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# Amination of Decyl Alcohol over the Binary Metal Oxide Catalysts

Yusaku Takita, Yasuo Nishida,* and Tetsuro Seiyama

*Department of Materials Science and Technology, Faculty of Engineering, Kyushu University, Higashi-ku, Fukuoka 812*
**Sumitomo Rubber Industry LTD., Fukiai-ku, Kobe 651*

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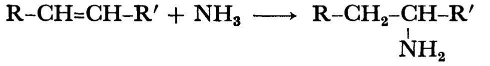
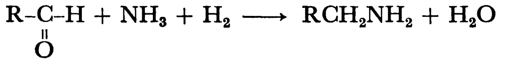
**Synopsis.** Catalytic amination of decyl alcohol was examined over binary oxide catalysts containing molybdenum, and the selective formation of decylamine was observed over $TiO_2$–, $SnO_2$–, and $Fe_2O_3$–$MoO_3$ catalysts. The reaction was often accompanied by the formation of 1-decene. It was found that catalytic activity for the amination of aliphatic alcohol was associated with the acidic property of metal oxide catalysts.

Olefins, alcohols and carbonyl compounds can be catalytically aminated by ammonia in the heterogeneous system.



$$\text{R-CH=CH-R}' + NH_3 \longrightarrow \text{R-CH}_2\text{-}\underset{\substack{|\\ NH_2}}{\text{CH}}\text{-R}'$$

$$\text{R-OH} + NH_3 \longrightarrow R_nNH_{3-n} + nH_2O \quad (n=1\text{—}3)$$



$$\text{R-}\underset{\substack{\|\\ O}}{\text{C}}\text{-H} + NH_3 + H_2 \longrightarrow RCH_2NH_2 + H_2O$$

Since the amination of aliphatic alcohols involves intermolecular dehydration, the catalytic activity might be associated with acidic property of catalysts, as in the case of intramolecular dehydration of alcohols. In fact, most of the catalysts such as $SiO_2$–$Al_2O_3$,[1] $Co_3O_4$–CuO–Kieselguhr,[2] metal sulfate[3] which are claimed to be effective for the reactions show notable acidity. Since only a few studies have been carried out on the catalytic amination of aliphatic alcohols, we have examined the amination of decyl alcohol by $NH_3$ over the various binary oxide catalysts containing molybdenum.

$$n\text{-}C_{10}H_{21}\text{-OH} + NH_3 \longrightarrow n\text{-}C_{10}H_{21}NH_2 + H_2O$$

## Experimental

$SnO_2$–$MoO_3$ catalyst was prepared by conventional methods from ammonium paramolybdate and tin(II) hydroxide precipitated from aqueous tin(II) chloride solution with ammonia. Other catalysts were prepared from respective metal nitrates and ammonium paramolybdate. The reaction was carried out in an ordinary flow reactor with a fixed catalyst bed under an atmospheric pressure at contact time of about 0.32 g s cm$^{-3}$. The composition of feed gas is given in Table 1. All the products were analyzed by gas chromatography except for didecylamine. The analysis of didecylamine was carried out chemically,[4] no didecylamine being detected.

## Results and Discussion

The results of amination of decyl alcohol over various catalysts are given in Table 1. Decylamine was formed in a considerable yield at temperatures below 350 °C over $TiO_2$–, $SnO_2$–, $Fe_2O_3$–$MoO_3$ catalysts. A small amount of decylamine was also obtained over the $Cr_2O_3$–$MoO_3$ catalyst but no amination proceeded over the $Mn_2O_3$–$MoO_3$ catalyst. In addition to the amination reaction, 1-decene and its decomposition products such as lower olefins and their aminated compounds were formed with increasing selectivity at higher temperature. This indicates that only 1-decene is formed by the intramolecular dehydration of decyl alcohol, without any further double bond isomerization of 1-decene. It was confirmed that no amination of 1-decene with ammonia took place under similar conditions.

