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Effect of preparation and reaction condition on the catalytic performance of Mo–V–Te–Nb catalysts for selective oxidation of propane to acrylic acid by high-throughput methodology

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ABSTRACT

Combinatorial screening technique has been applied to investigate the catalytic activity and selectivity of quaternary Mo–V–Te–Nb mixed oxide catalysts treated with various chemicals during preparation for selective oxidation of propane to acrylic acid. The catalyst libraries were prepared by the slurry method and catalytic activities were examined in 32-channel high-throughput screening reactor system coupled with a mass spectrometer and/or gas chromatograph.

The obtained results provided substantial evidence that the sample preparation condition would have strong effect on the catalytic performance for propane selective oxidation. Among screened samples, Mo–V–Te–Nb treated with HIO_3 solution presented a better performance. The reaction results of promising catalysts selected from the libraries were applied to further scale-up of the system and confirmed catalytic performance. Quantification of the result of Mo–V–Te–Nb treated with HIO_3 solution was realized by combination of GC and MS and relationship between the MS data and the GC results can be established.

1. Introduction

The economic advantages of switching to a propane feedback in the production of acrylic acid have been a motivating force for extensive research studies focused on developing alkane partial oxidation catalysts. Among these catalysts, MoVTe(Sb)NbO system is known to be efficient for selective oxidation of propane into acrylic acid [1–3]. In industry, acrylic acid and its esters are important monomers for the manufacture of homo- and co-polymers such as paints adhesives, textile finishing, leather processing, and superabsorbents [4]. The most important industrial process for the synthesis of acrylic acid involves two steps, which consist of the propene oxidation to acrolein followed by the oxidation of acrolein to acrylic acid [5].

The direct oxidation of propane to acrylic acid using molecular oxygen has attracted great attention as a single step process, since propane is much cheaper than propene. Botellar and coworkers [6,7] proposed that the MoVTeNb catalyst prepared by hydrothermal synthesis is active for acrylic acid production and Grasselli et al. [8] have confirmed the high performance of catalysts prepared by the hydrothermal process. Although the MoVTeNb catalyst is known to be effective for this reaction, catalytic performance of the same is not yet sufficiently investigated for industrial application [9]. In addition, the activity of this catalyst is affected by a wide range of working conditions (different gas compositions, temperature, etc.), and preparation condition. Considering these facts, one can concluded that not only the composition of catalysts but also some specific structures of the resulting catalysts are closely related to their catalytic performance. Therefore, it is clear that the improvement of the catalytic performance of these catalysts goes through a better knowledge of structural aspects and catalyst preparation procedure.

Combinatorial screening is efficient way to evaluate the catalytic performance within a short time and it is applied to search a new heterogeneous catalyst in many research fields [10–18]. We have successfully adopted the high-throughput screening method for selective oxidation of propane to acrylic acid by primary screening in previous report [19]. Here, we employed a home-built 32-channel tubular reactor to optimize the catalytic properties of the catalyst libraries based on Mo–V–Te–Nb. In addition, we focused on discussing the effect of preparation and reaction condition on the catalytic performance.

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2. Experimental

2.1. Catalyst preparation

1.261 g of ammonium molybdate tetrahydrate, 0.276 g of ammonium vanadate and 0.361 g of telluric acid were dissolved in 50 ml of distilled water with vigorous stirring (solution A, Mo–V–Te mixture). Predetermined amount of ammonium niobium oxalate, nickel nitrate, iron nitrate, cerium nitrate, copper nitrate, and cobalt nitrate, each dissolved in 4 ml of distilled water separately to obtain six different metal precursor solutions (solution B1–6). The solution A and each solution B1–6 were mixed and stirred for 3 h. After 3 h, 0.25 g of nitric acid added to the resulting solutions and continuous stirred for another 4 h (1st library). In this step, predetermined amount of chemicals (H_2O_2, Oxone, I_2, MCPBA, V_2O_5, $NaHB(OAc)_3$, N_2H_4, $LiAlH_4$, $NaBH_4$) were added instead of nitric acid for preparation of the 2nd library. I_2 and HIO_3 were added to Mo–V–Te–Nb mixed oxide catalyst for the 3rd library. After stirring, sample catalysts were dried in a rotary evaporator and any remaining moisture in the catalyst were removed overnight in an electric oven at 80 °C. After drying, the catalysts were calcined at 200 °C for 2 h in the ambient condition and at 600 °C for 2 h in nitrogen condition (heat—rate: 5 °C/min). Thus, the final $Mo_1V_{0.33}Te_{0.22}M_{0.11}O_x$ (M = Nb, Ni, Fe, Ce, Cu, and Co) catalysts were obtained.

2.2. Reaction system: 32-channel tubular reactor

A computer-controlled 32-channel tubular reactor system was developed for high temperature (>500 °C) catalytic reactions as shown in Fig. 1. We used quartz tubes with the external diameter size of 0.25 in. as an internal reactor in the heating block and the catalysts were loaded in the quartz reactor.

In order to maintain the same flow rate in the reactor channels, a capillary with 1.6 mm o.d., 0.12 mm i.d., and 500 mm long was connected between the 16-port 2-position valve and the inlet of each tubular reactor for dampening the effect of different pressure drop over the catalyst beds.

The reaction temperature was controlled by thermocouples placed inside each tubular reactor and independent PID controller. The preheated reactant feed could be introduced from the top of the reactor into each tubular reactor sequentially. During testing process, all the catalyst beds could be operated for an identical contact time that is a basis for comparing the results from different streams. When the reactant gas was flowing through one of the channels, He gas was flowing through the others to prevent the catalyst from being oxidized in the air (O_2) at the high reaction temperature. The product gas was analyzed by quadrupole mass spectrometer (QMS, Hiden HPR-20) and 10 masses (propane: $m/z = 29$; propene: $m/z = 41$; acrylic acid: $m/z = 72$; acetic acid: $m/z = 60$; acrolein: $m/z = 58$; carbon dioxide: $m/z = 44$; acetone: $m/z = 43$; carbon monoxide: $m/z = 28$; oxygen: $m/z = 32$; water: $m/z = 18$) were monitored. In order to obtain quantitative results, a GC equipped with two six-port valve was combined with the QMS. The GC analyses were performed with a HP-5890 using three columns: Porapok Q and Gaskuropack 54 columns in series, where CO, CO_2, O_2, and water were analyzed, and HP-1 capillary column for analysis of the condensate.

Propane conversion was calculated as the number of moles of 'C' in all products and the selectivity was taken as the fraction of the mole of 'C' in the product with respect to the total moles of 'C' in all products.

2.3. Characterization

Sample catalysts were characterized by the following analytical technique: X-ray diffraction (XRD) patterns were collected with Bruker-AXS X-ray diffractometer (D8 DISCOVER with GADDS for combinatorial screening) with Cu Kα radiation (λ = 1.5405 Å). Brunauer–Emmett–Teller (BET) surface areas were measured by through N_2 adsorption at 77 K using a Micromeritics ASAP 2010 instruments. Surface analysis was performed by X-ray photoelectron spectrometer (LHS-10, SPECS GmbH) equipped with a multiplate channel detector using Mg Kα radiation (200 W).

