

Comparison of Reaction Pathways for the Partial Oxidation of Propane over Vanadyl Ion-Exchanged Zeolite Beta and $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$

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The reaction pathways for the oxidation of propane over VO-H-beta and $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ are investigated. Two methods are used in this study: (i) overall product selectivities are recorded as a function of conversion, and (ii) those species observed or speculated to exist are reacted individually over the catalysts. With VO-H-beta, propene is the primary product of propane oxidation and acetic acid is a sequential oxidation product of the propene, possibly forming through an acetone intermediate. $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ also gives propene as the primary product of propane oxidation, and the propene thus formed oxidizes further to acrylic acid and acetone. Reactions of individual oxygenated compounds, e.g., propanal, acrolein, etc., confirm the superior oxidation features of the mixed metal oxide catalyst relative to the zeolite-based catalyst. © 2001

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Key Words: propane oxidation; vanadium-containing zeolites; Mo–V–Te–Nb–oxide catalyst; reaction pathway.

1. INTRODUCTION

Traditional industrial production of oxygenates, such as acids, alcohols, and unsaturated nitriles, is achieved by oxidation of olefins (1). A potentially less costly alternative to the use of olefins is the direct transformation of light alkanes into oxygenates through a partial oxidation process. The main challenge for partial oxidation is that light alkanes are usually less reactive than the desired products, and further oxidation to total oxidation products, CO_x , is thermodynamically favored. Despite this thermodynamic limitation, research on partial oxidation has yielded several successful processes that involve the partial oxidation of light alkanes, e.g., partial oxidation of *n*-butane to maleic anhydride by VPO (2) and ammoxidation of propane to acrylonitrile using V–Al–Sb–O (3).

Various catalyst systems have been studied for the partial oxidation of light alkanes including bulk mixed metal oxides (4–11), heteropolyacids (12–14), and molecular sieves (15–19). Zeolite-based catalysts have been investigated for the

partial oxidation of propane and were found to be suitable matrices for isolating transition metals (15, 18). Moreover, the uniform pore structure of the zeolite can be used as a host for stabilizing small metal oxide clusters (20–24). During initial oxidation studies with zeolite-based catalysts, we found that vanadyl ion-exchanged zeolite beta (VO-H-beta) produced a considerable amount of acetic acid when reacting propane with oxygen. It appeared possible that more valuable oxygenates, e.g., acrylic acid, were produced and overoxidized to CO_x , since feeding acrylic acid into this reaction system resulted in complete oxidation of the acid to CO_x at 350°C, and some acetic acid at lower reaction temperatures. These findings motivated us to study the reaction pathways for propane oxidation over VO-H-beta. For comparison, we also report reaction pathways of propane partial oxidation over a “Mitsubishi type” catalyst, $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$, one of the best catalysts for propane partial oxidation to acrylic acid (25).

2. EXPERIMENTAL SECTION

2.1. Catalysts Preparation

The starting materials used for the preparation of vanadyl ion-exchanged zeolite beta (VO-H-beta) were Na-zeolite beta (PQ Corp, Si/Al = 12), NH_4NO_3 (Aldrich), and VOSO_4 (Aldrich). VO-H-beta was synthesized in three steps as follows: (1) Na-zeolite beta was ion-exchanged with 1 M NH_4NO_3 solution (50 mL of NH_4NO_3 solution/g of zeolite) overnight at 80°C three times, and the resulting NH_4 -beta was washed with double-distilled water, filtered, and dried overnight in an 80°C oven; (2) H-beta was formed by heating NH_4 -beta at 500°C for 4 h in N_2 ; (3) VO-H-beta was prepared by ion-exchange of H-beta with 0.1 M VOSO_4 solution (50 mL of VOSO_4 solution/g of zeolite) for 10 h at 60°C twice (26), and the resulting mixture was washed with double-distilled water, filtered, and dried overnight in an 80°C oven. The composition of the VO-H-beta sample is Si : Al : V = 25.2 : 1 : 0.61, giving 1.66 wt% V (the elemental

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analysis of VO-H-beta was done by Galbraith Laboratories, Inc.).

$\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ was synthesized according to a Mitsubishi patent (25) and provided to us by BP Amoco. The XRD pattern of this catalyst is in good agreement with that described in the patent (25).

2.2. Catalytic Reactions

The catalytic reactions were carried out using a continuous-flow system (BTRS-Jr., Autoclave Engineers) with a fixed-bed stainless steel reactor. Before a reaction, the catalyst samples were pelletized and sieved to $-35/+60$ mesh size. A mixture of 0.5 mL of catalyst (0.20 g of VO-H-beta, or 0.70 g of $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$) and 1 mL of silicon carbide was used for each run. Catalysts were pretreated at 350°C for 1 h in a He flow. The reactions were carried out at temperatures from 250°C to 450°C under atmospheric pressure with a reactant molar ratio of propane : oxygen : H_2O : helium = 4 : 2 : 4 : 5 and a total flow of 15 mL/min.

