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Reaction pathways in the selective oxidation of propane over a mixed metal oxide catalyst

Manhua Lin*, Tejal B. Desai, Frederick W. Kaiser, Peter D. Klugherz

Rohm and Haas Company, Research Laboratories, Spring house, PA 19477, USA

Abstract

The catalytic properties of a Mo–V–Te–Nb–O mixed metal oxide catalyst were investigated in the selective oxidation of propane and its corresponding partial oxidation intermediates. Propane oxidation pathways are proposed based on experimental findings. © 2000 Published by Elsevier Science B.V.

Keywords: Propane; Oxidation; Reaction pathways; Mixed metal oxide catalyst; Acrylic acid

1. Introduction

The selective oxidation of lower alkanes to various functionalized molecules has attracted much interest in recent years [1]. In particular, reactions involving propane selective oxidation to propylene, acrolein, acrylic acid, or its ammoxidation to acrylonitrile have been heavily studied [2–5]. Propane partial oxidation to acrylic acid (AA) over vanadium pyrophosphate (VPO) catalysts [6–9] has been reported and reaction pathways were suggested by Ai [6] for a Te-modified VPO catalyst. Propane oxidation to AA with heteropolyacids or with their corresponding salts has also been reported [10–13]. In propane ammoxidation to acrylonitrile, V–Sb oxide catalysts were studied by several researchers [14–17] and Mo–V–Te–Nb–O oxide catalysts were studied by Ushikubo et al. [18–20]. Very recently, propane oxidation pathways with Ni–Mo–Te–P–O catalysts were also proposed by Kaddouri et al. [21]. We report here an investigation of the catalytic properties in propane selective oxidation to AA of a Mo–V–Te–Nb–O catalyst comparable to that reported by Ushikubo et al. [18]. To elucidate possible reaction pathways, we also studied the oxidation of key partial oxidation intermediates over this catalyst.

2. Experimental

2.1. Catalyst preparation

An aqueous mixture containing Mo, V, Te and Nb metal ions in the appropriate atomic ratio was prepared by mixing solution of the starting materials described by Ushikubo et al. [19]. This aqueous mixture was frozen in a dry-ice acetone bath and dried under vacuum to obtain the catalyst precursor in powder form. The precursor was pressed and sized to granules and calcined at 600°C for 2 h with a steady nitrogen flow. The resulting catalyst was pressed and sized to 12–20 mesh for testing.

2.2. Catalyst characterization

Catalyst bulk composition was determined using a Philips 2404 Wavelength dispersive XRF spectro-

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* Corresponding author. Fax: +1-215-659-0547.
E-mail address: mmandylin@netzero.net (M. Lin).

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meter. Catalyst surface composition was determined via ESCA on a Kratos Axis-Ultra instrument. A pass energy of 160 eV was used for running survey scans to determine the elements present in the catalyst and all binding energies were referenced by maintaining the C 1s peak at 284.6 eV. Catalyst surface morphology was obtained with a JEOL 840 Scanning Electron Microscope. Surface area and adsorption average pore diameter were measured by conventional BET methods. Catalyst crystalline phases were determined by XRD using a Philips X-ray powder diffractometer and Cu Kα radiation.

2.3. Catalyst evaluation

Approximately 20 g of catalyst was packed in an 11 mm ID stainless steel tubular reactor and tested over a wide range of temperatures at a substrate/air/water mole ratio of 3/50/47, a space velocity of 1200 h^{-1} and a pressure of 7 psig. The substrates were propane, propylene, isopropanol, acetone, acrolein, AA and acetic acid, respectively. The off-gas was separated from the liquid phase with cold traps. Product streams were analyzed by GC.

3. Result and discussion

3.1. Catalyst characterization

Table 1
Catalyst composition analysis

Measurement	Relative molar ratio			
	Mo	V	Te	Nb
Bulk composition based on starting material	1	0.30	0.23	0.12
Bulk composition based on XRF	1	0.25	0.18	0.09
Surface composition based on ESCA	1	0.30	0.19	0.15

As shown in Table 1, the bulk metal composition (measured by XRF) and surface metal composition (measured by ESCA) are reasonably close to the composition derived from the amount of starting material used in the preparation. The elemental analyzes served as a check on the catalyst preparation and these results confirmed our target catalyst compositions.

