binary catalysts, these catalysts may be good ones for producing AcOH from ethylene or propylene as from butenes, since they have strong activity for oxidation of

Cat.: 4 ml V/Cr (5/5) preparation as Cr-1 Feed;
olefin : air : H₂O = 1.33 : 44 : 55, SV = 5, 600 hr⁻¹,
△; *n*-Butene, □; Isobutene, ▲; Butadiene, ○;
Propylene, ◇; Ethylene, —; Conversion, ---;
Selectivity

Fig. 9 Reactivity of Olefins and Selectivity to Acid over V/Cr Catalyst

MEK to AcOH than the above MoO₃-SnO₂ and MoO₃-Co₂O₃ catalysts.

Figure 9 shows the results of oxidation of olefins over V-Cr (5 : 5) catalyst. The reactivity of each olefin decreased with the shortening of the chain length. This tendency is like that of hydration of olefins. As would be expected, ethylene and propylene formed AcOH with good selectivity as butenes. Butadiene formed only MA, and it did not form methyl vinyl ketone, diacetyl and AcOH, which should be obtained if butadiene was oxidized according to Scheme 1.

The selectivity to acid from these olefins increased with increasing conversion or reaction temperature as shown in the case of butenes. Each olefin had its critical temperature at which it gave acid with maximum selectivity. These results suggest that, with V-Cr catalyst, AcOH is formed from each olefin by consecutive oxidation. Mono-olefins may be oxidized in the reaction paths shown in Scheme 1 and 2. Even if a catalyst is effective for hydration of olefins and oxydehydrogenation of alcohols as V-Cr catalyst, it also has the active site that is effective for allylic type oxidation of olefins, as seen from the presence of a small amount of MA always

accompanying AcOH in the oxidation of *n*-butenes. Therefore, butadiene was oxidized to MA *via* allylic type oxidation and not to AcOH *via* oxydehydrogenation.

As to the oxidation mechanism of butenes over various catalysts, four mechanism have been proposed. (i) The formation of an allyl radical intermediate to produce butadiene, MA or methacrolein. (ii) The formation of an alcoholic intermediate by hydration of the carbonium ion intermediate to produce MEK, AcH and AcOH^{10,12}. (iii) The formation of a π -complex with the oxide surface and the subsequent scission of the carbon-carbon double bond of butenes with nickel oxide and cobalt oxide catalysts¹³. (iv) The formation of an σ -complex by nucleophilic attack of hydroxyl anion as accepted for oxypalladation of *n*-butene to form MEK¹⁴.

From the product patterns in the oxidation of *sec*-BuOH over various V₂O₅-binary catalysts as shown in **Fig. 4**, the properties of a catalyst changed with a second element. That is, V-Mo (5 : 5), V-Mn (8 : 2), V-P (7 : 3) and V-Al (9 : 1) catalysts were effective to producing MA by mechanism (i). With V-Pd (98.3 : 1.7) catalyst, the selectivity to MA was reduced to 5% but that to AcOH was increased to 38% in comparison with V₂O₅ catalyst in spite of a little addition of palladium. In this case, AcOH may be obtained partly by mechanism (iv). With V-Rh (5 : 5), V-Cr (3 : 7), V-Ti (4 : 6) and V-Nb (5 : 5) catalysts the selectivity to MA was low and the selectivity to AcOH was increased markedly by a second element. In these catalysts, AcOH may be obtained by mechanism (ii) or (iii).

As a representative catalyst that was effective to form AcOH from *n*-butenes and isobutene, V-Cr catalyst was studied comparing it with the V₂O₅ catalyst, as described in 3.4.1~3.4.5, mainly in reference to the reactivity of various olefins and plausible intermediates. Mechanism (ii) is the most plausible one to explain the reaction path of AcOH formation from *n*-butenes, isobutene, propylene and ethylene, but still sufficient experimental data are lacking to disregard mechanism (iii).

References

- 1) Moro-oka, Y., Takita, Y., Ozaki, A., *Bull. Chem. Soc. Japan*, **44**, 293 (1971).
- 2) Brockhaus, R., *Chemie Ing. Tech.*, **38**, 1,039 (1966).

- 3) Bretton, R. H. et al., *Ind. Eng. Chem.*, **44**, 594 (1952).
 - 4) Nihon Gosei, Japan 45-30,802; 31,165; 41,367; 41,570; 41,571; 41,569 (1970). Ajinomoto, Japan 47-10,691 (1972), U.S. 3,704,317 (1972), Brit. 1,234,896 (1971), Toa Nenryo Kogyo, Japan 49-40,446 (1974), Kuraray, Japan 47-10, 692~5 (1972).
 - 5) Mactadyen, D. A., *J. Boil. Chem.*, **158**, 107 (1945).
 - 6) JISK-1,351 (1956).
 - 7) Kaneko, K. et al., *Bull. Japan Petrol. Inst.*, **16**, 17(1974).
 - 8) Societe Edison, Ital., 640,456 (1962); Ruhchemie, Fr., 1,395,378 (1965).
 - 9) Buitin, J. *J. Catalysts*, **10**, 188 (1968), Japan 40-8,523, 10,569 (1965).
 - 10) Moro-oka, Y., Tan, S., Ozaki, A., *Bull. Chem. Soc. Japan*, **41**, 2,820 (1968); *J. Catalysis*, 12,291 (1968); **17**, 125,132 (1970).
 - 11) Batist, Ph. A. et al., *J. Catalysis*, **5**, 55 (1966).
 - 12) Takita Yu. et al., *Shokubai*, **18**, 13 (1976).
 - 13) Moro-oka Y. et al., *J. Am. Chem. Soc.*, **89**, 5124 (1967).
 - 14) Henry P. M., *ibid.*, **86**, 3246 (1964).
-