Propane oxidation over $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ was also conducted under conditions more similar to those of Example One in the Mitsubishi patent (25). A 1.75 g amount of $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ together with 2.5 mL of SiC was used for the reaction with a feed molar ratio of propane : O_2 : He = 1 : 3.15 : 11.85 and a total flow rate of 36.2 mL/min (space velocity of 1734 h^{-1} with a catalyst density of 1.4 g/cm^3); in the Mitsubishi patent (25), the amount of catalyst used was 0.37 g and the feed gas molar ratio was propane : air = 1 : 15 with a space velocity of 1734 h^{-1} .

Product analysis was performed using a gas chromatograph (Hewlett Packard G1800B) equipped with a mass spectrometer and a capillary column (Hewlett Packard, HP Plot-Q). Gaseous products were analyzed using online sampling, while liquid products were collected in an ice trap and analyzed after the completion of the run.

The conversion was defined as the fraction of consumed hydrocarbon of the moles of hydrocarbon fed to the reaction. Selectivities are the fractions of consumed hydrocarbon converted for each product. The contact times provided are the ratios of the catalyst volumes to the total flow rates of gaseous feeds.

2.3. Reaction Pathway Study

The reaction pathways were first studied by following the trends in product selectivities with respect to the reactant conversion. Both propane oxidation and propene oxidation were employed in this investigation. An amount of 0.20 g (0.5 mL) of VO-H-beta with 1.0 mL of SiC was used for this study, while only 17.5 mg to 105 mg of $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ with 0.5 mL of SiC was employed in order to keep the conversion of reactants low. The temperature was set to 350°C

and the molar feed gas ratio was propane (or propene) : O_2 : H_2O : He = 4 : 2 : 4 : 5. The contact time was varied to reach different conversion levels.

The reaction pathways were also studied by feeding oxygenates that are possible intermediates in the propane oxidation pathway to the reactor. These reactions were conducted at lower temperatures (250°C or lower), since most of the oxygenates investigated here are highly reactive. A 0.20 g amount of VO-H-beta (0.5 mL) or 0.35 g of $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ (0.25 mL) was used for this study with pretreatment at 350°C for 1 h in He. For water-soluble oxygenates, the reactant input ratio used was oxygenate (10 mol% aqueous solution) : O_2 : He = 4 : 2 : 9. For water-insoluble oxygenates, the reactant input ratio was oxygenate (pure) : O_2 : He = 0.4 : 2 : 12.6. The contact time was varied between 0.25 s to 4 s.

3. RESULTS AND DISCUSSION

3.1. Partial Oxidation of Propane

3.1.1. Propane partial oxidation reaction over VO-H-beta. The reaction products from propane oxidation over VO-H-beta were acetic acid, propene, CO, CO_2 , and trace amounts of ethylene. At 350°C, the conversion of propane was 1.6%, the selectivity to acetic acid 21.1%, and the selectivity to propene 20.9%. As the temperature was increased to 400°C, the conversion of propane increased to 4.3% and the selectivity to acetic acid decreased to 14%. The specific values of conversion and selectivity are summarized in Table 1.

The reactivity for propane oxidation over VO-H-beta is not high under the conditions investigated. The turnover frequency per vanadium atom (TOF) of propane consumption is $7.4 \times 10^{-4} \text{ s}^{-1}$ for VO-H-beta at 350°C. Assuming an activation energy of 100 kJ/mol and first-order dependence on propane concentration, these data extrapolate to a propane consumption rate of $2.3 \times 10^{-4} \text{ s}^{-1}$ at 333°C. This rate is comparable to results of previous studies on isolated monovanadate species by Khodakov and co-workers (27).

TABLE 1

Propane Oxidation over VO-H-beta^a

Temp (°C)	Conv (%)		Selectivity (%)				
	C_3H_8	O_2	C_3H_6	C_2H_4	Acetic acid	CO	CO_2
350	1.62	9.12	20.9	0	21.1	28.3	29.7
400	4.27	25.4	13.6	1.2	13.9	38.0	33.4
450	13.0	83.3	11.1	1.5	8.12	45.4	33.9

^aReaction conditions: 0.20 g of catalyst, molar feed ratio propane : O_2 : H_2O : He = 4 : 2 : 4 : 5, and 15 mL/min total flow rate.

TABLE 2
Propane Oxidation over $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$

Temp (°C)	Conv (%)		Selectivity (%)						
	C_3H_8	O_2	C_3H_6	Acetone	Acetic acid	Propanoic acid	Acrylic acid	CO	CO_2
250 ^a	4.00	12.2	27.9	7.3	10.8	2.6	43.4	5.0	3.2
300 ^a	12.3	44.9	19.8	3.2	12.6	1.7	51.0	6.1	5.6
350 ^a	27.2	79.8	9.30	0.8	15.2	1.4	64.7	4.4	4.3
400 ^b	58.3	63.3	3.16	0.0	4.6	0.0	39.2	26.2	26.6
400 ^c	75.3						42.4		

^a Reaction conditions: 0.70 g of catalyst, molar feed ratio propane : O_2 : H_2O : He = 4 : 2 : 4 : 5, and 15 mL/min total flow rate.

^b Reaction conditions: 1.75 g of catalyst, molar feed ratio propane : O_2 : He = 1 : 3.15 : 11.85, and 36.2 mL/min total flow rate.