The measured BET surface area of 3.6 m^2/g and pore size of 180 Å are typical of mixed metal oxide catalysts. The SEM imaging (Fig. 1) revealed that the catalyst consists of primary sub-micron particles and their porous aggregates. The X-ray diffraction patterns of the Mo–V–Te–Nb–O catalyst we prepared exhibited major diffraction peaks at 2θ of 22.4°, 28.6°, 36.5°, 45.4° and 50.4° as reported by Ushikubo et al. [18].

3.2. The selective oxidation of propane

The results of propane oxidation with the Mo–V–Te–Nb–O catalyst are presented in Table 2. As a comparison, propane oxidation results Te/VPO carried out by Ai [6] and Te–P/NiMoO, carried out by Kaddouri et al. [21] are also included in the table. Besides the

Fig. 1. SEM imaging of the $Mo_1V_{0.3}Te_{0.2}Nb_{0.1}$ catalyst.

Table 2
Selective oxidation of propane

Catalyst	Temperature (°C)	Propane conversion (%)	Selectivity (%)					
			Propylene	Acetone	Acetic acid	Acrolein	AA	Co$_x$
Mo–V–Te–Nb–O	391	18	0	1	8	0	26	54
Te/VPO [6]	390	23	0	0	0	0	37	63
Te–P/NiMoO [21]	460	12	22	0	0	13	23	40

common products of AA and CO$_x$, the selectivities to other partial oxidation products are very different with respect to the three catalysts compared, which suggests that propane might follow very different pathways with these catalysts.

3.3. Propane oxidation pathways

Using what is known about the oxidation of *n*-butane on VPO catalysts, Ai [6] speculated that propane oxidation to AA on the Te-modified VPO catalyst follows the pathways shown in Fig. 2a. He proposed that propane was oxidized first to propylene, which was further oxidized to AA through acrolein intermediate, or is oxy-hydrated to acetone through isopropanol intermediate. Acetone was further oxidized to acetic acid and CO$_x$. Note that in his paper, the only products observed were AA and CO$_x$.

With respect to Te–P/NiMoO catalysts, since both acrolein and propylene were both obtained as products, Kaddouri et al. [21] concluded that propane oxidation involves different reaction pathways as shown in Fig. 2b. The authors excluded acetone or acetic acid as possible intermediates, since they were not detected. However, pathways to acrolein and acetaldehyde were supported by product collected, although only trace of later was detected. In addition, Kaddouri et al. [21] also speculated the direct oxidation of propylene to CO$_x$.

Since the Mo–V–Te–Nb–O mixed metal oxide catalyst reported here is compositionally and structurally different from either Te/VPO or Te–P/NiMoO catalysts, it is likely to have oxidation pathways different from proposed in Fig. 2. Results in Table 2 also suggest the existence of different pathways. To better elucidate the propane oxidation pathways, the oxidation behavior of several possible intermediates mentioned in Fig. 2 were also studied as feed substrates over the Mo–V–Te–Nb–O catalyst.

3.3.1. Relative reactivity of oxidation substrates

As expected for a saturated hydrocarbon, propane is much less reactive than propylene or other oxygenate substrates as we have studied. Fig. 3 shows the conversions of these substrates over a range 250–390°C. With the Mo–V–Te–Nb–O catalyst, the order of relative reactivity of these substrates was

$$\text{propane} \ll \text{acetic acid} \approx \text{AA} < \text{propylene} < \text{acetone} < \text{acrolein} \approx \text{isopropanol}$$

Except for the relative reactivity of AA and acetic acid, this agrees with the order suggested by Ai [6] for the Te-modified VPO catalyst:

$$\text{propane} < \text{acrylic acid} < \text{acetic acid} < \text{propylene} < \text{acrolein}$$