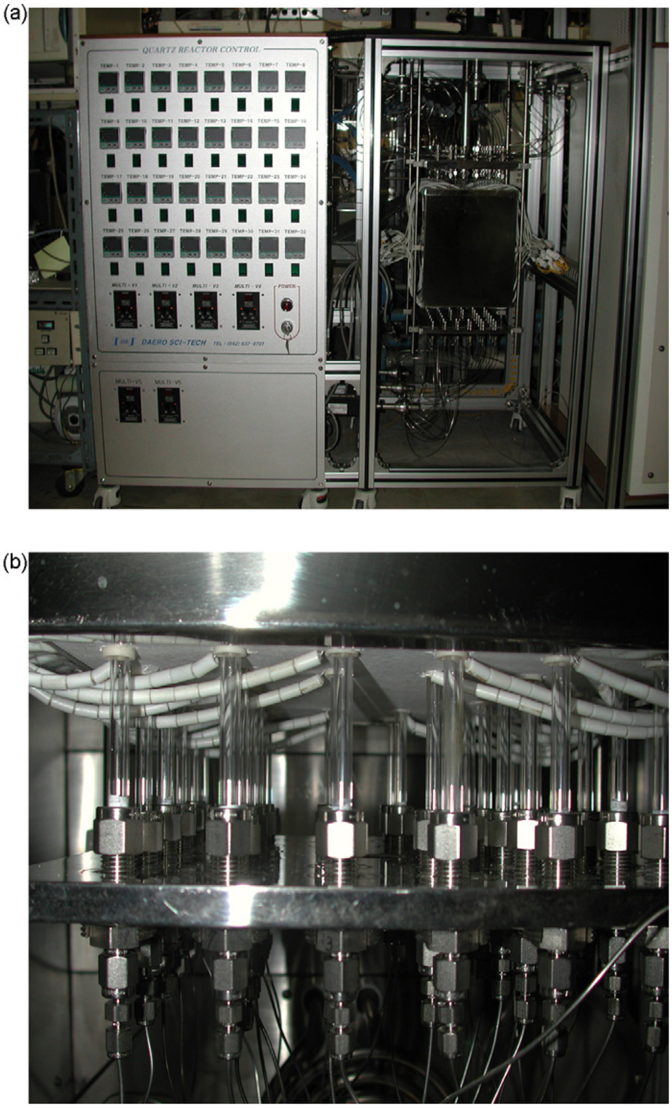

Fig. 1. 32-Channel tubular reactor system (a) front view and (b) inside view.

3. Results and discussion

3.1. Combinatorial screening of 1st and 2nd libraries and validation of results by conventional method

3.1.1. Effect of metal components on catalytic performance of Mo–V–Te–M (M = Nb, Ni, Fe, Ce, Cu, and Co) catalysts—1st library

Table 1 shows the catalytic performance of Mo–V–Te–M (M = Nb, Ni, Fe, Ce, Cu, and Co) catalysts. Only Mo–V–Te–Nb catalyst shows considerable conversion of propane and yield of acrylic acid (AA). As the temperature is elevated from 350 to 425 °C, the conversion of propane increases from 23 to 56%, and yield of AA increases at first, passing through the maximum at 400 °C, then, decreases at 425 °C. Meanwhile, selectivity of AA

Table 1

Catalytic performance of Mo–V–Te–M (M = Nb, Ni, Fe, Ce, Cu, and Co) mixed oxide catalysts 520 °C (C_3H_8:O_2:H_2O:He = 5.3:9.3:0:85.4; GHSV = 6470 h^{-1}; AA: acrylic acid; AcA: acetic acid; ACR: acrolein)

Sample	Temperature (°C)	C_3H_8 conversion (%)	AA yield (%)	Selectivity (%)					
				C_3H_6	AcA	AA	ACR	CO	CO_2
Nb	350	23.3	16.8	9.5	5.9	72	0	6	6.7
Ni	350	0.5	0	44.5	0	0	0	0	55.2
Fe	350	0.5	0	27.2	0	0	0	8.6	64.2
Ce	350	0.5	0	39.6	0	0	0	0	60.4
Cu	350	0.3	0	41.1	0	0	0	0	58.9
Co	350	0.5	0	36.6	0	0	0	0	63.4
Nb	375	32.5	23.39	7	5	72	0	7	9.1
Ni	375	0.8	0	50.4	0	0	0	5.8	43.8
Fe	375	1.2	0	20.2	0	0	0	8.8	71
Ce	375	1	0	38.6	0	0	0	0	61.4
Cu	375	0.6	0	48.7	0	0	0	0	51.3
Co	375	1	0	34.9	0	0	0	0.64	58.7
Nb	400	48	32.67	4.4	3.6	68.1	0	10.5	13.4
Ni	400	1.2	0	51.6	0	0	0	6	42.4
Fe	400	2.5	0	13.8	0	0	0	9.4	76.7
Ce	400	2.5	0	36	0	0	0	2.9	61
Cu	400	1.1	0	46.7	0	0	0	6	47.3
Co	400	2.1	0	30.7	0	0	0	7.2	62.1
Nb	425	56	27.74	3.3	2.7	49.5	0	18.1	26.4
Ni	425	2	0	46.3	0	0	0	6.8	46.9
Fe	425	5.5	0	9	0	0	0	8.8	82.2
Ce	425	5.4	0	29.7	0	0	0	2.9	67.3
Cu	425	2.3	0	41.4	0	0	1.9	7.1	49.6
Co	425	3.7	0	25.5	0	0	0	7.4	66.3

decreases from 72 to 49.5% with a relative increase of the selectivity of CO_x (CO + CO_2) from 13 to 45%. The selectivity of propylene and acetic acid (AcA) also decreases slightly and the amount of acrolein (ACR) formation is negligible. Lin et al. [20] reported that the order of reactivity of reactants was propane < AcA = AA < propylene < acetone (ACT) < ACR on the MoVTeNb catalyst. In this regard, increasing temperatures would accelerate the overoxidation of AA and other intermediate to CO_x, which leads to a decrease of AA selectivity and increase of CO_x formation. On the other hand, Nb-free Mo–V–Te catalysts show a lower catalytic performance and propane conversion is below 6% at all the reaction temperatures. The major product is propylene and CO_x, which indicates that Nb-free Mo–V–Te–M (M = Ni, Fe, Ce, Cu, and Co) catalysts induced the dehydrogenation of propane and total oxidation. Ueda et al. reported that similar propane conversion was observed for Mo–V–Te, and Mo–V–Te–Nb oxide catalysts over a large temperature ranges (280–400 °C); the AA selectivity, however, was highly dependent on the constituents. The highest selectivity of AA was observed for the quaternary oxide than that of ternary oxide [21]. These results indicate that Mo–V–Te systems form the active site for propane selective oxidation and the role of Nb as a constituent element is clarified. Moreover, it has been observed that Nb-containing catalysts present a better yield of AA than the corresponding Nb-free catalysts, probably due to a consequence of the different reaction product stabilities in the presence or in the absence of Nb in the catalysts. As a result, the catalytic performance of Mo–V–Te–Nb catalyst seems to be enhanced in the presence of Nb.

In order to compare the structures of Mo–V–Te–M (M = Ni, Fe, Ce, Cu, and Co) and Mo–V–Te–Nb, XRD analysis were performed as shown in Fig. 2. The pattern of Mo–V–Te–Nb is very similar to that reported for the most efficient catalysts, which correspond well to the mixture of 60% M1 and 40% M2 [22]. Two intense peak at $2\theta = 22.1^\circ$ and 28.2° related to M1 + M2 phase in addition to more than five peaks (the most intense peak appear at $2\theta = 22.1^\circ$, 28.2°, 24.8°, 36.1°, 45.1°, and 50.1°) are observed in Mo–V–Te–Nb.