^c Results reported in the Mitsubishi patent (25), with 0.37 g of catalyst, and a molar feed ratio propane : air = 1 : 15 at a space velocity of 1734 h^{-1} .

3.1.2. Propane partial oxidation reaction over $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$. $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ is one of the best catalysts reported for the partial oxidation of propane to acrylic acid. The reaction results obtained here with $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ are compared to those reported in the patent literature (Table 2). The major products observed under the reaction conditions used in the patent are acrylic acid and CO_x . At oxygen-rich conditions like those reported in the patent literature, the conversion of propane was 58.3% and the selectivity to acrylic acid 39.2% at 400°C. This selectivity is close to the results reported by Mitsubishi (propane conversion 75.3% and acrylic acid selectivity of 42.4%) (25).

The propane oxidation reaction was also performed in the presence of water with $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ under reaction conditions similar to those used with VO-H-beta. At 350°C, the conversion of propane reached 27.2% and the selectivity to acrylic acid was 64.7%. Additionally, propane could be activated even at temperatures as low as 250°C (Table 2).

3.2. Reaction Pathways: Trends in Product Selectivities

The reaction pathways of propane oxidation over VO-H-beta and $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ were first examined by analyzing product selectivities as a function of propane conversion, and the oxidation behavior of propene at low conversions.

3.2.1. Reaction pathways for propane oxidation over VO-H-beta. The detected products from propane oxidation over VO-H-beta are propene, acetic acid, CO_x , and trace amounts of acetone (less than 0.5% selectivity). At very low (<1%) propane conversion, the main product is propene. With an increase in the conversion, the selectivity to propene decreases while the selectivity to acetic acid increases (Fig. 1). In general, the primary products of

a given reaction can be discriminated from higher-order products by extrapolating product selectivities to zero conversion. Primary products have non-zero intercepts, while secondary and higher-order products have zero intercepts (5). For the case of propane oxidation over VO-H-beta, the data (Fig. 1) do not conclusively distinguish between zero or very low selectivities to acetic acid and CO_x at low conversion; however, it is clear that the dominant primary product is propene, and the main routes to acetic acid and CO_x involve secondary oxidation of propene.

Propene oxidation over VO-H-beta was investigated in order to gain further insights into the formation of acetic acid. At 350°C, the main products are CO_x , acetic acid, and acetone (Fig. 2). CO_x are the major products of propene oxidation, with extrapolated selectivities to acetic acid and acetone of around 22% and 13%, respectively. At temperatures

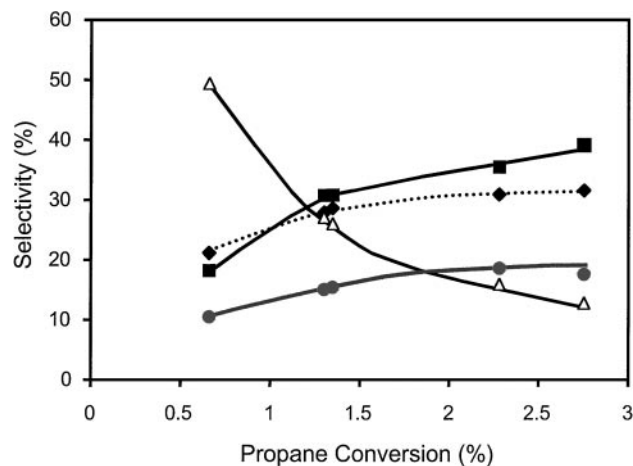


FIG. 1. Product selectivity profiles for propane oxidation over VO-H-beta: (Δ) propene; (\bullet) acetic acid; (\blacklozenge) CO; (\blacksquare) CO_2 . Reaction temperature was 350°C. The molar feed gas ratio was C_3H_8 : O_2 : H_2O : He = 4 : 2 : 4 : 5.

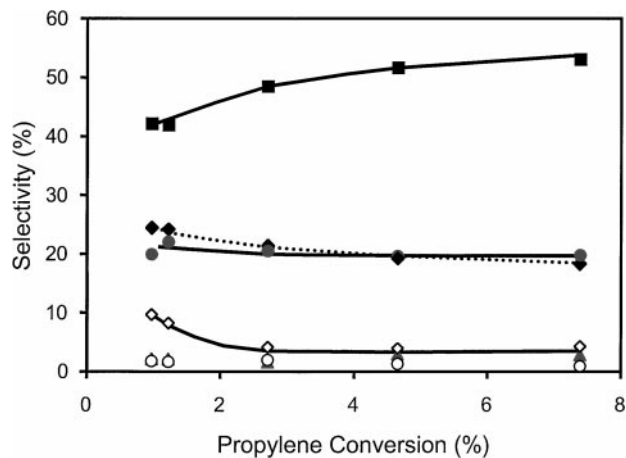


FIG. 2. Product selectivity profiles for propane oxidation over VO-H-beta: (●) acetic acid; (▲) acetaldehyde; (◇) acetone; (○) propanal; (◆) CO; (■) CO₂. Reaction temperature was 350°C. The molar feed gas ratio was C₃H₈:O₂:H₂O:He = 4:2:4:5.