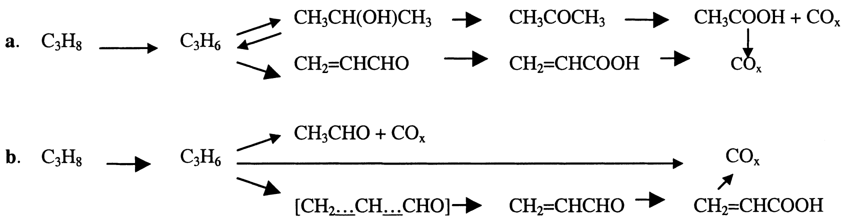


Fig. 2. Oxidation pathway on (a) Te/VPO [6] and (b) Te–P/NiMoO [21] catalysts.

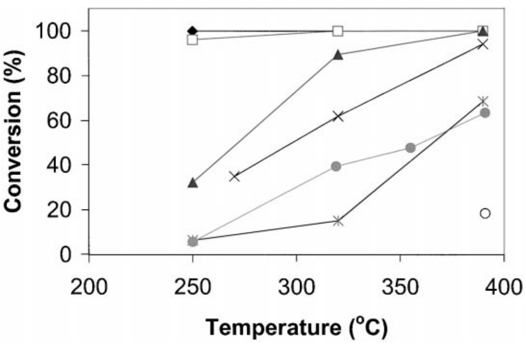
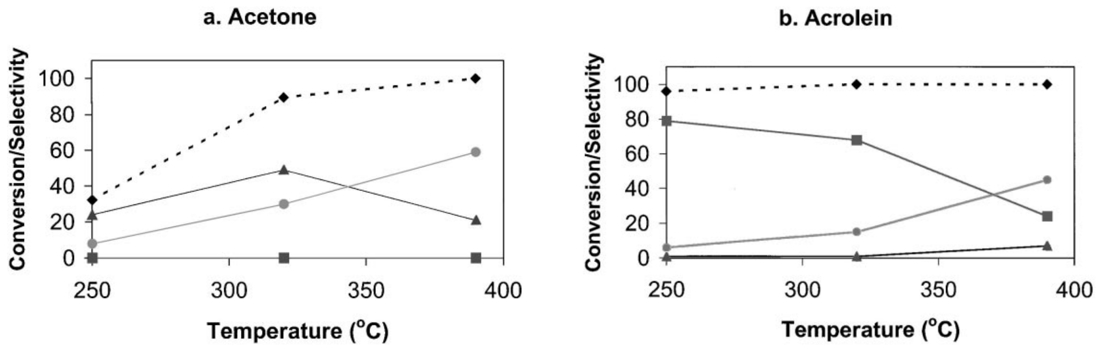


Fig. 3. Relative reactivity of propane (○), propylene (×), acrolein (□), acrylic acid (●), acetone (▲), acetic acid (∗) and isopropanol (◆).

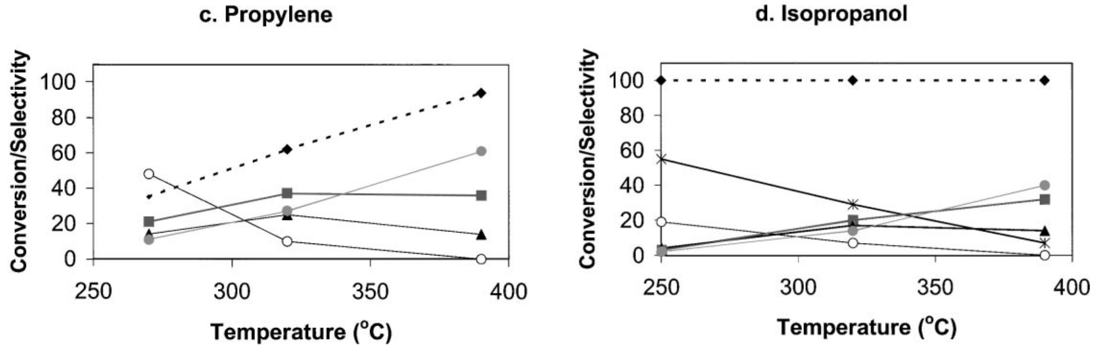
Here, the different ranking of the two acids could be due to the difference in catalysts studied. Based on Fig. 3, at 390°C or above, acrolein, acetone, isopropanol and propylene are too reactive to be detected. Indeed, only total oxidation products CO_x, acrylic acid and some small amount of acetic acid were detected in propane oxidation at 390°C (Table 2). At such temperatures, propylene, isopropanol or acrolein may well be intermediates but not detectable in the product stream. Even if they do exist as intermediates, they may exist for an extremely short time, and possibly only as surface-adsorbed species.