On the other hand, the peak at $2\theta = 23.4^\circ$, 25.8°, 27.2°, and 36.1° are related to M2 phase observed in the catalysts without Nb while the peak at $2\theta = 27.2^\circ$ is not observed in Mo–V–Te–Nb catalyst. It is concluded that unique performance of Mo–V–Te–Nb catalyst is related to M1 + M2 where M1 phase is richer than M2 because the catalysts contained more M2 phase are inactive to propane dehydrogenation and have only a positive effect on the selectivity of acrylic acid [23].

3.1.2. *Effect of chemical treatment on catalytic performance of Mo–V–Te–Nb during preparation—2nd library*

Based on the results from 1st library, the effects of different chemical treatment on catalytic performance of Mo–V–Te–Nb during preparation were studied. The catalyst library is composed of Mo–V–Te–Nb catalysts treated with nine different chemicals during preparation, four reference catalyst (Mo–V–Te–Nb mixed oxide prepared by various sol–gel method donated by LG Chem.), and catalyst without nitric acid treatment during preparation, as shown in Table 2. Commercial alumina powder was loaded to channels numbered of 1, 3, 5, 6, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29 for background.

The actual results of screening test at 450 °C are presented in Fig. 3. In this figure, the mass abundances are presented in terms of arbitrary units as a function of reactor channel number or time. MS signal peak corresponds to levels present in the reactor effluent and the increase and/or decreases represent signal acquired during the transit of the multi-position valve from one channel to another. As evident from Fig. 3, decrease in propane signals are always associated with the decrease in the oxygen signal, suggesting the close coupling of these species in the propane oxidation, which is the basic reaction to produce AA. However, for some catalysts while propane and oxygen signals are significantly decreased, only small AA signals are observed. An example of this behavior can be seen in channel #22. The catalysts loaded in channels #2, #4, #16, #18, #22, and #30 have the tendency to make the byproducts (acetic acid (AcA), $m/z = 60$) and CO_2. Because the CO_2 is a product

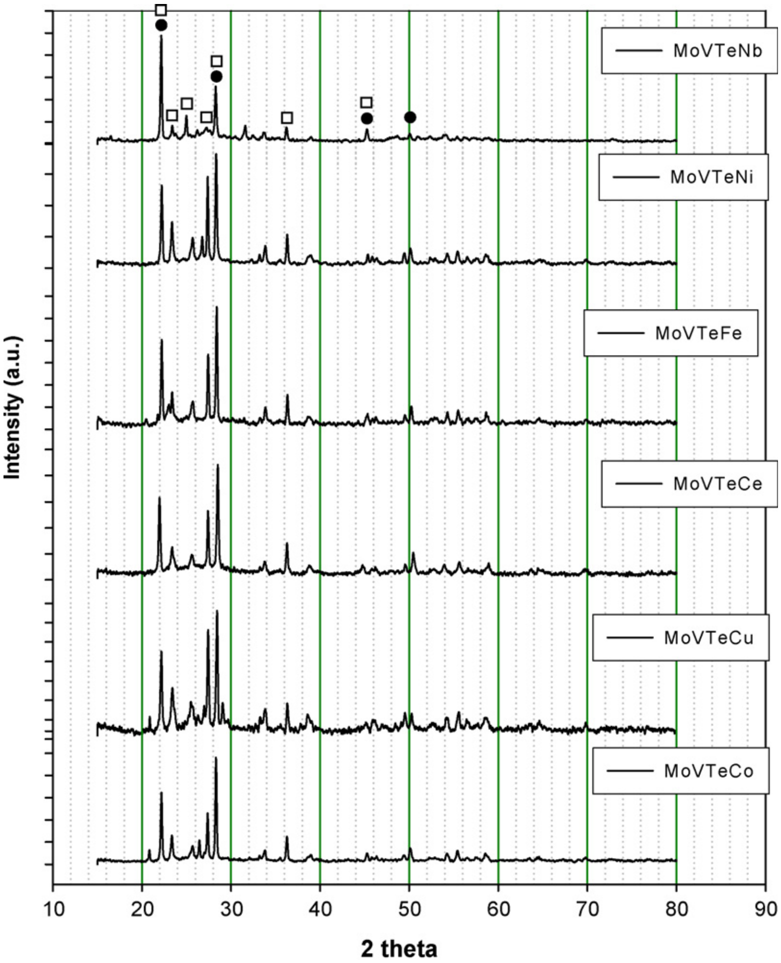

Fig. 2. XRD patterns of Mo–V–Te-based catalysts ((●) M1 phase; (□) M2 phase).

originated from undesirable total oxidation reaction, these samples have been excluded from potential candidate. Among these catalysts, #8 and #12 show the high AA and ACR formation associated with low formation of CO_2 and AcA. Comparing these two catalysts, #8 (treated with H_2O_2) shows higher propane conversion and oxygen consumption than that of #12 but shows similar AA and ACR formation. These results indicate that the selectivity of AA and ACR is higher for #12 than that of #8. Therefore, we have selected the catalyst (#12, treated with I_2) as a potential candidate. In order to test the effect of reaction temperature of #12 on the formation of AA, the catalytic activity of this library was tested at a reaction temperature of 430–490 °C as shown in Fig. 4. The catalyst #12 shows the highest formation of AA in the range of all the reaction temperatures. The formation of AA is greatly affected by the reaction temperature and a similar result was obtained from #18 (Ref-3).

Table 2
Mo–V–Te–Nb mixed oxide catalysts library (2nd library) treated with different chemicals during preparation

Channel no.	Added chemical during preparation	Channel no.	Added chemical during preparation
1	Alumina	17	Alumina
2	Ref-1	18	Ref-3
3	Alumina	19	Alumina
4	Ref-2	20	$NaHB(OAc)_3$
5	Alumina	21	Alumina
6	Alumina	22	N_2H_4
7	Alumina	23	Alumina
8	H_2O_2	24	HNO_3
9	Alumina	25	Alumina
10	Oxone	26	$LiAlH_4$
11	Alumina	27	Alumina
12	I_2	28	$NaBH_4$
13	Alumina	29	Alumina
14	MCPBA	30	Ref-4
15	Alumina	31	Alumina
16	V_2O_5	32	No nitric acid treatment

3.1.3. *Conventional testing of MoVTeNb treated with I_2 solution without H_2O addition*

High-throughput techniques are very valuable in a preliminary stage of the screening of large libraries of catalysts. However, the key-experiments should be repeated with conventional set-up, so as to allow independent validation by other research groups. In the current case, our reactor system has a drawback; mass transfer limitation cannot be considered to be negligible in the miniature reactor and the unexpected slowing down or speeding up of the reaction upon GHSV. Therefore, the most promising catalyst (Mo–V–Te–Nb, I_2 treatment) as selected from 1st library was re-investigated. GHSV changed from 6470 to 2500 h^{-1} to adjust the conventional scale and reactant composition is the same as high-throughput screening.