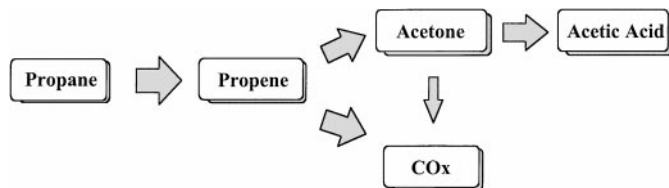
lower than 250°C, 2-propanol is the major product (Table 3). For example, the selectivity to 2-propanol is 88.3% at a propane conversion of 0.4% at 150°C. As the temperature is increased from 150°C to 350°C, the selectivity to 2-propanol decreases monotonically to zero, the selectivity to acetone first increases to a maximum (6.7% selectivity) and decreases thereafter, and the selectivity to acetic acid increases to 19.6% at a propene conversion of 4.7%. Moro-oka suggests that olefin oxidation over acidic metal oxides occurs through an oxyhydration mechanism in which olefins are first hydrated to corresponding alcohols on acid sites and then oxidatively dehydrogenated to form ketones (28). The observations for propene oxidation over VO-H-beta are consistent with this oxyhydration reaction pathway. A study of the oxidation of acetone (Section 3.3.1) indicates that acetic acid is a major product from acetone. Although no direct relationship between acetic acid and acetone is demonstrated from the data shown in Fig. 2, we suggest that acetone is an intermediate for the formation of acetic acid. Since the selectivity to acetone declines steeply

TABLE 3

Propene Oxidation over VO-H-beta^a

Temp (°C)	Conv (%)		Selectivity (%)				
	C ₃ H ₈	O ₂	2-Propanol	Acetone	Acetic acid	CO	CO ₂
150	0.41	0.33	88.3	0.41	0	8.32	2.97
200	0.67	1.87	59.3	5.10	6.91	16.0	12.7
250	1.05	5.71	10.5	6.66	17.0	22.0	43.8
350	4.65	38.6	0	3.92	19.6	19.3	51.6

^a Reaction conditions: 0.20 g of catalyst, molar feed ratio propene: O₂:H₂O:He = 4:2:4:5, and 15 mL/min total flow rate. Trace amounts of acetaldehyde and propanal were observed.



SCHEME 1. Main reaction pathways for propane oxidation over VO-H-beta.

with degree of conversion (Fig. 2) that corresponds to an increasing contact time, some formation of CO_x directly from acetone is also possible.

Oxygenates other than acetic acid and acetone, such as acetaldehyde, propanal, propanoic acid, acrolein, and traces of oligomer products, are observed from propene oxidation. The selectivities to these oxygenates are very low, generally below 2% under the reaction conditions used here. Thus, the formation of acetic acid from these oxygenates is not likely important.

The results from the oxidation of both propane and propene suggest that the reaction pathway for propane oxidation over VO-H-beta is that shown in Scheme 1. Propene is the primary product of propane oxidation, and acetic acid is mainly produced by sequential oxidation of propene, possibly through acetone. Intermediate oxygenates, such as acetone, can survive only at very low conversion. CO and CO₂ are major products of propene oxidation.

3.2.2. Reaction pathways for propane oxidation over Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x. The products from the oxidation of propane in the presence of water over Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x at 350°C are acrylic acid, propene, acetic acid, CO_x, and small amounts of acetone and propanoic acid. The selectivity to propene decreases while the selectivity of acrylic acid increases with increasing propane conversion (Fig. 3). For example, as propane conversion increases from 2.1% to 12.9%, the selectivity to propene decreases from 73.4% to 20.9%, and the selectivity to acrylic acid increases from 22.1% to 60.0%. When extrapolating to zero propane conversion, the selectivity to propene is 100%. Thus, propene is the primary product of propane oxidation; acrylic acid and other oxygenates (acetic acid, trace amount of acetone, and propanoic acid) are secondary or higher-order products. The rate of propane consumption at 350°C with C₃H₈:O₂:H₂O:He = 4:2:4:5 at low conversions is 1.23 × 10⁻⁴ mol/(g_{cat} · min) and is approximately an order of magnitude higher than that for VAPO-5 under the same conditions (1.9 × 10⁻⁵ mol/(g_{cat} · min)) (18).

Propene oxidation was also carried out over Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x at 350°C to study the reaction pathways on going from propene to oxygenates (since propene is the only primary product of propane oxidation). The major products detected are acetone and acrylic acid. Smaller