Table 1. Amination of decyl alcohol over the binary oxide catalysts

| Catalyst | Temperature (°C) | Conversion of decyl alcohol (%) | Selectivity (%) | | |
|---|---|---|---|---|---|
| | | | Decylamine | 1-Decene | Others |
| $TiO_2$–$MoO_3$ | 260 | 11.2 | 68.7 | 31.3 | |
| | 300 | 26.6 | 46.6 | 53.4 | |
| | 340 | 49.2 | 14.5 | 85.5 | Tr |
| | 380 | 52.9 | Tr | 91.1 | 8.9 |
| $SnO_2$–$MoO_3$ | 250 | 15.1 | 50.3 | 49.7 | |
| | 300 | 47.9 | 26.5 | 73.5 | |
| | 350 | 57.4 | 1.9 | 97.2 | 0.9 |
| $Fe_2O_3$–$MoO_3$ | 300 | 13.2 | 37.1 | 62.9 | |
| | 350 | 37.7 | 10.8 | 79.2 | 10.0 |
| $Cr_2O_3$–$MoO_3$ | 300 | 7.3 | 13.5 | 86.5 | |
| | 350 | 30.0 | 5.7 | 92.3 | |
| $Mn_2O_3$–$MoO_3$ | 300 | — | — | — | |
| | 380 | 17.2 | — | 97.1 | 2.9 |

Catalyst; 1.20 g, Feed gas; decyl alcohol 4.2 cm$^3$/min, ammonia 8.4 cm$^3$/min, $H_2$ 4.2 cm$^3$/min, $N_2$ 2.1 cm$^3$/min.

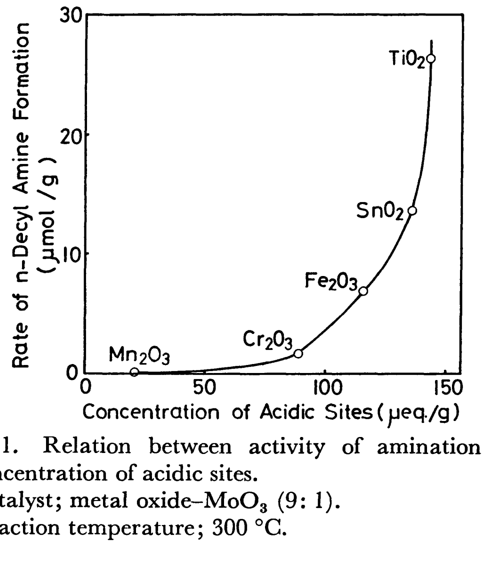


Fig. 1. Relation between activity of amination and concentration of acidic sites.
Catalyst; metal oxide–$MoO_3$ (9: 1).
Reaction temperature; 300 °C.

This suggests that ammonia, a stronger base than olefin, retards the adsorption of 1-decene onto acidic sites. It is unlikely that decyl cation is formed from decyl alcohol in the course of amination, although it is known that such a cation can be an intermediate in the usual isomerization of olefin over an acidic catalyst.

The acidity of the catalysts measured by butylamine titration using Dimethyl Yellow indicator ($\mathrm{p}K_a < +3.3$) is correlated with the catalytic activity at 300 °C (Fig. 1). We see that catalytic activity increases with the acidity of catalysts, though the dependence far exceeds a linear relation. It is difficult to analyze the deviation from linearity. However, an explanation might be given by taking into account the acid strength. The acidic sites actually effective for the amination might be limited to only those with sufficient acid strength and such sites might increase with the change of catalysts more steeply than the measured total acidic sites. X-Ray diffraction patterns of these catalysts show formation of no solid solution. Appearance of $Fe_2(MoO_4)_3$ was detected only in the case of $Fe_2O_3$–$MoO_3$. However, metal oxides combined with molybdenum oxide are not considered as simple carriers, since acidic properties of catalysts were shown to be enhanced in the mixed systems. We consider from Fig. 1 that the intermolecular dehydration process involved in the amination is catalyzed by acidic sites. This is in contrast to the Ni–$Al_2O_3$ or Fe catalyzed amination of aliphatic alcohol by ammonia under hydrogen pressures, for which it was reported[5] that the catalysis is irrespective of acidic property of the catalyst.

## References

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