Catalytic performance of Mo–V–Te–Nb (I_2) catalyst as a function of the reaction temperature without water in conventional testing is given in Table 3. It is clear that the reaction temperatures have strong effects on the product distribution. As the temperature is elevated from 430 to 520 °C, the conversion of

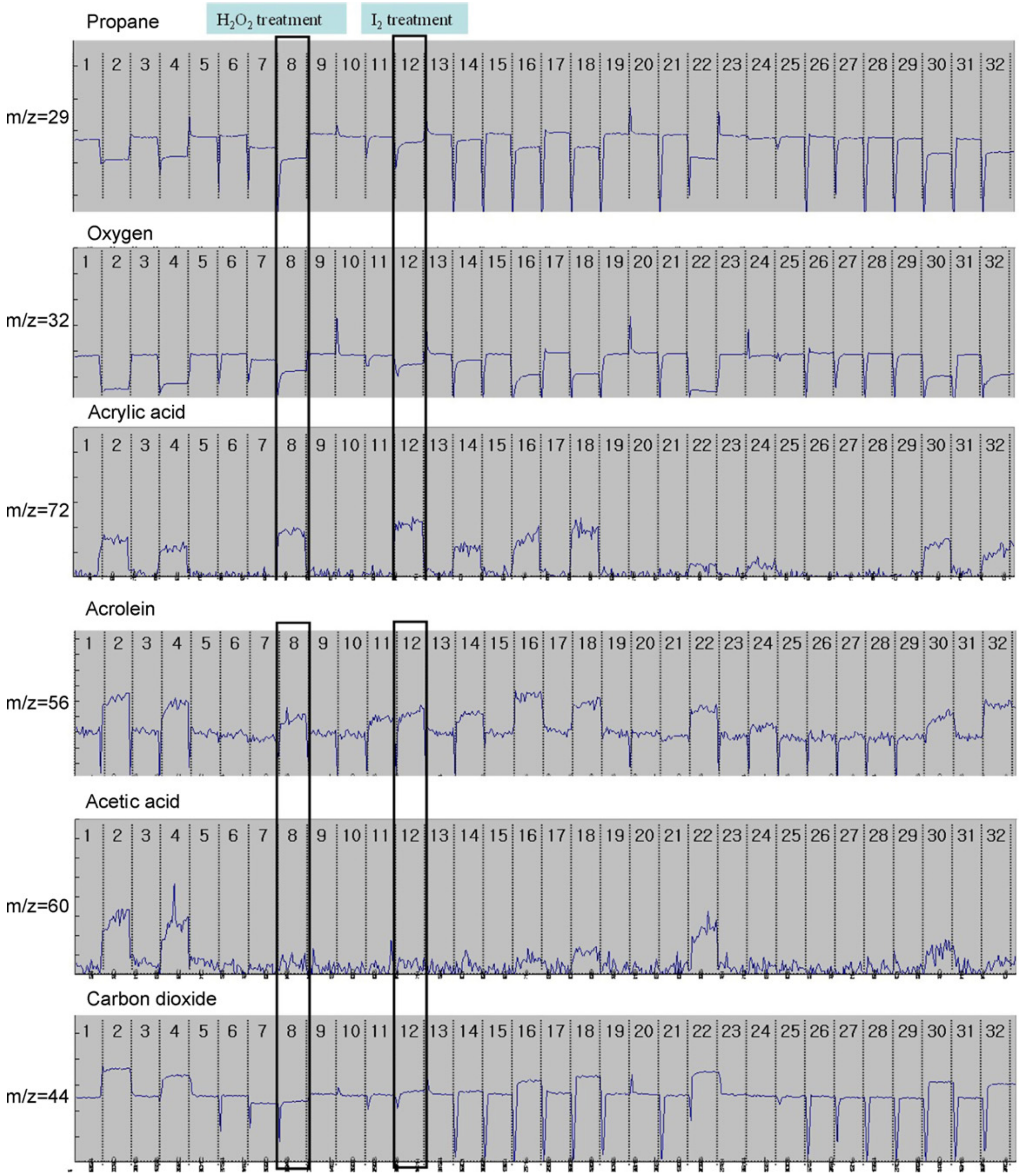

Fig. 3. MS signal intensity of products of propane selective oxidation at 450 °C. (C_3H_8:O_2:H_2O:He = 5.3:9.3:0:85.4, GHSV = 6470 h^{-1}).

propane increases from 0.4 to 22.7%, and the selectivity of AA increases from 7.5 to 19.2% until 460 °C, but it decreases above 460 °C. The selectivity of ACT, and ACR + AcA also decreases slightly. The increased CO_x selectivity from 16.5 to 65.8% is at the expense of propene and AA above 430 °C. It is well known that propane has low activity under low reaction temperature [24,25]. Therefore, high reaction temperatures are necessary to propane activation, which lead to increase the conversion of propane with the temperature elevation. Meanwhile, higher temperature would accelerate the overoxidation of AA, propene, and other intermediate to CO_x, resulting in a decrease the selectivity of them. Due to the reversed contribution of reaction temperature to AA selectivity and propane conversion, the yield of AA reaches the maximum at 490 °C. However, the yield of AA is very low (2.6%). It means that overoxidation of AA occurs in the absence of water in the feed, resulting in negligible AA yield.

Table 3
Catalytic performance of Mo–V–Te–Nb (I_2) in water free reaction at temperatures between 370 and 520 °C at GHSV = 2500 h^{-1} (C_3H_8:O_2:H_2O:He = 5.4:16.1:0:78.5; AA: acrylic acid; AcA: acetic acid; ACR: acrolein; ACT: acetone)

Temperature (°C)	C_3H_8 conversion (%)	AA yield (%)	Selectivity (%)					
			CO_2	C_3H_6	CO	AA	ACR + AcA	ACT
370	0.4	0.1	12.3	53.5	0	7.5	18.0	8.7
400	2.4	0.4	9.3	57.5	0	16.4	9.6	7.3
430	4.9	0.9	8.8	54.8	7.7	19.3	6.2	3.2
460	9.5	1.8	9.9	41.4	24.7	19.2	3.3	1.5
490	14.7	2.6	15.2	33.6	30.8	17.8	1.9	0.8
520	22.7	0.5	26.5	31.6	39.3	2.4	0.3	0.1

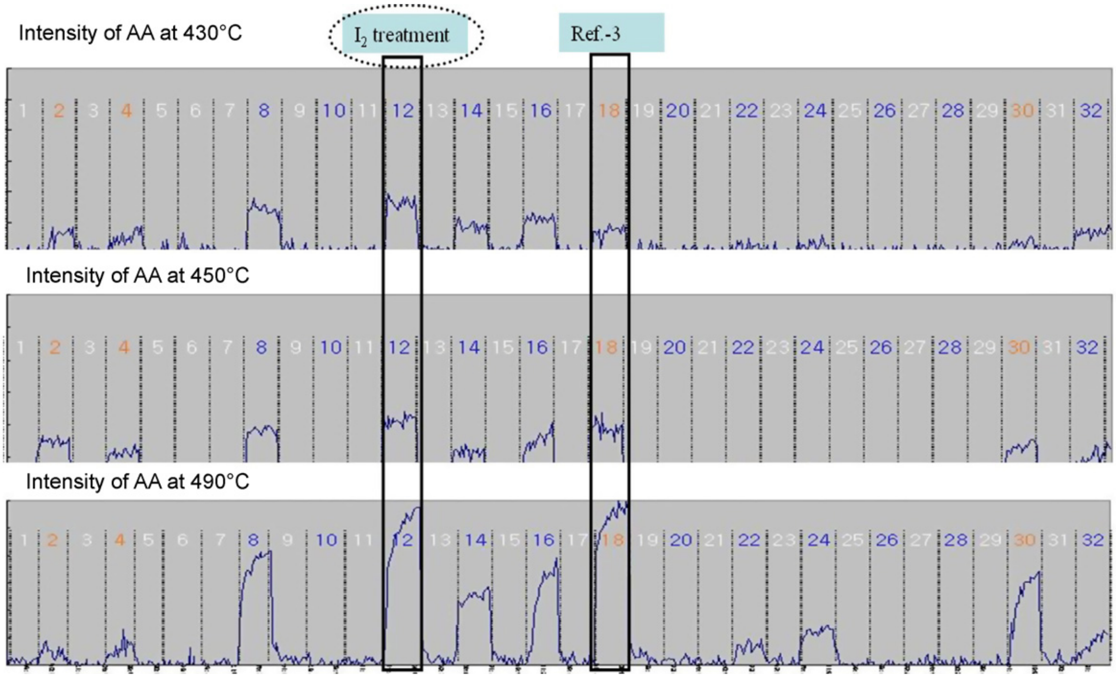

Fig. 4. MS signal intensity of AA of propane selective oxidation as a function of reaction temperature (C_3H_8:O_2:H_2O:He = 5.3:9.3:0:85.4, GHSV = 6470 h^{-1}).