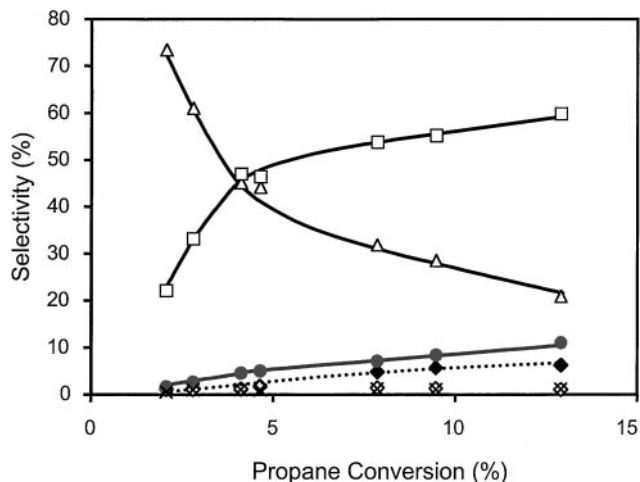


FIG. 3. Product selectivity profiles for propane oxidation over $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$: (Δ) propene; (\square) acrylic acid; (\bullet) acetic acid; (\diamond) acetone; (\times) propanoic acid; (\blacklozenge) CO_x . Reaction temperature was 350°C . The molar feed gas ratio was $\text{C}_3\text{H}_8:\text{O}_2:\text{H}_2\text{O}:\text{He} = 4:2:4:5$.

amounts of acrolein, acetic acid, propanoic acid, and CO_x are also observed (Fig. 4). The selectivities to acetone and acrylic acid do not vary significantly with propene conversion. Upon extrapolating to zero propene conversion, the selectivities to acrylic acid and acetone are 67% and 18%, respectively. The other compounds have small but non-zero selectivity at zero propene conversion. Thus, it is reasonable to conclude that two major routes exist for propene oxidation over $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$: (1) propene is oxidized to acrylic acid and (2) propene is oxidized to acetone.

By combining the propene and propane oxidation data, the main reaction pathways for propane oxidation are pro-

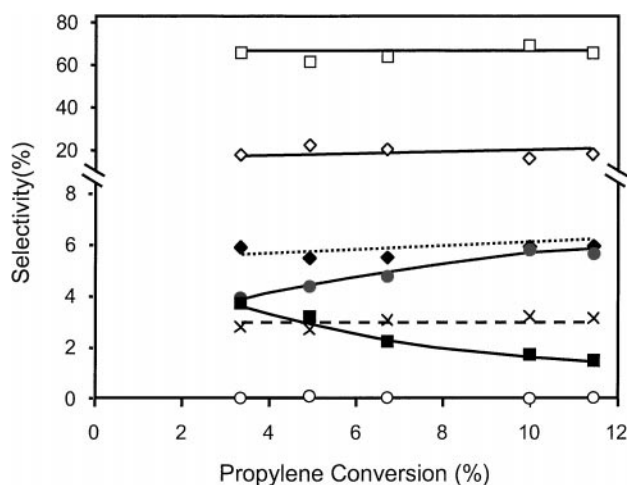
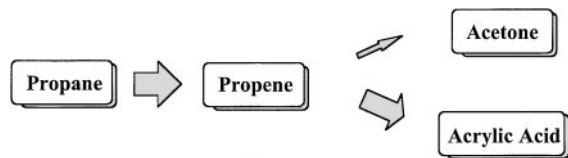


FIG. 4. Product selectivity profiles for propene oxidation over $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$: (\square) acrylic acid; (\diamond) acetone; (\blacksquare) acrolein; (\times) propanoic acid; (\circ) propanal; (\bullet) acetic acid; (\blacklozenge) CO_x . Reaction temperature was 350°C . The molar feed gas ratio was $\text{C}_3\text{H}_6:\text{O}_2:\text{H}_2\text{O}:\text{He} = 4:2:4:5$.



SCHEME 2. Main reaction pathway scheme for propane oxidation over $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$.

posed in Scheme 2: propane is first oxidized to propene that is then oxidized to acetone and acrylic acid.

It is interesting to note the differences in selectivities to acetone for propane and propene oxidation. The selectivity to acetone is very low ($<2\%$ under all conditions tested) in the former case, while it is relatively high ($\sim 19\%$) in the latter case. In a separate experiment, propane and propene were simultaneously fed to the reactor at ratios varying from 0 to 0.75 ($\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$). The selectivity to acetone did not vary with the introduction of propane. Additionally, the rate of consumption for pure propane for low conversions at 350°C with $\text{C}_3\text{H}_8:\text{O}_2:\text{H}_2\text{O}:\text{He}$ of 4:2:4:5 is approximately an order of magnitude lower than the propene consumption rate ($\text{C}_3\text{H}_6:\text{O}_2:\text{H}_2\text{O}:\text{He} = 4:2:4:5$). These data suggest the presence of two different sites on $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$; one site is able to activate propane and propene to acrylic acid, while the other converts only propene to acetone.

3.3. Reaction Pathway Method II: Oxidation of Possible Oxygenates

3.3.1. Oxidation of individual possible intermediates. The oxidation of oxygenated species that are possibly involved in the propane oxidation reaction was investigated over VO-H-beta and $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$. The oxygenated species chosen are those observed in the reaction results presented above. Acetic acid and trace amounts of acetone are observed in the propane oxidation over VO-H-beta (Table 1), while acrylic acid, acetic acid, acetone, and trace amounts of propanoic acid are obtained from propane oxidation over $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ (Table 2). 2-Propanol is observed from propene oxidation over VO-H-beta at temperatures under 250°C , and small amounts of propanal and acrolein are observed from propene oxidation over $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$. These compounds may also be involved in propane oxidation; however, they appear to be too reactive or in too low concentration to be detected under our reaction conditions. The detection of propanal and propanoic acid may indicate the presence of 1-propanol as an intermediate species. Hence, individual transformations of 2-propanol, 1-propanol, propanal, acrolein, acetone, acrylic acid, and acetic acid over VO-H-beta and $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ were investigated.

