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# Selective oxidation of propane over nickel molybdate modified with telluromolybdate

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## Abstract

It was observed that nickel molybdate modified with telluromolybdate catalyzed the oxidation of propane to acrylic acid and acrolein. The selectivity and activity increased with the amount of loading up to 6%. The synergistic effects between nickel molybdate and telluromolybdate were observed. © 2001 Published by Elsevier Science B.V.

*Keywords:* Propane; Oxidation; Nickel molybdate; Telluromolybdate

## 1. Introduction

In the last decade, much progress has been made in the selective partial oxidation of light alkanes with molecular oxygen in gas phase. Among various catalysts, nickel molybdate with a slight excess of $MoO_3$ has been reported to have good performance in oxidative dehydrogenation of propane [1–6] and butanes [7–15]. But their yields of oxygenates were not enough for an industrial production. In the variation of Ni–Mo catalysts, Mazzocchia and coworkers [16] found Ni–Mo–Te–P–O mixed oxide for selective oxidation of propane to acrylic acid and acrolein; the reported yields were still low. Based on the above prospect, we investigated the combination of molybdate supports and other elements which are able to perform allylic oxidation of propylene. In the present study, we examined nickel molybdate catalysts modified with telluromolybdate [17] and antimony complexes and observed that propane was catalytically oxidized to acrylic acid and acrolein with molecular oxygen in good yield.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

The precursor of $Ni_{0.92}MoO_{3.92}$ was prepared by precipitation method. The desired amount of ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] aqueous solution and nickel nitrate [$Ni(NO_3)_2\cdot 6H_2O$] aqueous solution were mixed at 80°C with pH adjusted at 5 by the addition of aqueous ammonia solution. The slurry was evaporated at 80°C, dried at 120°C for 24 h and crashed. Another precursor of $Ni_{0.38}MoO_{3.38}$ was obtained from the same starting materials, but the slurry was condensed to quarter amount, filtrated and dried.

Ammonium telluromolybdate (Te-HPA) was obtained from ammonium heptamolybdate aqueous solution and telluric acid [$Te(OH)_6$] aqueous solution. The solutions were mixed at 60°C and condensed until crystallization at 30°C. The crystals were filtrated

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and washed with a small amount of cold water. Analytically calculated for [$(NH_4)_6TeMo_6O_{24}\cdot 7H_2O$]: N, 6.4; Te, 9.7; Mo, 43.6; $H_2O$, 9.5; found: N, 6.1; Te, 9.5; Mo, 43.5; $H_2O$, 9.7.

Antimonyl complex [$(NH_4)_2Sb_2(C_4H_2O_6)_2\cdot 5H_2O$] was used as starting material for Sb-containing catalyst. Antimony oxide ($Sb_2O_3$) was added to ammonium hydrogen oxalate aqueous solution. The mixture was stirred and heated at 80°C for 24 h. The solution was filtrated and recrystallized at 0°C. Analytically calculated for [$(NH_4)_2Sb_2(C_4H_2O_6)_2\cdot 5H_2O$]: N, 4.2; Sb, 36.8; C, 14.5; $H_2O$, 13.6; found: N, 4.3; Sb, 37.0; C, 14.8; $H_2O$, 14.0.

The loaded nickel molybdate catalysts were prepared by conventional impregnation method. The desired amount of Te-HPA or Sb-complex suspension was added to nickel molybdate slurry at room temperature. The mixture was evaporated at 37°C and dried at 120°C for 24 h and calcined at 500°C for 2 h under air atmosphere.

The characterizations of the prepared catalysts were carried out using inductively coupled plasma spectroscopy, atomic absorption. The X-ray diffraction (XRD) experiments have been carried out with a Rigaku apparatus using Cu Kα radiation (Ni filter) from 10 to 80°C at 1°/min. The surface areas of all the catalysts were determined by BET method using nitrogen.

### 2.2. Catalytic test

The catalytic experiments were carried out in a fixed bed stainless-steel tube reactor (ID 10 mm) with a coaxial-centered thermocouple. The catalyst charge was 1 g without dilution. The reaction was performed at atmospheric pressure between 400 and 420°C. The feedstock composition was: propane/$O_2$/steam/$N_2$ = 12/8/40/40. A total feed gas flow rate of 3000 $cm^3$ g-catalyst$^{-1}$ $h^{-1}$ was employed.