3.1.4. Conventional testing of MoVTeNb treated with I_2 solution with H_2O addition

The effect of water presence on the catalytic performance was studied at a reaction temperature of 370–520 °C as shown in Table 4. AA and CO_x are major products; ACR, AcA, and ACT of byproducts are produced in a small amount. Compared with results in Table 3, propane conversion increases at all temperature when water is introduced and the enhanced production of AA is accompanied by a large reduction in propene selectivity. The major effect of water presence appears to be in the selectivity of AA, 59.8% of AA selectivity was obtained at 400 °C and byproduct ACT formation is decreased. From these results, water has a beneficial effect on the formation of oxygenate products from propane, in particular AA. Considering the selectivity to AA, the suitable reaction temperature was below 490 °C.

Table 4

Catalytic performance of Mo–V–Te–Nb (I_2) in the presence of water at temperatures between 370 and 520 °C at GHSV = 2500 h^{-1} (C_3H_8:O_2:H_2O:He = 5.4:16.1:11.5:67; AA: acrylic acid; AcA: acetic acid; ACR: acrolein; ACT: acetone)

Temperature (°C)	C_3H_8 conversion (%)	AA yield (%)	Selectivity (%)					
			CO_2	C_3H_6	CO	AA	ACR + AcA	ACT
370	8.3	2.8	10.1	11.3	0	33.2	6.6	4.2
400	11.4	6.8	12.5	19.6	8.6	59.8	3.2	2.9
430	14.6	5.7	19.7	18.9	36.5	38.9	0.7	0.6
460	22.1	7.5	27.7	18.1	44.3	33.9	0.2	0.2
490	32.1	8.1	35.0	9.5	48.7	7.5	0.1	0.1
520	34.1	8.6	39.2	7.9	54.2	25.3	0	0

Table 5

Catalytic performance of Mo–V–Te–Nb (I_2) by changing GHSV from 2500 to 1070 h^{-1} at temperatures between 370 and 490 °C (C_3H_8:O_2:H_2O:He = 5.4:16.1:11.5:67; GHSV = 1070 h^{-1}; AA: acrylic acid; AcA: acetic acid; ACR: acrolein; ACT: acetone)

Temperature (°C)	C_3H_8 conversion (%)	AA yield (%)	Selectivity (%)					
			CO_2	C_3H_6	CO	AA	ACR + AcA	ACT
370	10.0	0.4	45.5	10.9	9.0	4.0	0	20.7
400	14.5	3.7	28.1	13.8	23.3	25.5	0.4	1.7
430	30.9	14.5	31.6	9.8	20.2	47.1	0.2	0.6
460	39.7	6.5	44.8	7.0	33.5	16.4	0.1	0.2
490	54.5	5.7	55.0	4.8	30.7	10.6	0.1	0.2

3.1.5. Catalytic performance of Mo–V–Te–Nb by changing GHSV

The catalytic performance of Mo–V–Te–Nb (I_2) by changing GHSV was studied at a reaction temperature of 370–490 °C as shown in Table 5. The results were obtained by increasing the amount of the catalyst used from 0.3 to 0.7 g. Compared with the results in Table 4, as the space velocity is decreased from 2500 to 1070 h^{-1} with the same reactant composition, the conversion of propane increases and the AA yield increases at all the reaction temperatures. Meanwhile, selectivity of propene and AA is decreased.

Previous studies [20,26,27] suggest that propane oxidative dehydrogenation to propylene is the first step of the reaction. The Mo–V–Te–Nb oxide catalyst has high reactivity to propylene oxidation, and propylene is quickly consumed in the sequential steps of the reaction as soon as it is produced. As the GHSV increases, the contact time of reactant (propane and propylene) with the catalyst becomes short and some of them leave the catalyst surface without reaction. Therefore, propane conversion decreases and the concentration of propylene in product gases increase with the increasing GHSV. Simultaneously, the contact times of AA and other intermediates with the catalyst also become short, which prevent them from staying for a long period on the catalyst surface, thus decreasing the chance of being further oxidized to CO_x. In this regard, with the GHSV decreasing, the selectivity to propene and AA decreases. The observed yield of AA is a product of propane conversion and AA selectivity, while the effect of GHSV on them is opposite.

3.1.6. Catalytic performance of Mo–V–Te–Nb by changing water concentration

The reaction was conducted by fixing the GHSV (1070 h^{-1}) and changing steam ratio V(steam)/V(C_3H_8) from 2.1 to 3.8. Table 6

Table 6
Catalytic performance of Mo–V–Te–Nb (I_2) by changing the water concentration from 11.5 to 20.7 at temperatures between 370 and 490 °C at GHSV: 1070 h^{-1} (C_3H_8:O_2:H_2O:He = 5.4:16.1:20.7:57.8; AA: acrylic acid; AcA: acetic acid; ACR: acrolein; ACT: acetone)

Temperature (°C)	C_3H_8 conversion (%)	AA yield (%)	Selectivity (%)					
			CO_2	C_3H_6	CO	AA	ACR + AcA	ACT
370	16.2	9.8	8.8	8.2	7.4	60.4	1.8	15.7
400	18.9	11.3	15.7	8.3	10.0	59.8	1.2	8.0
430	29.7	16.2	19.4	5.2	19.1	54.5	0.6	3.9
460	42.0	18.1	30.2	3.6	23.8	43.2	0.9	1.0
490	52.2	13.2	41.3	2.0	33.3	25.3	0.8	0.1

shows the catalytic performance of Mo–V–Te–Nb (I_2) as a function of reaction temperature. One can see that the major effect appear to be in the selectivity of AA and CO_x. Compared with Table 5, selectivity of AA increases and selectivity of CO_x decreases at all the reaction temperatures. As the temperature is elevated from 370 to 490 °C, the conversion of propane increases from 16.2 to 52.2% which is similar with the obtained results in Table 5 and selectivity of AA decreased from 60.4 to 25.3% accompanied by increasing the selectivity of CO_x.

It can be seen that AA already formed even in a steam-free condition as shown in Section 3.1.3, which indicates that steam is important but not the indispensable for the formation of AA. The most likely reason for the positive effect is that steam enhances the desorption of the strongly adsorbed AA on the catalyst surface to prevent it from overoxidation to CO_x [28,29].

