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Observation of nitriles formed in the oxidative dehydrogenation of carboxylic acids over metal-oxygen cluster catalysts

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At reaction temperatures of 300–350 °C isobutyronitrile and methacrylonitrile, in addition to the expected products of oxidative dehydrogenation, methacrylic acid, acetone, propene, CO and CO_2, are produced from isobutyric acid passed over ammonium salts of 12-molybdophosphoric acid.

Keywords: Oxidative dehydrogenation; nitriles; carboxylic acids; isobutyric acid; metal-oxygen cluster catalysts; heteropoly oxometalates

1. Introduction

Nitriles are an important family of organic molecules which are utilized extensively in the chemical industry. For example, acrylonitrile is undoubtedly the most commercially important nitrile monomer and is used in the manufacture of acrylic fibres, synthetic rubbers and resins. Acrylonitrile is produced almost exclusively by the ammoxidation of propylene over bismuth molybdate or multicomponent oxide catalysts [1]. The ammoxidation technology has been extended to prepare other important nitrile intermediates from paraffinic and olefinic hydrocarbons including methacrylonitrile from isobutane or isobutene and atroponitrile from α-methylstyrene (2).

The technologies available for the preparation of nitriles are not limited to hydrocarbon ammoxidations. Indeed, a large portion of nitrile production relies on oxygen containing organic molecules such as alcohols, aldehydes and carboxylic acids to serve as the nitrile precursor. Alumina supported zinc oxide has been utilized in the synthesis of aliphatic nitriles from aldehydes and alcohols

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that are co-fed over the catalyst with ammonia [3,4]. Similar reactions of carboxylic acids with ammonia over acidic catalysts result in the production of nitriles. Probably the best known reaction of this type is that of adipic acid with ammonia over BPO_4/Al_2O_3 to yield adiponitrile [5], although short chain nitriles can also be prepared using this method [6].

Each of the catalysts that has been mentioned in conjunction with ammoxidation processes and the formation of nitriles possesses some degree of Brönsted acidity which along with the oxidation-reduction properties of the catalyst appear to be the most important factors. Heteropoly oxometalates are ionic solids that possess both acidic and redox properties [7]. In particular, the 12-heteropoly oxometalates that contain the Keggin anion can exist in the protonic form (solid acid) or as one of a number of organic or inorganic salts. Several of the salts have shown to contain residual protons leading to distributions of acid strengths and numbers of sites that differ significantly from the parent acids [8]. In addition, the Keggin anion is composed to twelve octahedra of oxygen atoms with peripheral metal atoms near their centres that surround a tetrahedron of oxygen atoms with a heteroatom at its centre. The peripheral atoms are commonly tungsten, molybdenum or vanadium present in their highest oxidation state. The Keggin anions have been shown to undergo a series of reversible reductions both in solution [9] and the solid state [10]. These factors suggest that 12-heteropoly oxometalates possess chemical and physical requirements of ammoxidation catalysts.

In this paper we report the formation of isobutyronitrile (IBN) and methacrylonitrile (MAN) from the reaction of isobutyric acid (IBA) over some 12-heteropoly oxometalate catalysts. The route to the formation of the nitriles is discussed with regard to the structure of the catalysts and the reaction conditions studied in the present investigation.

2. Experimental

The catalysts employed in the current study included 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$), the ammonium and cesium salts that were prepared from precipitation reactions [$(NH_4)_3PMo_{12}O_{40}$ and $Cs_3PMo_{12}O_{40}$, respectively] and a series of salts containing both cesium and ammonium cations that were prepared using an ion exchange modification technique [11]. In addition, ammonium-12-tungstophosphate was studied. The measured numbers of cations as determined from ion chromatographic analysis are presented in table 1.

Reactions were carried out in a continuous flow microcatalytic reactor that has been described previously [12]. Isobutyronitrile and methacrylonitrile were analyzed by HP5890 gas chromatographs equipped with a 30 m DBFFAP capillary column (J&W Scientific) and flame ionization or mass spectrometric detectors.