3.3.2. Oxidation profiles of some possible intermediates

Fig. 4 shows the oxidation profiles of acetone, acrolein, propylene and isopropanol as substrates. As shown in Fig. 4a, acetone has a fairly simpler oxidation pathway; it leads only to acetic acid and CO_x. Acetic acid is the major product at lower temperatures, while CO_x is the major product at higher temperatures. The decrease of acetic acid selectivity at higher temperature is likely due to its further oxidation to CO_x. As shown in Fig. 4b, at low temperatures, acrolein was oxidized mostly to AA. The gradual decrease in AA


a. Acetone

b. Acrolein


c. Propylene

d. Isopropanol

Fig. 4. Oxidation profiles for various substrates. Conversion (◆) and selectivities to acrylic acid (■), acetic acid (▲), acetone(○), propylene(∗), and CO_x (●).

selectivity with increasing temperature is also likely caused by the further oxidation to CO_x. At 390°C, a few percent of acetic acid, which is believed to be an oxidation product of AA, is also detected.

Results in Fig. 4c suggest that propylene is oxidized via two competing pathways:

(a) propylene→acrolein→acrylic acid, and
(b) propylene→acetone→acetic acid.

Here in path (a), propylene is oxidized to AA through acrolein, while in path (b), the oxidation of propylene to acetone could proceed through oxy-hydration as Ai [6] suggested. But, the direct oxidation from propylene to acetone is also possible and both pathways eventually lead to CO_x. Since the acetone pathway does not lead to AA as discussed above, and acrolein produces mostly AA at low temperatures. The results shown indicate that propylene favors the acetone pathway at lower temperatures and favors the acrolein pathway at higher temperatures. It should be noted that the reaction mechanisms are likely different for the two pathways, with acetone forming through propylene hydration and acrolein through oxygen insertion. The results in Fig. 4d show that isopropanol also reacts via two competing pathways: (a) dehydration to propylene, and (b) oxidation to acetone. The increasing AA selectivity with increasing temperature indicates that the propylene pathway is favored at higher temperatures.

The oxidation profiles of acetic acid and acrylic acid are relatively simple. As expected, carbon oxides were the only products detected from acetic acid oxidation. However, a significant amount of acetic acid was formed from the oxidation of AA, supporting the argument made in the discussion of acrolein oxidation profile.

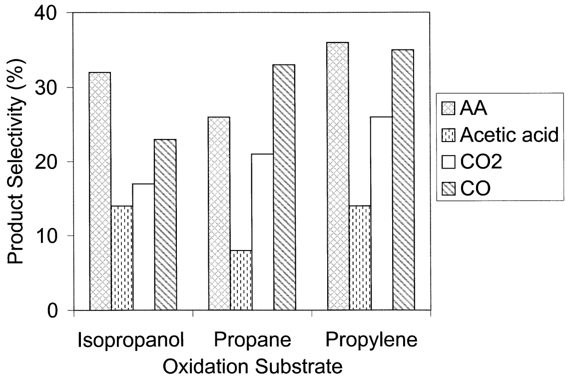


Fig. 6. Pattern of selectivity at 390°C.

3.3.3. *The elucidation of propane oxidation pathways*

From propane, one can envision at least three possible reaction pathways leading to various partial oxidation products. Based on the oxidation profiles of possible intermediates discussed, three possible pathways are described in Fig. 5. Note that oxidation of 1-propanol is analogous to that of isopropanol.