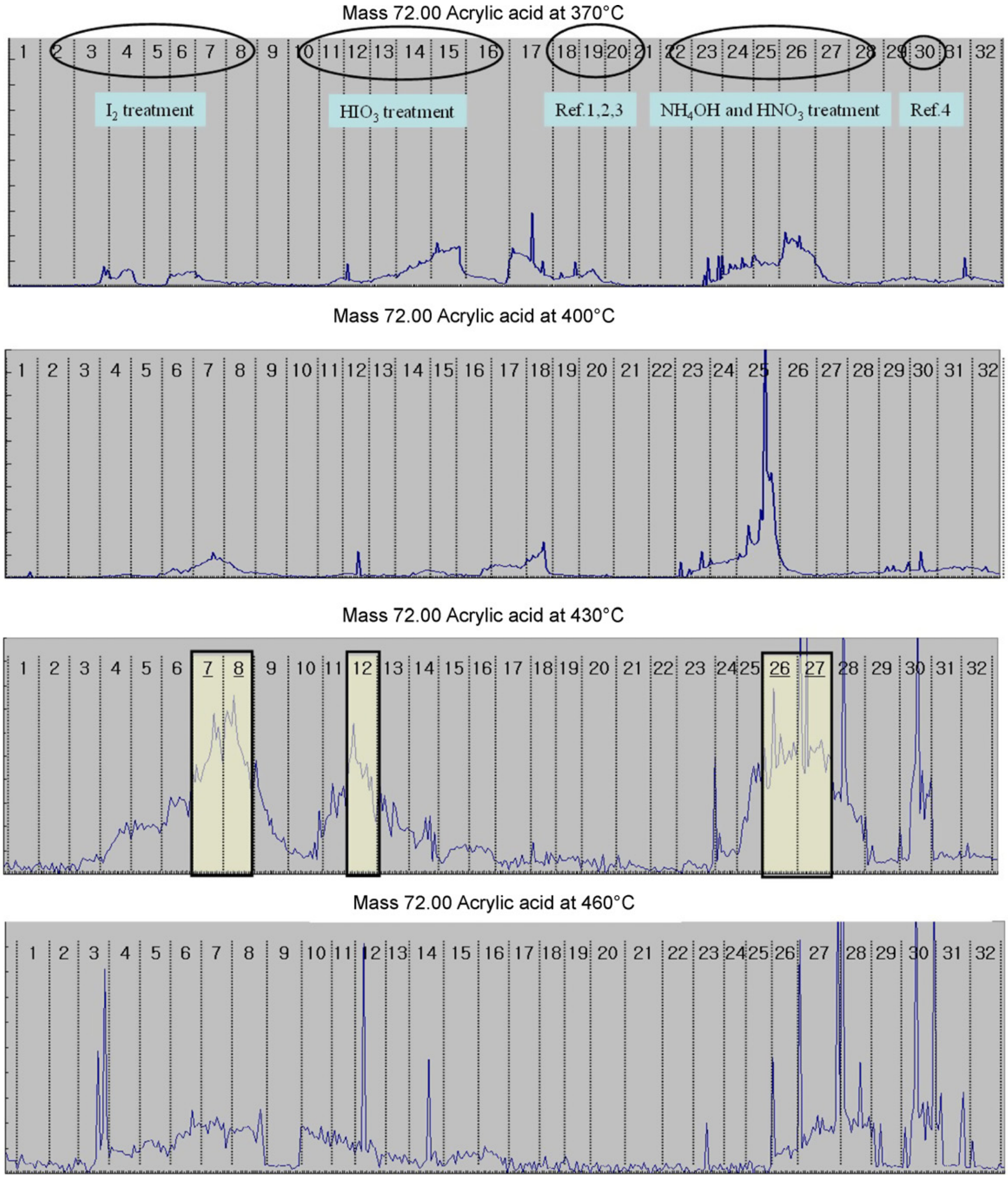

Fig. 5. MS signal intensity of AA of propane selective oxidation as a function of reaction temperature (C_3H_8:O_2:H_2O:He = 5.4:16.1:20.7:57.8, GHSV = 6470 h^{-1}).

Table 7
MoVTeNb mixed oxide catalyst library treated by various chemicals

Channel no.	Catalyst name, treated with	Channel no.	Catalyst name, treated with
1	Alumina (blank)	17	Alumina
2	I_2 = 0.006 g	18	Ref-1
3	I_2 = 0.012 g	19	Ref-2
4	I_2 = 0.025 g	20	Ref-3
5	I_2 = 0.051 g	21	Alumina (blank)
6	I_2 = 0.100 g	22	pH 1
7	I_2 = 0.200 g	23	pH 2
8	I_2 = 0.400 g	24	pH 3
9	Alumina (blank)	25	pH 4
10	HIO_3 = 0.050 g	26	pH 5
11	HIO_3 = 0.200 g	27	pH 6
12	HIO_3 = 0.300 g	28	pH 7
13	HIO_3 = 0.400 g	29	Alumina (blank)
14	HIO_3 = 0.500 g	30	Ref-4
15	HIO_3 = 0.600 g	31	Alumina (blank)
16	HIO_3 = 0.800 g	32	Alumina (blank)

3.2. Mo–V–Te–Nb oxide catalysts treated with prospective chemicals (I_2, HIO_3), the catalysts prepared by precursor solution of different pH—3rd library

We have found that I_2 treatment during preparation made a positive effect on the catalytic activity of Mo–V–Te–Nb catalyst for selective oxidation of propane to AA. In order to confirm the effect of different iodine precursors during preparation on catalytic performance, the catalyst library of Mo–V–Te–Nb oxide catalysts treated with I_2, and HIO_3 have been prepared. As shown in Table 7, catalysts treated with different amounts of I_2 are loaded from channel # 2 to # 8 and HIO_3 from #10 to # 16. The pH of resultant slurry (pH 2.6) is varied by incorporating an aqueous nitric acid (pH 1.0) and ammonium hydroxide solution (pH 10.0) in order to achieve desired pH (from 1.0 to 7.0), loaded from #22 to #28. Four-reference Mo–V–Te–Nb catalysts have been loaded at the channel #18, #19, #20, and #30.

In Fig. 5, the AA ion partial pressure signals determined by QMS during the screening process are presented as a function of channel number at a temperature range from 370 to 460 °C. The MS signal of AA of each channel shows increasing trend with increase temperature until 430 °C, then decreases at 460 °C, suggesting overoxidation of AA to CO_x. At 430 °C, the catalysts loaded at the channel #7, #8, #12, #26 and #27 show a high catalytic activity to AA. The resolution and quality of MS signals of AA are low because of water vapor, which caused signal fluctuation. However, it allows us discrimination of the individual site and the relative activities of the different catalyst sites are readily discernable, presenting the potential utility of the system as a high-throughput screening tool.

3.2.1. Conventional testing of MoVTeNb treated with I_2, HIO_3 solution and prepared by different pH condition

Selected Mo–V–Te–Nb oxides treated with I_2 solution (#7, 8) from the 3rd library have been tested under conventional scale for propane selective oxidation to AA and presents in Fig. 6. As shown in Fig. 6(a), both AA and CO_x ($CO + CO_2$) are major products; AcA + ACR and ACT are byproducts in small amounts. The conversion of propane augmented with the increasing temperature and the yield of AA reaches to the maximum value of 12% at 400 °C. When the reaction temperature is higher than 400 °C, conversion of propane and selectivity of CO_x increases, but AA yield quickly decreases. According to Fig. 6(b), conversion of propane is similar to that of Mo–V–Te–Nb (I_2 = 0.2 g, #7), but the AA yield reaches the maximum value of 19% at 430 °C. Above 430 °C, propane and CO_x conversion increases and the AA yield decreases from 19 to 11% accompanied by the great decrease of the selectivity of AA.