2-Propanol. Almost all the 2-propanol fed is consumed over both catalysts (>99.5% conversion) at 250°C; however, the product distributions are quite different for these two catalysts. With VO-H-beta, the dehydration product, propene, is dominant (more than 90% selectivity at contact time 2 s) at 250°C. Only small amounts of acetone, acetic acid, and CO_x are observed at this temperature (Fig. 5). At 150°C, the product distribution is similar to that at 250°C, with the addition of the condensation product, diisopropyl ether.

For Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x, the major products are acetone, acrylic acid, propene, and acetic acid at 250°C (Fig. 5). At a contact time of 2 s, the selectivity to propene is 11%, while the selectivities to acetone and acrylic acid are 41% and 25%, respectively. At 150°C, acetone and propene are the major products with selectivities of 66% and 21%, respectively, at 50% 2-propanol conversion. No acrylic acid is observed at 150°C.

1-Propanol. Similar to the case of 2-propanol, 1-propanol is almost completely consumed over both catalysts at 250°C (>99.5% conversion) (Fig. 6). For VO-H-beta, the dehydration product, propene, is the dominant product (selectivity higher than 95% under our test conditions). Small amounts of propanal are observed with a selectivity of 0.8% at 2 s contact time. Additionally, there are trace amounts of other products, such as acetone, acetic acid, and acetaldehyde. These products each have selectivities less than 0.5% and may result from the oxidation of propene. At 150°C, ether formation from intermolecular dehydration is the major product from 1-propanol.

For Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x, the dominant product is propanoic acid with a selectivity of 79.0% at 250°C (contact time of 2 s). Only small amounts of propene are observed (selectivity of 1.8%). No propanal is obtained at 250°C, while a large amount of propanal (selectivity of 38.7% at

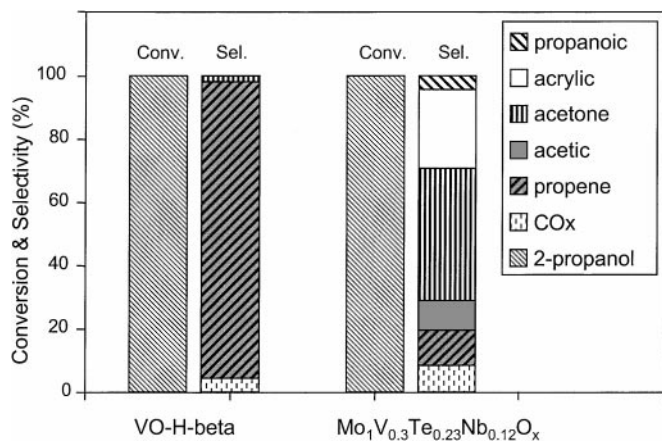


FIG. 5. Conversion and product distribution of 2-propanol oxidation over VO-H-beta and Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x at 250°C and 2 s contact time with a molar feed gas ratio of 2-propanol: H₂O: O₂: He = 0.4: 3.6: 2: 9.

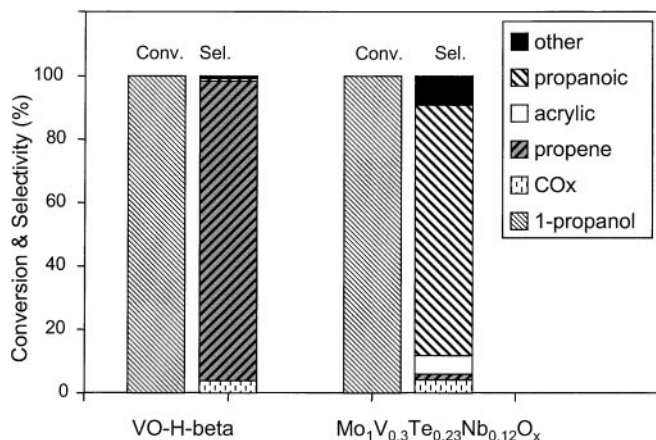


FIG. 6. Conversion and product distribution of 1-propanol oxidation over VO-H-beta and Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x at 250°C and 2 s contact time with a molar feed gas ratio of 1-propanol: H₂O: O₂: He = 0.4: 3.6: 2: 9. "Other" here refers to acetic acid, acetaldehyde, and acetone.

a conversion of 20.6%) is produced at 150°C. Thus, it is reasonable to consider propanal as an oxidation product of 1-propanol, and propanoic acid as a further oxidation product of propanal.

Propanal. The detected products of propanal oxidation over VO-H-beta are propanoic acid, acetic acid, acetaldehyde, and large amounts of CO_x (Fig. 7). The selectivity to propanoic acid is 19.5% (contact time 2 s and 250°C) at 60% conversion. The formation of propanoic acid from propanal indicates that VO-H-beta has oxidation capability for terminal HC=O. However, total oxidation products are dominant in propanal oxidation over this catalyst under the conditions tested here (selectivity to CO_x is 54%).