The compositions of all products were confirmed by an on-line gaschromatograph system. Capillary column (TC-FFAP) with a flame ionization detector was used for analysis of oxygenates. Molecular sieve columns and Porapak columns with a thermal conductivity detector were utilized for the analysis of inorganic gases and hydrocarbons.

## 3. Results and discussion

### 3.1. Catalyst characterization

The physical properties of nickel molybdates modified with Te-HPA are summarized in Table 1. The surface area decreased slightly with the loading of Te-HPA and markedly with decrease in Ni/Mo ratio.

The physical structures of unloaded nickel molybdate catalysts with various Ni/Mo ratio were studied by XRD at room temperature (21°C) (Fig. 1). It was found that all the prepared catalysts show the diffraction patterns of α-phase [18]. The XRD patterns of $Ni_{0.92}MoO_{3.92}$ catalyst (spectrum b) and the stoichiometric compound ($Ni_{1.0}MoO_{4.0}$, spectrum a) were almost the same. On the other hand, the strong peaks corresponding to $MoO_3$ (spectrum d) phase were found in the diffraction patterns of $Ni_{0.38}MoO_{3.38}$ catalyst (spectrum c).

Table 1
Physical properties of Te-HPA/nickel molybdates

| Ni/Mo ratio (mol) | Te-HPA loading (wt.%) | Surface area ($m^2$/g) | Composition of catalyst (wt.%) | | |
|---|---|---|---|---|---|
| | | | Mo | Ni | Te |
| 0.91 | 0 | 33.8 | 42.9 | 24.1 | – |
| ↑ | 3 | 25.7 | 43.1 | 23.6 | 0.27 |
| ↑ | 6 | 22.1 | 43.5 | 22.7 | 0.45 |
| ↑ | 9 | 19.7 | 43.6 | 22.4 | 0.89 |
| 0.38 | 0 | 18.6 | 55.7 | 12.9 | – |
| ↑ | 3 | 16.5 | 55.7 | 12.6 | 0.29 |
| ↑ | 6 | 17.0 | 55.7 | 12.3 | 0.59 |
| ↑ | 9 | 13.9 | 52.5 | 12.2 | 0.95 |

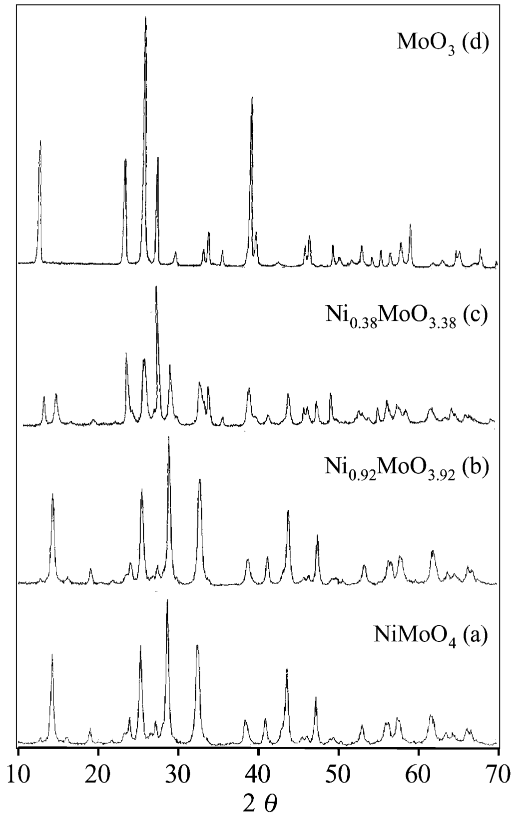

Fig. 1. XRD of nickel molybdates with various Ni/Mo atomic ratio.

Fig. 2 shows a comparison of XRD patterns of $Ni_{0.92}MoO_{3.92}$ catalyst (spectrum a), 6 wt.% Te-HPA/$Ni_{0.92}MoO_{3.92}$ catalyst (spectrum b) and 0.58 wt.% Sb/$Ni_{0.92}MoO_{3.92}$ catalyst (spectrum c). Te- or Sb-containing phases were not detected probably due to the low loading amount or low degree of crystallinity.

