



# Oxidation, oxidative esterification and ammoxidation of acrolein over metal oxides: Do these reactions include nucleophilic acyl substitution?



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## ABSTRACT

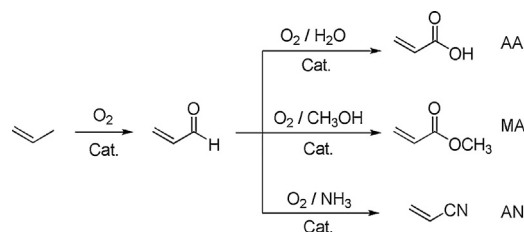
It is known that nucleophilic acyl substitution in the RCOX compounds with “good leaving” groups X is a fundamental and energetically favorable route to carboxylic acid derivatives. When water, alcohols and ammonia are used as nucleophiles, carboxylic acids, esters and amides (or nitriles) are obtained, respectively. On the other hand, the same products are derived from aldehydes upon their catalytic aerobic oxidation, on condition that water, alcohols and ammonia are present in the feed gas. Therefore, one can surmise that nucleophilic substitution reactions are involved intrinsically in the catalytic oxidation reactions. In agreement with this hypothesis we have shown, as an example, that the selfsame catalyst, MoVTeNb mixed oxides, enables successful oxidation, oxidative esterification and ammoxidation of acrolein. The mechanistic aspects of these reactions are considered based on established organic and general chemistry principles.

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## 1. Introduction

Acrylic acid (AA), methyl acrylate (MA) and acrylonitrile (AN) are important bulk chemicals. Their production is currently based on propylene oxidative transformations, while propane is also considered as a promising feedstock to obtain AA and AN. It is important in this connection that acrolein plays a key role as an isolated or in situ intermediate in these reactions. For example, aerobic oxidation of acrolein to AA over a molybdenum–vanadium oxide catalyst is a part of the two-step propylene oxidation process (Scheme 1) [1–4]. Notably, this reaction proceeds normally in the presence of 20–40 vol% of water at 250–310 °C.

MA is usually obtained by the acid-catalyzed esterification of AA with methanol. However, MA can be synthesized directly from acrolein or even propylene as a result of oxidative esterification, on condition that methanol is added to the feed (Scheme 1) [5,6].



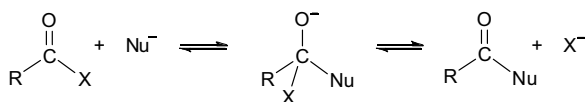
Scheme 1. Oxidative transformations of propylene and acrolein.

AN is mainly produced by ammoxidation of propylene over bismuth molybdate catalysts at 400–500 °C (Sohio process) [7–9]. There is no generally accepted opinion whether this reaction proceeds via in situ formation of acrolein or not [10–15]. Nevertheless, acrolein itself undergoes oxidation in the presence of ammonia to yield AN, the rate of this reaction is at least several times as high as the rate of propylene ammoxidation (Scheme 1) [10–15].

It should be noted that in spite of significant practical value of the propylene/acrolein oxidation reactions, their mechanism is not clear so far and is still under debate. However, taking into account a striking similarity in the acrolein conversions to AA, MA and AN (Scheme 1), a common mechanism for these reactions can be

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**Scheme 2.** Nucleophilic acyl substitution (general reaction pattern). X = halide (acid halides), acyloxy (anhydrides), alkoxy (esters), and other “good leaving” groups.

surmised. The evident difference in the reactions at **Scheme 1** is the presence of various reagents, such as water, methanol and ammonia.

However, the presence of water is often neglected or at least underestimated in mechanistic considerations for the acrolein oxidation. Usually, the role of water is reduced to influence on the AA desorption from a catalyst surface [16,17] regardless of the fact that more significant impact and even direct water participation in the reaction mechanism definitely occurs [18]. Notably, even though water is absent in the initial feed gas, it can be generated as an intermediate during the oxidation reaction.

Furthermore, production of MA upon oxidative conditions has been mainly explained by preliminary oxidation of acrolein to AA followed by the in situ acid-catalyzed esterification reaction. In actual fact, the mechanism of oxidative esterification of aldehydes remains uncertain and a few alternative mechanisms for this reaction have been suggested [6,19–30].

Amoxidation of acrolein is typically attributed to intermediate formation of an imine or acrolein–ammonia complexes, which undergo dehydrogenation and dehydration reactions [10–15]. One more reaction mechanism suggests initial oxidation of acrolein to AA followed by reaction of AA with ammonia to give AN [10,31]. However, this idea was discarded on account of quite low selectivity toward nitriles in reactions of carboxylic acids upon drastic amoxidation conditions [31].

The mechanism of propylene “direct” amoxidation to AN is a more widely discussed topic in the literature [32]. Ammonia is usually considered as a source of complexes pertinent to ammonia fixation on the transition metal oxides. Such complexes are believed to react with allylic radicals or the like species to give finally AN [33]. This version is mainly based on IR observation of surface species, such as  $\text{Me}^{+n}\text{—NH}_2$  and  $\text{Me}^{+m}\text{=NH}$ , formed by ammonia dissociative adsorption and concurrent reactions. However, the suggested reaction mechanism is not unambiguously supported by theoretical calculations, which show that reaction of allylic radical with  $\text{Me}^{+m}\text{=NH}$  species is finally energetically unfavorable [34].