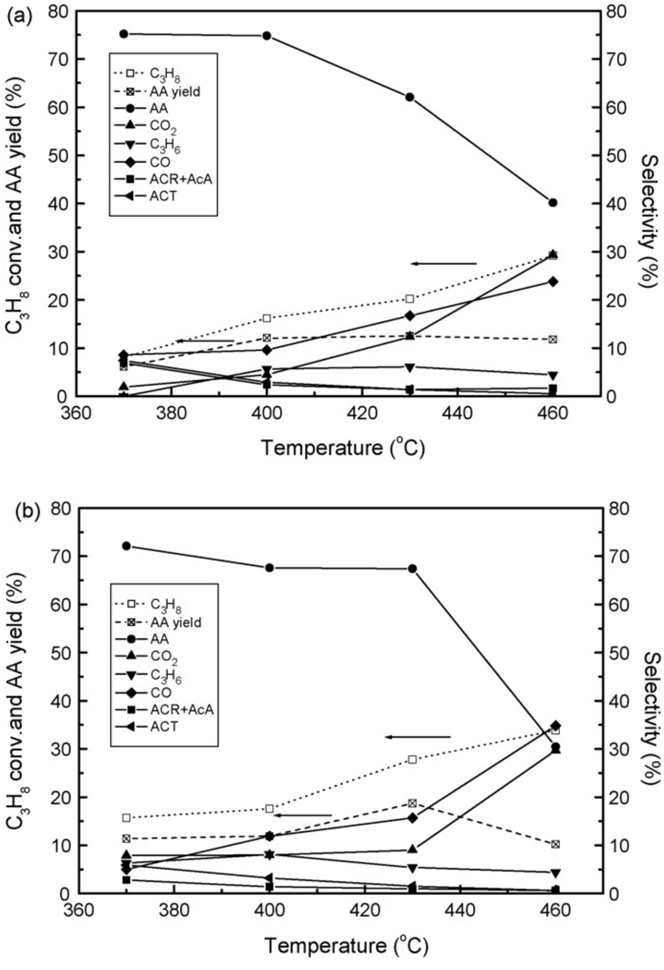

Fig. 6. Conversion and yield/selectivity vs. reaction temperature for propane selective oxidation over: (a) Mo–V–Te–Nb (I_2 = 0.2 g, #7) and (b) Mo–V–Te–Nb (I_2 = 0.4 g, #8).

The reaction results of Mo–V–Te–Nb oxides treated with HIO_3 solution (HIO_3 = 0.3 g, #12) is shown in Fig. 7. The beneficial effect

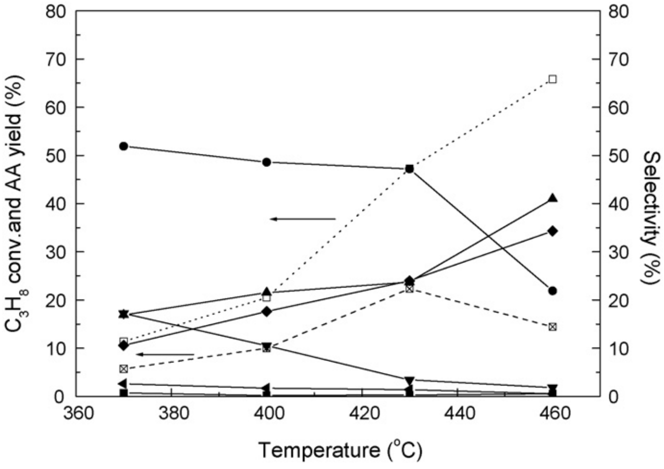

Fig. 7. Conversion and yield/selectivity vs. reaction temperature for propane selective oxidation over Mo–V–Te–Nb (HIO_3 = 0.3 g, #12) (symbols as the same in Fig. 6).

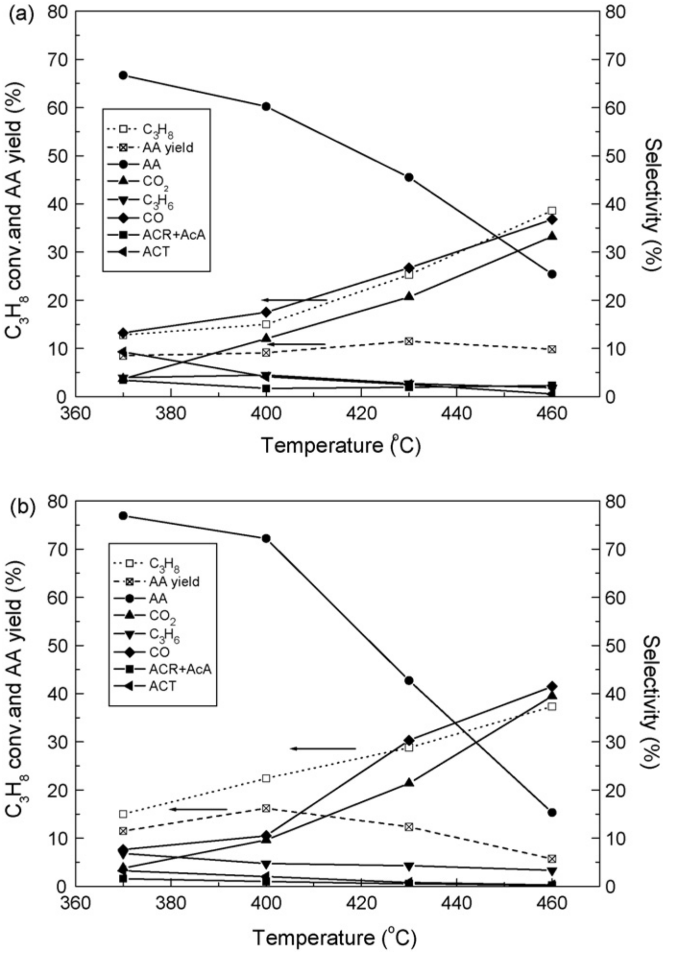

Fig. 8. Conversion and yield/selectivity vs. reaction temperature for propane selective oxidation over: (a) Mo–V–Te–Nb (pH 5, #26) and (b) Mo–V–Te–Nb (pH 6, #27).

of HIO_3 treatment on the conversion of propane is very pronounced in the range of all the reaction temperatures, resulting in 65% at 460 °C. Meanwhile, CO_x formation also increases by elevating the temperature, accompanied by decreasing AA selectivity. Due to opposite contribution of reaction temperatures to AA selectivity and propane conversion, the yield of AA reaches maximum of 21% at 430 °C. Considering the selectivity and yield of AA, the suitable reaction temperature of Mo–V–Te–Nb (HIO_3 = 0.3 g, #12) is around 430 °C.

Fig. 8 shows the catalytic performance of Mo–V–Te–Nb oxides prepared under pH 5 and 6 condition. The AA yield of each catalyst is 10 and 16% at 430 and 400 °C where the selectivity of AA is 46 and 73%, respectively. Considering the selectivity and yield of AA, Mo–V–Te–Nb (pH 6, #27) shows better catalytic performance than Mo–V–Te–Nb (pH 5) even though the conversion of propane is lower than that of Mo–V–Te–Nb (pH 5, #26). Consequently, the trends observed with the high-throughput technique are in agreement with the results obtained from a conventional testing. Among the re-investigated catalysts, Mo–V–Te–Nb (I_2 = 0.4 g, #8) and Mo–V–Te–Nb (HIO_3 = 0.3 g, #12) show the highest yield 12% and at 430 °C.

3.2.2. Characterization of MoVTeNb catalyst

The specific surface area of Mo–V–Te–Nb (I_2 = 0.4 g), Mo–V–Te–Nb (HIO_3 = 0.3 g), and Mo–V–Te–Nb (ref., HNO_3 = pH 2.6) were 3.6, 4.3, and 3.0 m^2/g, respectively. Iodine treated catalysts show slightly higher surface area than that of reference catalysts but it cannot be sufficient evidence to explain the role of iodine to the catalytic performance of Mo–V–Te–Nb oxides. The XRD patterns of these catalysts are given in Fig. 9. It is known [30,31] that the effective Mo–V–Te–Nb–O mixed metal oxide catalyst for the partial oxidation of propane to acrylic acid should have XRD peaks at diffraction angles of $2\theta = 22.1^\circ, 28.2^\circ, 36.1^\circ, 45.1^\circ$, and 50.0°. All the five characteristic peaks of the prepared catalysts are present in the pattern, which indicates that effective catalysts are formed in our experiment. XRD peaks of Mo–V–Te–Nb treated by HIO_3, I_2 are more intense than that of the reference catalyst. It means that the degree of crystallization of Mo–V–Te–Nb oxides treated with HIO_3 and I_2 is higher than Mo–V–Te–Nb (ref.). As a result, the addition of iodine species during preparation affects the phase of the catalyst.