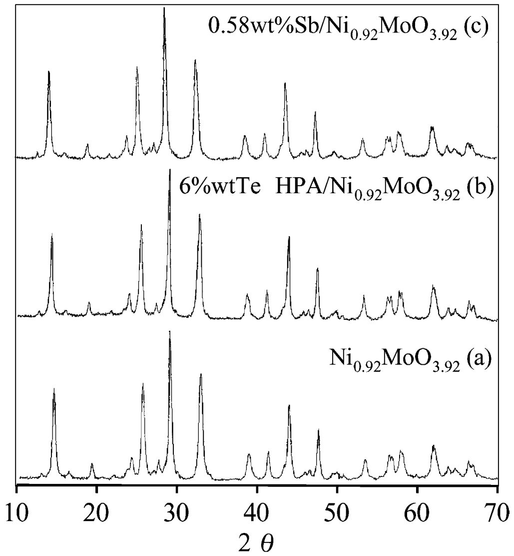

Fig. 2. Comparison of XRD patterns for modified nickel molybdates.

### 3.2. Effect of Te-HPA loading on nickel molybdates

Fig. 3 shows the results of oxidation of propane over the catalyst with various loading amounts of Te-HPA on $Ni_{0.92}MoO_{3.92}$. On the unsupported catalyst, dehydrogenation towards propylene and cracking to acetic acid proceeded, but the desired products (acrylic acid and acrolein) were hardly formed. The total selectivity to acrylic acid and acrolein increased markedly with increasing the amount of loading, and also the catalytic activity gained with loading up to 6 wt.%. This suggests that a synergistic effect exists between nickel molybdate and telluromolybdate. The yield of the desired products achieved to 16.9% (based on propane)

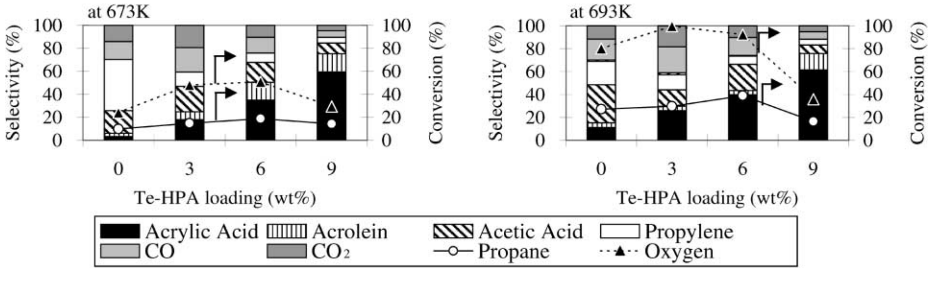

Fig. 3. Effect of Te-HPA loading on $Ni_{0.92}MoO_{3.92}$. Propane/$O_2$/steam/$N_2$ = 12/8/40/40; total feed gas flow rate, 3000 $cm^3$ g-catalyst$^{-1}$ $h^{-1}$; catalyst amount, 1 g.

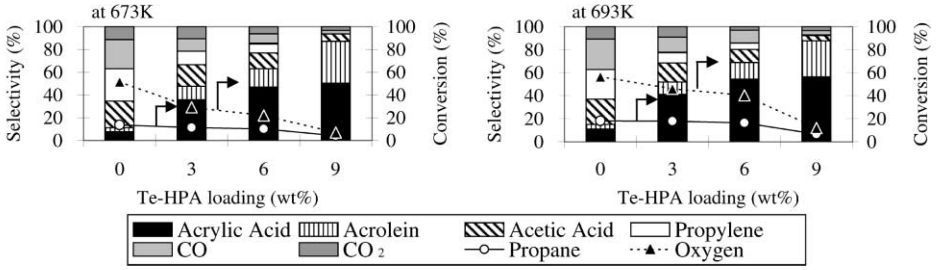

Fig. 4. Effect of Te-HPA loading on $Ni_{0.38}MoO_{3.38}$. Propane/$O_2$/steam/$N_2$ = 12/8/40/40; total feed gas flow rate, 3000 $cm^3$ g-catalyst$^{-1}$ $h^{-1}$; catalyst amount, 1 g.

at 6 wt.% loading (propane conversion, 38.9%; selectivity to acrylic acid, 39.8%; selectivity to acrolein, 3.6%).