Thus, no general mechanism for the reactions on **Scheme 1** is suggested so far. On the other hand, if water, methanol and ammonia are considered as typical nucleophilic reagents, we can find very close analogy to these reactions in the field of organic chemistry. For instance, it is known that nucleophilic acyl substitution in the RCOX compounds (with good leaving groups X) is a fundamental and energetically favorable route to carboxylic acid derivatives. When water, alcohols and ammonia are used as nucleophiles, carboxylic acids, esters and amides are produced, respectively (**Scheme 2**) [35].

It should be noted also that non-substituted amides are thermally unstable compounds, which can convert readily into nitriles via dehydration at elevated temperatures [31]. AN, for example, was first prepared by heating of acrylamide with phosphorus pentoxide [36], while the latter reagent is not essential and various metal oxides are more efficient promoters for the same reaction [37].

In view of the aforesaid, the aim of this article was to suggest a mechanism, which can connect all three reactions shown in **Scheme 1**. Therefore, we have considered the idea that catalytic oxidation of acrolein to AA, MA and AN involves inherently nucleophilic substitution reactions with water, alcohols and ammonia. A general stage of these reactions could be the formation of an acyl type intermediate on the catalyst surface resulting from partial oxidation of acrolein. This intermediate will undergo transformations analogous to nucleophilic acyl substitution in homogeneous reactions of organic compounds.

It is evident that in order to establish the proposed reaction pathway it has to be shown initially that all the reactions can be carried out over the same catalyst. Therefore, in our experimental part of the work we have studied gas phase oxidation of acrolein in the presence of water, methanol and ammonia over the selfsame catalyst, MoVTeNb mixed oxides. The results obtained are most plausibly interpreted in terms of HAT theory and nucleophile–electrophile interactions. Recently, similar consideration was applied to catalytic oxidation of methanol over vanadia and this gave a robust explanation for predominant selectivity towards each product among formaldehyde, formic acid, dimethoxymethane and methyl formate depending on reaction conditions [38].

## 2. Experimental

The preparation and characterization of the sample of mixed MoVTeNb oxides, was described elsewhere [39]. A sample of nominal composition  $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$  (obtained by spray drying at 190 °C) was calcined in He flow at 600 °C to ensure the formation of the targeted active phase. After calcination, specific surface area of the sample was  $7.3\text{ m}^2\text{ g}^{-1}$ ; the final chemical composition of the sample was  $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.12}\text{Nb}_{0.12}\text{O}_x$ ; two major phases including M1 orthorhombic (80%) and M2 hexagonal (15%) phases were detected [39].

The gas-phase oxidation reactions were performed in a quartz tube flow reactor with an internal diameter of 6 mm, using shaped catalyst granules ( $d = 0.25\text{--}0.5\text{ mm}$ ; 2.1 g, ca. 3 mL). The reactive gas mixtures were fed into the reactor filled with the catalyst; the reactor was operated under atmospheric pressure. The gas mixtures were preheated by mixing acrolein/He,  $\text{H}_2\text{O}/\text{He}$ , methanol/He,  $\text{NH}_3$  and air in gas mixing device at 150 °C followed by passing the mixtures through a spiral quartz tube with an internal diameter of 6 mm at the catalyst bed temperature. The reaction temperature was measured inside the reactor ( $\pm 1\text{ }^\circ\text{C}$ ) using a thermocouple inserted into the catalyst bed. During the catalytic runs, gas samples were analyzed by integrated online gas chro-

**Table 1**  
Aerobic oxidation of acrolein over MoVTeNb catalyst in the presence of water, methanol and ammonia.

No.	Feed composition	Conv. of acrolein (%)	Sel. to AA (%)	Sel. to MA (%)	Sel. to AN (%)
1	Acrolein/ $\text{H}_2\text{O}/\text{air}$ 5/10/85	99.5 <sup>a</sup>	95.0 <sup>b</sup>	–	–
2	Acrolein/ $\text{CH}_3\text{OH}/\text{air}$ 5/10/85	99.7 <sup>a</sup>	14.5	78.2 <sup>c</sup>	–
3	Acrolein/ $\text{NH}_3/\text{air}$ 7/8/85	98.5 <sup>d</sup>	–	–	87.6 <sup>e</sup>
4	Acrolein/ $\text{NH}_3/\text{H}_2\text{O}/\text{air}$ 7/8/10/75	98.4 <sup>d</sup>	–	–	87.5 <sup>e</sup>

<sup>a</sup> Reaction conditions:  $T = 250\text{ }^\circ\text{C}$ , contact time is 1.3 s (GHSV = 2770  $\text{h}^{-1}$ ).

<sup>b</sup> The balance is acetic acid and  $\text{CO}_x$ .

<sup>c</sup> The balance is acetic acid and  $\text{CO}_x$ ; conversion of methanol is 65.4%.

<sup>d</sup> Reaction conditions:  $T = 410\text{ }^\circ\text{C}$ , contact time is 0.2 s (GHSV = 18000  $\text{h}^{-1}$ ).

<sup>e</sup> The balance is HCN, acetonitrile, and  $\text{CO}_x$ .

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