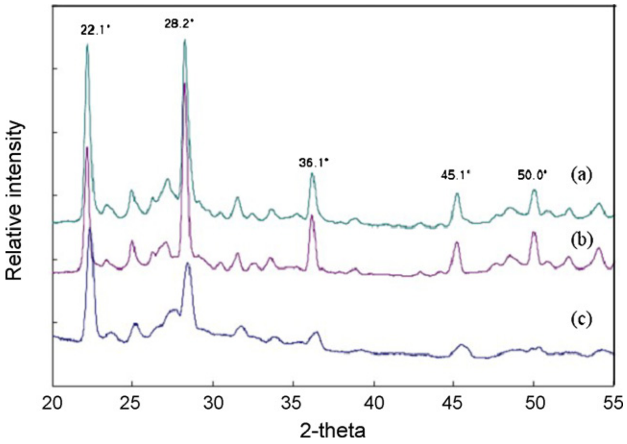

Fig. 9. XRD patterns of the Mo–V–Te–Nb mixed oxide catalyst treated with (a) 0.3 g of HIO_3, (b) 0.4 g of I_2, and (c) HNO_3 which is adjusted to pH 2.6.

The XPS analysis provided the further evidence that the effect of HIO_3 and I_2 addition on the surface metal concentration. The experimental precision on the quantitative measurements was considered to be around 10%. Even though the iodine species were not observed in the XPS analysis, which may be due to sublimation during calcination step, the surface concentration of Te and Nb of (Mo/V/Te/Nb = 1/0.21/0.27/0.19, HIO_3 = 0.3 g) and (Mo/V/Te/Nb = 1/0.25/0.24/0.15, I_2 = 0.4 g) were richer than the reference catalyst (Mo/V/Te/Nb = 1/0.33/0.22/0.11, HNO_3 (pH 2.6)) while concentration of V is comparatively lower than that of reference catalyst. It is reported that Nb play roles for stabilizing the AA formed on the catalyst surface and preventing further oxidation by assisting quick desorption and it concerns the stabilization of Te on the catalyst surface [32]. Te was considered to be a key element in the catalysts for the propene oxidation to ACR and the stabilization of AA. Therefore, it is supposed that iodine species during preparation enhanced the concentration of Nb and Te on the surface, resulting in enriched Te that promoted the stabilization of AA.

3.2.3. Quantified MS analysis combining with results of GC

To obtain quantitative results, MS combined with GC was applied to analyze the conversion of propane, oxygen and the yield, selectivity of AA over Mo–V–Te–Nb (HIO_3 = 0.3 g, #12) mixed oxide catalyst. In order to accelerate the data acquisition process and to minimize the volume of the data acquired, He ($m/z = 4$), AA ($m/z = 72$), propane ($m/z = 29$), and oxygen ($m/z = 32$) were monitored during the testing process. It is well known that the relative MS signal intensity of a selected ion ($I_{\mathrm{product}}/I_{\mathrm{He}}$) of a given compound where I indicates the intensity of the MS signal is proportional to the mole ratio of the compound to He in the mixture. By simultaneously analyzing the same effluent of the gas

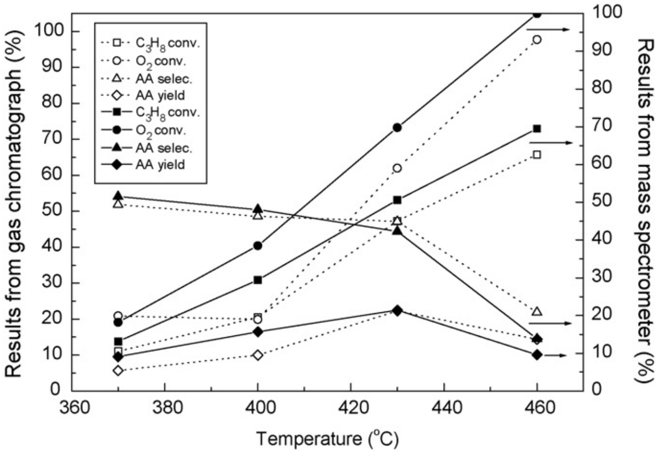

Fig. 10. Results from GC vs. MS as a function of reaction temperature for propane selective oxidation over Mo–V–Te–Nb (HIO_3 = 0.3 g, #12).

with MS and a GC equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID), a correction coefficient relating $I_{\text{product}}/I_{\text{He}}$ to the relative mole ratio of a product (product/He) corresponding to GC analysis can be obtained. In this way, all the compounds in the mixed gases can be corrected by the corresponding coefficient as shown in Fig. 10. Even though fluctuations of the MS signals are significantly influenced by the detector mode (Faraday detector) and water condensation, deviation of conversion, selectivity, and yield are maintained within below 10% at all the reaction temperatures. These results provide that the screening method using the 32-channel tubular reactor system is reliable and useful for the high-throughput screening. Moreover, the combination of MS and GC suggests a possible means for the rapid quantification of the MS data.

4. Conclusions

Combinatorial screening methodologies have been used to screen Mo–V–Te-based catalysts for the selective oxidation of propane. All the mixed oxide catalysts were prepared slurry method and tested in the home-built 32-channel tubular reactor system.

In order to develop new compositions of the catalysts, 1st library composed of Mo–V–Te–M (M = Nb, Ni, Fe, Ce, Cu, and Co) oxide catalysts have been prepared and tested, and the only catalyst containing Nb showed the catalytic activity to AA. Based on these results, we have prepared the 2nd library composed of Mo–V–Te–Nb treated with different chemical treatment during the preparation step. Among these catalysts, Mo–V–Te–Nb treated with I_2 showed high performance to selectivity and yield of AA.

Scale-up testing were performed in a conventional gas flow reactor by using optimal catalyst confirmed the results from the 2nd library. In this case, we have confirmed that the catalytic performance of propane selective oxidation to AA is influenced by the reaction condition. The main role of water is to enhance the formation of AA and prevent it from total oxidation to CO_x. And we also observed that low GHSV (1070 h^{-1}) results in low conversion of propane accompanied by high yield of AA at low temperature.

The 3rd library composed of Mo–V–Te–Nb catalysts treated with 0.006–0.4 g of I_2, 0.05–0.8 g of HIO_3, and 1–7 of pH control were prepared and tested under the optimized reaction conditions. Good catalytic performance was observed at samples treated with 0.4 g of I_2, 0.3 g of HIO_3, and pH 6 during preparation.

XRD results indicate that the effective catalysts have five characteristics peaks at $2\theta = 22.1^\circ, 28.2^\circ, 36.1^\circ, 45.1^\circ$, and 50.0° and degree of crystallization is higher than that of the reference catalyst. The XPS analysis provided that these samples showed enriched Nb and Te concentration on the surface of catalyst than that of reference catalyst, which suggested that the addition of iodine precursor during preparation process made an effect on the Nb, Te concentration on the surface.

Quantification of the results was realized by combination of GC with MS which provided a possible route to quantitative analysis of MS data by calibrating the MS data by GC results.

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