On the other hand, further loading caused decrease in the activity and striking increase in the selectivity. It was considered that the catalysts with low concentration of surface Ni species show low activity and high selectivity. From the above consideration, we expected that highly selective catalyst could be obtained using nickel molybdates with low Ni/Mo ratio.

Fig. 4 shows the results of the same reaction over modified $Ni_{0.38}MoO_{3.38}$ catalysts. The activity of catalyst decreased in comparison with $Ni_{0.92}MoO_{3.92}$-based catalyst, but the reaction proceeded more selectively. At 9% loading, we have the highest selectivity towards the desired products (total, 87.8%; acrylic acid, 56.4%; acrolein, 31.4%). By the result, we attained the highly selective oxidation of propane in spite of the insufficient yield (propane conversion, 6.6%; total yield of desired products, 5.8%).

Although it was reported that volatilation of Te was often observed using Te-containing catalyst during reaction [19], any deactivation or volatilation of Te was not observed using Te-HPA/nickel molybdate catalysts during each reaction. From these results, we consider that Te was strongly stabilized as Te–Ni–Mo mixed oxide on the catalyst surface and played as very active species for the selective oxidation of propane.

### 3.3. *Effect of precipitator*

For it was suggested that the properties of nickel molybdate affect catalytic performance largely, we studied the influence of precipitator which was used for preparation of the supports.

Fig. 5 shows the effect of precipitators. The concentration of each precipitator was 1.9 M except for ammonium hydrogen carbonate (0.5 M). Using 6 wt.% Te-HPA/$Ni_{0.92}MoO_{3.92}$ catalyst prepared with $NH_4HCO_3$ solution as precipitator, we have the highest yield of the desired products (17.6%). Although the details of the effect of precipitator were not clarified, we considered that the precipitators affected the aqueous Ni and Mo species in the solutions and, as a consequence, the surface species of the nickel molybdate crystals could be changed. The effects

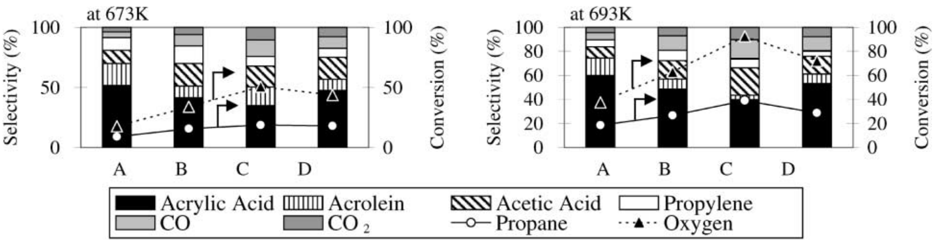

Fig. 5. Effect of precipitator (catalyst, 6 wt.% Te-HPA/$Ni_{0.92}MoO_{3.92}$; propane/$O_2$/steam/$N_2$ = 12/8/40/40; total feed gas flow rate, 3000 $cm^3$ g-catalyst$^{-1}$ $h^{-1}$; catalyst amount, 1 g): (A) urea, (B) $(NH_4)_2CO_3$, (C) aqueous $NH_3$ solution (28 wt.%) and (D) $NH_4HCO_3$.

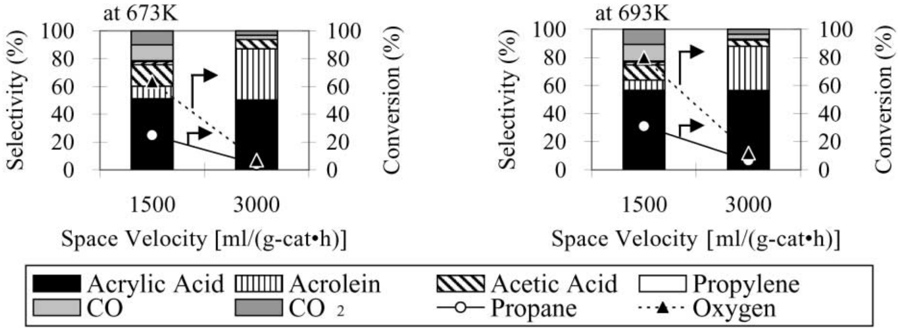

Fig. 6. Effect of space velocity. Catalyst, 9 wt.% Te-HPA/$Ni_{0.38}MoO_{3.38}$; propane/$O_2$/steam/$N_2$ = 12/8/40/40; total feed gas flow rate, 3000 $cm^3$ g-catalyst$^{-1}$ h$^{-1}$; catalyst amount, 1 g.

of other parameters of preparation, such as pH and temperature, are now under investigation.

