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ABSTRACTS

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Oxidation, Oxidative Esterification and Ammoxidation of Acrolein over Metal Oxides: Do these Reactions Include Nucleophilic Acyl Substitution?

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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 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). Notably, this reaction proceeds normally in the presence of 2 to 40 vol% of water at $250-310^{\circ}C$.

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).

AN is mainly produced by ammoxidation of propylene over bismuth molybdate catalysts at $400-500^{\circ}C$ (Sohio process). There is no generally accepted opinion whether this reaction proceeds via in situ formation of acrolein or not. 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).
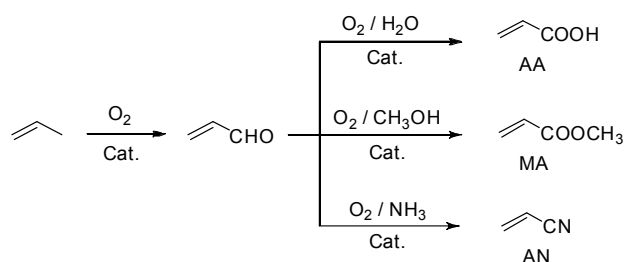
Scheme 1. Oxidative transformations of propylene and acrolein.

Taking into account a striking similarity in the acrolein conversions to AA, MA and AN, it can be surmised a common mechanism for these reactions. Obviously, a general stage should be an oxidation of acrolein into the same intermediate, which will undergo different transformations depending on the reaction conditions. The evident difference in the reactions at Scheme 1 is the presence of various reagents, such as water, methanol and ammonia.

However, no general mechanism for the reactions on Scheme 1 is suggested so far. On the other hand, it is known that nucleophilic acyl substitution in the RCOX compounds (with good leaving groups X) is a fundamental and energetically favourable route to carboxylic acid derivatives. When water, alcohols and ammonia are used as nucleophiles, carboxylic acids, esters and amides (or nitriles) are produced, respectively (Scheme 2).
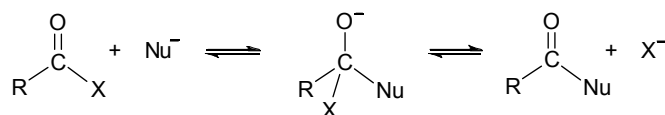
Scheme 2. Nucleophilic acyl substitution (general reaction pattern). X = halide (acid halides), acyloxy (anhydrides), alkoxy (esters), and other "good leaving" groups.

In our presentation we reasoned that catalytic oxidation of acrolein to AA, MA and AN can involve inherently nucleophilic substitution reactions with water, alcohols and ammonia. Therefore, we have shown initially that the selfsame catalyst, MoVTeNb mixed oxides, provides all three reactions, such as oxidation, oxidative esterification and ammoxidation of acrolein. The results obtained can be 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 [1].

2   Results and discussion

The gas-phase acrolein oxidation reactions were performed using MoVTeNb oxides chosen as powerful and versatile vanadium catalyst. As expected, AA is mainly produced in the presence of water. When methanol is present in the feed, MA becomes the main product, while minor amounts of AA are also formed. When ammonia is present in the feed, AN becomes the main product. Moreover, addition of water in the feed in amount of 10 vol% practically does not influence the result of the latter reaction. Accordingly, the same catalyst provides quite efficiently oxidation, oxidative esterification and ammoxidation of acrolein (the experimental details will be disclosed in presentation). Therefore, one may propose that all these reactions are relative and, moreover, they may be happen within the same catalytic sites.
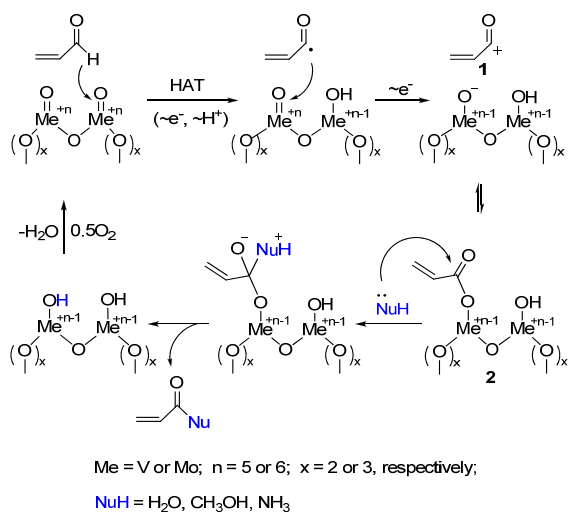
For a simplified theoretical consideration, a hypothetical sequence of the reaction steps in acrolein oxidative transformations can be outlined by the example of a monolayer dimeric metal oxide (Scheme 3). The oxidation step leads to formation of intermediates such as **1** and **2**.

Scheme 3. Proposed mechanism for oxidation of acrolein in the presence of water, methanol and ammonia over monolayer dimeric metal oxide.

Me = V or Mo; n = 5 or 6; x = 2 or 3, respectively;

NuH = H_2O, CH_3OH, NH_3

Even though ion **1** does not react with a nucleophile immediately, it binds to the anion surface to form meta-stable compound **2**. Intermediate **2** is in fact a semiorganic ester, which is electrophilic enough to react with water, methanol and especially with ammonia to give AA, MA and acrylamide, respectively. Obviously, acrylamide undergoes immediate dehydration upon the reaction conditions (T > 400°C) to yield AN.

3   Conclusion

We suggest that transient acryl-vanadia/molybdenum surface complexes (formed in the oxidation stage) can react readily with typical nucleophiles, such as water, methanol and ammonia to yield the expected AA, MA and AN. The concept suggested is universal; it plausibly explains the formation of various products over the same catalyst upon oxidation conditions and is in accord with established organic and general chemistry principals.

References

[1]   K.Yu. Koltunov, V.I. Sobolev, *Adv. Chem. Lett.* 1 (2013) 280.