Table 1
Cation composition of some 12-heteropoly oxometalate catalysts

	Number of NH_4^+ cations per Keggin anion	Number of Cs^+ cations per Keggin anion
$Cs_3PMo_{12}O_{40}$	–	2.78
NH_4PMoCs1	1.75	1.15
NH_4PMoCs3	1.30	1.53
CsPMo$NH_4$1	0.04	2.59
CsPMo$NH_4$3	0.14	2.44
NH_4PMo$NH_4$1	2.5	–
NH_4PMo$NH_4$3	2.51	–
$(NH_4)_3PMo_{12}O_{40}$	2.17	–

3. Results and discussion

Isobutyric acid was reacted over the 12-heteropoly oxometalate catalysts at 250, 300 and 350 ° C and apparent residence times of 0.85 and 1.4 mg mL min^{-1} in the absence and presence of co-fed oxygen (O_2/IBA = 2.65). Over $H_3PMo_{12}O_{40}$ and $Cs_3PMo_{12}O_{40}$ products of the oxidative dehydrogenation of IBA (methacrylic acid, acetone, propene, CO, CO_2) were formed. Interestingly, the 12-molybdophosphate catalysts that contained ammonium as one of the cations yielded isobutyronitrile and methacrylonitrile in addition to the oxidative dehydrogenation products. The nitrile selectivities are shown in table 2. The production of nitriles was particularly evident at the highest reaction temperature, although some of the catalysts also displayed a propensity for nitrile formation at the lower reaction temperatures.

In the absence of co-fed oxygen at 300 ° C, nitrile production was also observed over the ammonium containing 12-molybdophosphate salts (table 3).

Table 2
Initial selectivities [a] to nitrile products over 12-heteropoly oxometalate catalysts in the presence of oxygen

W/F [b]	250 ° C		300 ° C		350 ° C	
	0.85	1.4	0.85	1.4	0.85	1.4
$(NH_4)_3PMo_{12}O_{40}$	–	0.1	1.2	0.6	3.4	0.7
NH_4PMoCs1	tr	–	tr	1.2	1.0	1.0
NH_4PMoCs	–	–	tr	–	2.8	4.1
CsPMo$NH_4$1	–	–	–	–	–	–
CsPMo$NH_4$3	tr	tr	–	–	–	tr
NH_4PMo$NH_4$1	tr	–	0.7	2.1	0.6	0.4
NH_4PMo$NH_4$3	–	–	–	–	0.6	0.6

[a] After 15 min reaction time (mol%).
[b] mg min ml^{-1}.

Table 3
Initial selectivities [a] to nitrile products over some 12-heteropoly oxometalate catalysts at 300 ° C in the absence of oxygen

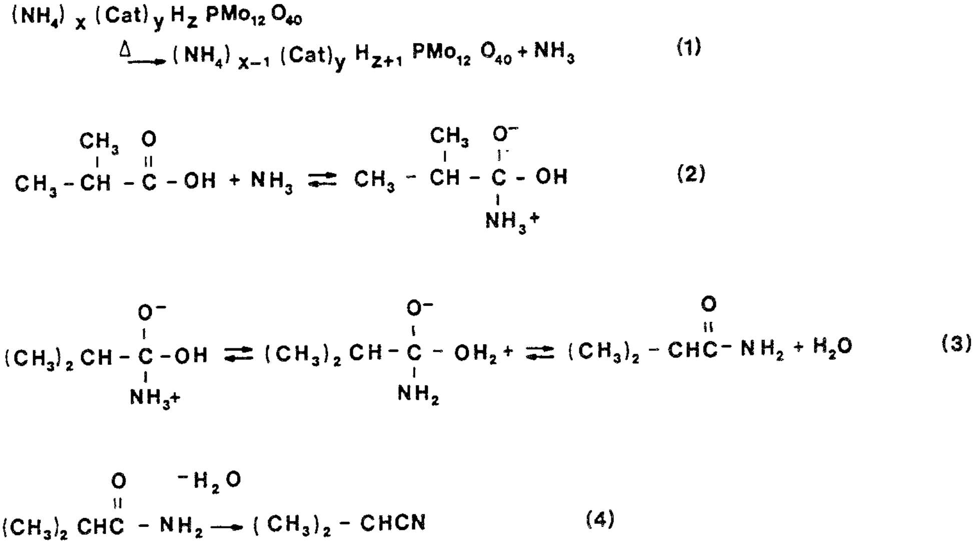
Catalyst	Selectivity [b] to nitriles
$(NH_4)_3PMo_{12}O_{40}$	8.0
$Cs_3PMo_{12}O_{40}$	–
$NH_4PMoCs1$	5.5
$NH_4PMoCs3$	5.0
$CsPMoNH_41$	–
$CsPMoNH_43$	1.0
NH_4PMoNH_41	8.5
NH_4PMoNH_43	22.0