### 3.4. Effect of space velocity

As mentioned above, the total selectivity to the desired products (acrylic acid and acrolein) achieved 87.7% at 6.6% conversion using 9 wt.% Te-HPA/$Ni_{0.38}MoO_{3.38}$ catalyst under standard conditions. In order to improve the yield of the desired products, we examined the reaction under 1500 $cm^3$ g-catalyst$^{-1}$ h$^{-1}$ which was half of the standard space velocity (Fig. 6).

Under this condition, the conversion increased markedly although selectivity to acrolein decreased. The yield of acrylic acid and acrolein achieved to 19.7% at 693 K. It was suggested that decrease of the space velocity caused a hot-spot formation on the catalyst surface. If the hot spot was formed, propane was highly converted, but the desired products which were less stable under higher temperature tend to oxidize further to decompose. In order to increase the yield of the desired products, the dilution of the catalyst or the reactant gas might be needed.

### 3.5. Non-Te catalyst (Sb/$Ni_{0.38}MoO_{3.38}$)

Because of toxicity of tellurium compounds, it is certainly an improvement in the preparation of the catalysts to replace telluromolybdate by antimony species which is less toxic. We synthesized antimony–tartate complex and used it for the source of Sb and examined Sb/$Ni_{0.38}MoO_{3.38}$ catalyst for propane oxidation.

The main products were propylene and acetic acid in case of Sb/$Ni_{0.38}MoO_{3.38}$ as shown in Fig. 7. Although the selectivity to acrylic acid and acrolein were low compared with Te-modified catalysts, it slightly increased with increasing the amount of Sb-loading.

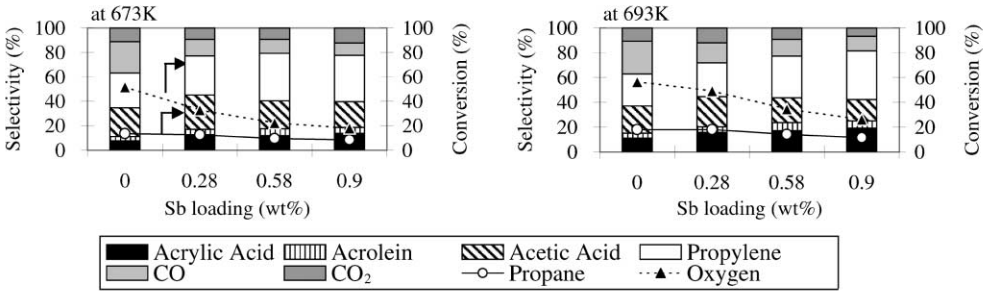

Fig. 7. Effect of Sb-loading on $Ni_{0.38}MoO_{3.38}$. Propane/$O_2$/steam/$N_2$ = 12/8/40/40; total feed gas flow rate, 3000 $cm^3$ g-catalyst$^{-1}$ h$^{-1}$; catalyst amount, 1 g.

The yield of the desired products was 2.9% at 693 K at 0.9 wt.% Sb-loading. From these results, it was found that the nickel molybdate catalysts could be modified with Sb-species.

## 4. Conclusions

1. Nickel molybdates modified with telluromolybdate was found to be a good catalyst for selective oxidation of propane to acrylic acid and acrolein.
2. Synergistic effects between nickel molybdates and telluromolybdate were observed, and the selectivity (acrylic acid and acrolein) of 87% was achieved at 9% loading of telluromolybdate (Ni/Mo ratio, 0.38 mol).
3. The maximum yield of desired products (acrylic acid and acrolein, 20%) was obtained at 420°C, 1500 $cm^3$ $g\text{-catalyst}^{-1}$ $h^{-1}$.
4. Sb-modified nickel molybdate was also found to be effective for this reaction, although the yields were low compared with Te-modified catalysts.

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