In path (a), 1-propanol is formed by insertion of one oxygen into the methyl C–H bond, which dehydrates to propylene or is oxidized to propionic acid through propionaldehyde. Path (b) is a direct oxidative dehydrogenation from propane to propylene followed by oxidation to AA through acrolein. In path (c), isopropanol is formed by insertion of one oxygen into the methylene C–H bond, which can dehydrate to

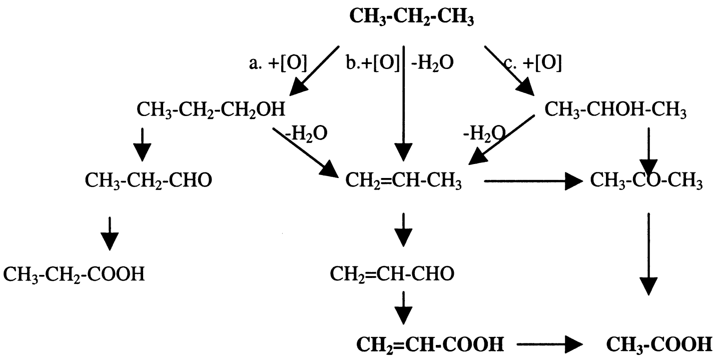


Fig. 5. Possible oxidation pathways of propane (CO_x formation not included; the observed partial oxidation products are highlighted).

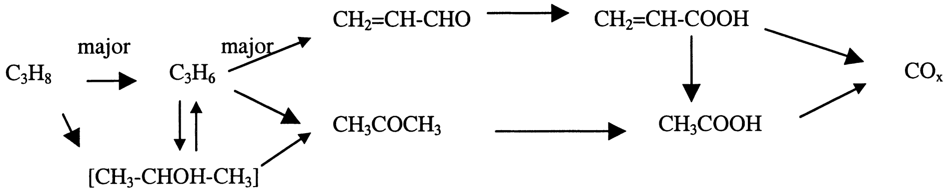


Fig. 7. Proposed oxidation pathway on Mo–V–Te–Nb–O catalyst.

propylene or further oxidize to acetone. In the oxidation of propane, acrylic acid and acetic acid were both obtained in substantial quantity, but propionic acid was not detected at all. This result suggests that path (a) is less likely. In fact, oxygen insertion to methyl C–H bond (path a) should be harder than to methylene C–H bond (path c) since the bond strength of latter is a few kcal weaker.

Currently, we are unable to conclude if pathway (c), or isopropanol intermediate truly exists. However, the patterns of oxidation product distribution of propane, propylene and isopropanol (Fig. 6) at 390°C with this catalyst may allow some speculation. While the product distribution patterns of propane and isopropanol are significantly different, the product distribution patterns of propane and propylene are very much alike, which suggests that propylene is likely the dominant first oxidation intermediate of propane over this catalyst. Therefore, we believe that the oxidation of propane over this catalyst likely goes first to propylene, followed by subsequent oxidation reactions as indicated in Fig. 6.

4. Conclusion

Based on our results, we conclude that propane oxidation over the Mo–V–Te–Nb–O catalyst follows the reaction pathways shown in Fig. 7. In this proposed scheme, the existence of isopropanol as an oxidation intermediate of propane is speculative while the existence of other intermediates is supported by our findings. Compared with the oxidation pathways proposed for Te/VPO (Fig. 2a), the major difference for the oxidation pathways shown in Fig. 7 involves the formation and reaction of isopropanol as possible intermediate from propane or propylene to acetone. Compared with the oxidation pathways proposed for Te–P/NiMoO catalysts (Fig. 2b), the major differences include the existence of acetone path for Mo–V–Te–Nb–O and proposed direct oxidation of propylene to CO_x as well as the acetaldehyde path for Te–P/NiMoO. It is unclear whether these differences are caused by the differences in the catalysts studied. However, to prove if an equilibrium exists between propylene and isopropanol, one might be able to use D_2O or H_2O^{18} as vapor feed for propylene oxidation since a hydration step was proposed by Ai (Fig. 2a).

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