High selectivity to propanoic acid and little CO_x are observed for propanal oxidation over Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x.

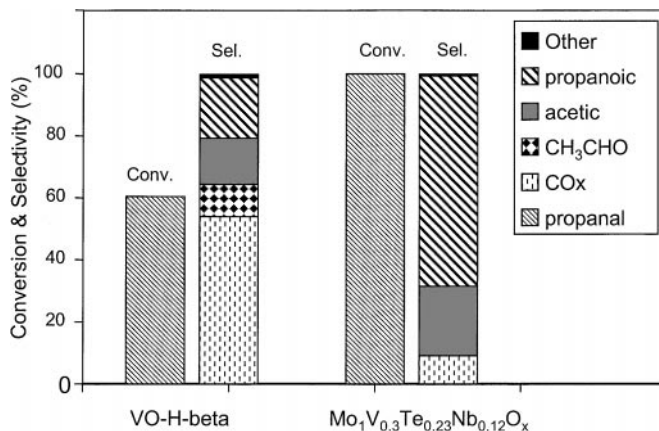


FIG. 7. Conversion and product distribution of propanal oxidation over VO-H-beta and Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x at 250°C and 2 s contact time with a molar feed gas ratio of propanal: O₂: He = 0.4: 2: 12.6. "Other" here refers to ethylene.

Even at complete consumption of propanal, the selectivity to propanoic acid at 250°C is 58% at a contact time of 2 s and 79% at a contact time of 1 s. At 150°C and a contact time of 1 s, the selectivity to propanoic acid increases to 91% with a propanal conversion of 44%.

Acrolein. When acrolein is oxidized over VO-H-beta, only small amounts of acrylic acid (3.1% selectivity at a conversion of 7.8%) are observed at 250°C (contact time 2 s) and total oxidation products are dominant (Fig. 8). These results suggest that the oxidation of the double bond of acrolein is easier than the oxidation of HC=O at the allylic position.

Acrolein is very reactive over $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ and acrylic acid is the dominant product at 250°C (Fig. 8). When the contact time is 2 s, the conversion of acrolein is 92% and the selectivity to acrylic acid is 94%. Thus, the double bond of acrolein is preserved. These results indicate that $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ has superior allylic oxidation character.

Since acrylic acid is the dominant product of acrolein oxidation with $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ and the oxidation of propene yields a selectivity to acrolein that decreases significantly with increasing conversion of propene (Fig. 4), it is likely that acrolein is an intermediate in the oxidation of propene to acrylic acid.

Acetone. The products of acetone oxidation over VO-H-beta are CO_x , acetic acid, and isobutene (Fig. 9). The selectivity to isobutene is 28% at 250°C at 20% conversion. The formation of isobutene is catalyzed by the acidity of VO-H-beta. The acetone conversion to isobutene can take place via acid-catalyzed aldolization and dehydration with subsequent cracking (29–31). For the $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ catalyst, acetic acid and CO_x are the only products formed, and no isobutene is observed. This suggests that $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ has a lower acidity than VO-H-beta.

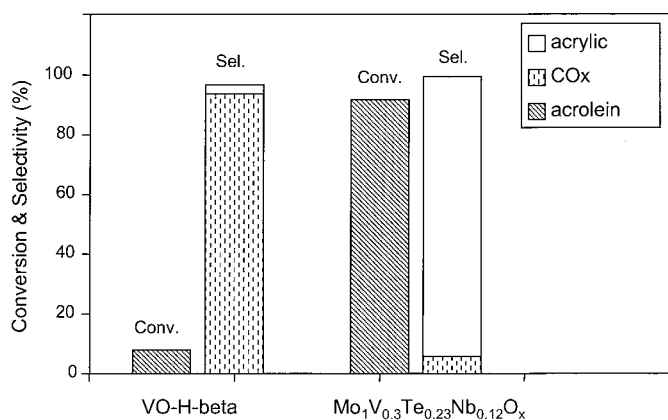


FIG. 8. Conversion and product distribution of acrolein oxidation over VO-H-beta and $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ at 250°C and 2 s contact time with a molar feed gas ratio of acrolein : O_2 : He = 0.4 : 2 : 12.6.

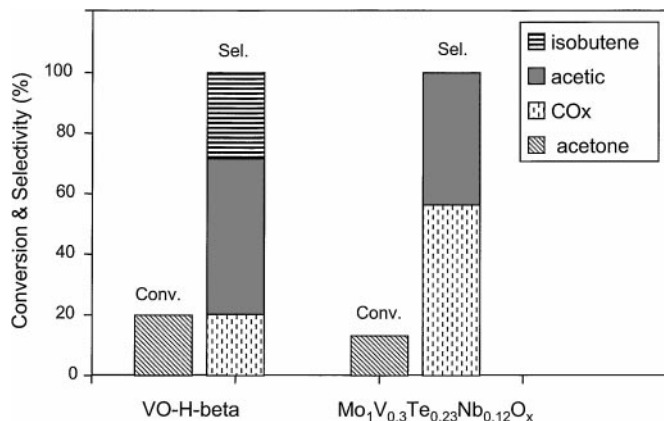


FIG. 9. Conversion and product distribution of acetone oxidation over VO-H-beta and $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ at 250°C and 2 s contact time with a molar feed gas ratio of acetone : H_2O : O_2 : He = 0.4 : 3.6 : 2 : 9.