[a] After 15 min reaction time (mol%).
[b] $W/F = 0.85$ mg min mL^{-1}.

In several cases the selectivities to the nitrile products formed in the absence of oxygen exceeded those obtained when oxygen was present in the feed stream. It is interesting to note that neither IBN nor MAN was formed following the reaction of IBA over $(NH_4)_3PW_{12}O_{40}$ either in the presence or absence of oxygen at 300 ° C. The marked difference in the behaviour of the 12-molybdophosphate and 12-tungstophosphate catalysts containing ammonium emphasizes the important role of the peripheral atoms in these isostructural heteropoly compounds.

The mechanism whereby the nitriles form evidently involves nitrogen initially present as ammonium cations in the 12-heteropoly salts. The production of the nitriles was unexpected since previous studies of the thermal stability [13,14] and the catalytic activity over $(NH_4)_3PMo_{12}O_{40}$ and $(NH_4)_3PW_{12}O_{40}$ did not suggest that decomposition of the ammonium cation and occurred. Catalytic reactions such as the conversion of methanol [14] and ethanol [15], hydrocarbon cracking [16] and the alkylation of toluene [17] showed no evidence for the formation of nitrogen-containing compounds although it is acknowledged that HCN can be produced from the reaction of methanol and ammonia over zeolite catalysts [18]. This suggests that there is a specific interaction between the isobutyric acid and the surface of the ammonium containing 12-molybdophosphate catalysts that leads to the nitrile formation.

A speculative mechanism for nitrile formation over the ammonium 12-molybdophosphate salts is outlined in fig. 1. It is conceivable that thermal activation of the catalysts leads to a weakened interaction between the ammonium ions and the Keggin anions with the potential existing for the formation of ammonia and a proton as shown in step (1). Following the formation of ammonia, the interaction with isobutyric acid either in the gas phase or in the proximity of the catalyst surface can lead to the formation of an ammonium



where (Cat) refers to a cation

and $x+y+z = 3$

Fig. 1. Step (1)–(4).

carboxylate salt (step (2)). At elevated temperatures the carboxylate salt with be susceptible to thermal degradation to the corresponding amide (step (3)).

The NH bond of the amide group is relatively labile [19] and hence the amide function can be readily dehydrated to yield the nitrile (step (4)). Heteropoly oxometalate catalysts have proven to be efficient dehydration catalysts [10,14,15] suggesting that this step should proceed with relative ease.

While it is evident from the data presented in table 2 that the production of the nitriles is relatively small, it must be remembered that the feed did not contain a source of nitrogen, limiting nitrile production to that which resulted from the decomposition of ammonium ions in the catalyst. Evidently, under the conditions studied, the production of nitriles is limited to the ammonium ions of the catalyst that are available to participate in the reaction. Since no source was available for replacement of the ammonium ions, the nitrile production decreased with time on stream as would be expected with only trace amounts, if any, present after a four hour reaction time.

It is important to note that, in contrast to the observations with other catalysts such as faujasite, which has been exchanged with ammonia, ammonium 12-molybdophosphate desorbs nitrogen, ammonia and water on heating beginning at approximately 400 ° C [20] in temperature programmed desorption experiments. However, in the present experiments it is expected that the ammonium content of the heteropoly salts will be largely intact at the temperatures of reaction.

The effect of the differences in surface areas and pore structures among the various solids listed in table 1 on the production of nitriles is unclear at this time, although there appears to be no correlation between the former and latter quantities.

The results of the present study suggest that 12-heteropoly catalysts containing molybdenum peripheral atoms may be effective for the preparation of nitriles from carboxylic acids.

Acknowledgement

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