To confirm that acetic acid results from C–C(=O) cracking of acetone, the oxidation of 3-pentanone was performed over VO-H-beta and $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$. As expected, propanoic acid, acetic acid, and acetaldehyde are the major oxidation products for both catalysts.

Acids. Compared to alcohols and aldehydes, acrylic acid and acetic acid are very stable at 250°C over both VO-H-beta and $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ catalysts. The conversions of acrylic acid over both VO-H-beta and $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ are less than 6.5% at a contact time of 2 s. However, much more total oxidation products are formed with VO-H-beta. The conversions of acetic acid over both VO-H-beta and $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ are less than 5% at a contact time of 2 s and CO_x are the only products.

3.3.2. Reaction network and catalytic behavior of propane oxidation over $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$. The exact reaction pathway of propane oxidation may vary from one catalyst to another. Broadly speaking, three major reaction routes are possible starting from propane (Scheme 3) (32). In the first route, propane is oxidized to 1-propanol, then to propanal, and finally to propanoic acid. In the second route, propane forms propene by oxidative dehydrogenation, that is oxidized to allyl alcohol, acrolein, and acrylic acid. In the third route, propane is oxidized to 2-propanol, and 2-propanol is oxidized to acetone and acetic acid. This reaction network may be further complicated by transformations between intermediates of different routes.

Based on the study of individual oxygenates (Section 3.3.1) and the trends in product selectivities as a function of conversion (Section 3.2), the reaction pathway described by route II (Scheme 3) is favored over routes III and I for propane oxidation over $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$. A more detailed reaction network is shown in Scheme 4. Propane is first dehydrogenated to propene and most of the formed

The results from reacting individual oxygenates over VO-H-beta indicate that acidity plays a major role in catalysis. Dehydration is an important step over VO-H-beta when 1-propanol and 2-propanol are the reactants. This leads to high selectivity for propene through intramolecular dehydration and formation of ether through intermolecular dehydration at lower temperature (150°C). The acidity also plays a critical role in the formation of isobutene from the oxidation of acetone over VO-H-beta. Large amounts of CO_x are observed in the oxidation of propanal and acrolein over VO-H-beta, with relatively little of their expected partial oxidation products, propanoic acid and acrylic acid, respectively.

3.4. Comparison of Catalytic Behavior of Propane

Oxidation over VO-H-beta and Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x

By investigating the reactivity of individual oxygenates over VO-H-beta and Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x, it is found that the main differences between these two catalysts are their acidity, capability for allylic oxidation, and the extent of total oxidation. As stated above, VO-H-beta has a much higher acidity than Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x. Most reactions over VO-H-beta are acid-driven, while for Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x oxidation is more important. Comparing 2-propanol and 1-propanol oxidation over VO-H-beta and Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x, the dehydration products are almost the only products formed over VO-H-beta, while oxidation products (acetone and acrylic acid for 2-propanol, and propanal and propanoic acid for 1-propanol) are dominant products over Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x.

The allylic oxidation capability of VO-H-beta is poor compared to the excellent performance of Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x. For VO-H-beta, no acrylic acid is observed from propene oxidation and only small amounts of acrylic acid are formed from the oxidation of acrolein. As allylic oxidation is an important step in the oxidation of propane to acrylic acid, this function needs to be greatly enhanced for further improvement of VO-H-beta.

Total oxidation is more severe over the zeolite-based catalyst compared to the bulk oxide catalyst. Besides deep oxidation from propane and propene, large amounts of CO_x are observed in the oxidation of individual oxygenates over VO-H-beta. This could be due to factors such as acidity, high surface area, and long diffusion time in contact with the catalytic active sites resulting from the microporous structure of zeolites. The behavior of VO-H-beta in oxidation of propanal and acrolein is particularly notable. These reactions involve oxidations of relatively weak C-H bonds and hence should be relatively facile, yet both exhibit relatively low activity and give little of the expected products, the respective carboxylic acids, compared to Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x (Figs. 7 and 8). In contrast, for other apparently more difficult oxidations (e.g., C-C bond cleavage of acetone, Fig. 9) the VO-H-beta catalyst

is as active as or more so than Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x. Such substrate-specific behavior is obviously crucial in determining successful catalysts for complex reactions, such as oxidation of propane to acrylic acid, and presumably is intimately connected with the detailed active site structure. Understanding these connections will be a major challenge for future research in the field.

4. CONCLUSION

By investigating the trends in product selectivities as a function of propane and propene conversion and the transformation of individual oxygenates, propene is found to be the primary product for propane oxidation over VO-H-beta, and acetic acid is a sequential oxidation product of the formed propene possibly through an acetone intermediate. With Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x, propene is the primary product for propane oxidation and the propene thus formed oxidizes further to acrylic acid and acetone. Reaction of individual oxygenates also reveals the superior partial oxidation features of the mixed metal oxide catalyst relative to the zeolite-based catalyst.

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