JOURNAL OF CATALYSIS **142**, 430–436 (1993)

Synthesis of Butyronitrile via Ammonolysis of Butylalcohol and Dehydrogenation of Butylamine over Mo_2N

HIROSHI ABE AND ALEXIS T. BELL

Center for Advanced Materials, Materials Sciences Division, Lawrence Berkeley Laboratory, and Department of Chemical Engineering, University of California, Berkeley, California 94720-9989

Received December 15, 1992; revised March 15, 1993

Investigations were carried out of the synthesis of butyronitrile via the ammonolysis of butylalcohol and the dehydrogenation of butylamine over Mo_2N. At 573 K butyronitrile is produced with virtually 100% yield by both reactions. The ammonolysis of butyalcohol proceeds via dehydrogenation of the butylalcohol to form butyraldehyde, which then reacts with ammonia to produce butylimine. Butyronitrile is formed by butylimine dehydrogenation. The formation of butyronitrile from butylamine occurs via the stepwise dehydrogenation of the amine. The presence of ammonia in the gas phase suppresses the hydrogenolysis of either butylalcohol or butylamine.

INTRODUCTION

Nitriles are important chemical intermediates that can be used to produce amines by hydrogenation and carboxylic acids by hydration. The industrial production of nitriles is generally by ammonolysis of carboxylic acids over catalysts such as Al_2O_3 and ZnO (*1, 2*); however, there is a growing interest in the production of nitriles by ammonolysis of alcohols. Several classes of catalysts have been reported to be active for the ammonolysis of primary alcohols (*3–7*). Raney nickel combined with rhodium, ruthenium, or palladium has been used to produce amines from alcohols and ammonia (*3*), and nickel–copper bimetallic catalysts have been used to form amines from alcohols or aldehydes (*4*). Iron sulfide has been reported to give 92–95% alcohol conversion and 83–89% nitrile selectivity at 718 K for the production of C_{2-12} nitriles from the corresponding alcohols and ammonia (*5*). Butyronitrile formation by ammonolysis of butylalcohol has been achieved over a Zn–Cr oxide with 83.6% butyronitrile selectivity and 100% butylalcohol conversion at 633 K (*6*). A copper-based catalyst for the production of octanenitrile from octanol and ammonia gives 87% nitrile selectivity at 598 K (*7*). Yet another approach to the synthesis of nitriles is the dehydrogenation of primary amines. ZrO_2, MgO, and SiO_2 exhibit activity for the dehydrogenation of propylamine to propylnitrile, with the highest activity and selectivity being reported for MgO (*8*).

In this work, the ammonolysis of butylalcohol and other alcohols was examined over Mo_2N catalyst with the objective of achieving high butyronitrile selectivity and high conversion of butylalcohol at relatively low reaction temperatures. The reaction mechanism for the formation of nitrile from an alcohol and ammonia, the effect of alkyl chain length of the alcohol on conversion and product selectivity, and the catalyst life were also investigated. A further objective of this study was to examine the activity and selectivity of Mo_2N for the dehydrogenation of butylamine.

EXPERIMENTAL

Mo_2N was prepared by NH_3 reduction of MoO_3 following the procedure of Volpe and Boudart (*9*). MoO_3 powder, obtained from Aldrich Chem. Co., Inc., was pressed, ground, and sieved to yield granules of 30–60 mesh. The granules were weighed, and 1.4 g were placed in a quartz microreactor. NH_3 was fed to the reactor at a rate of 250

0021-9517/93 $5.00

cm^3/min while the temperature of the reactor was increased from room temperature to 623 K in 3.5 h. The temperature was then held at 623 K for 1 h, increased to 723 K in 3 h, then increased again to 973 K in 2 h, and finally held at 973 K for 1 h. The reactor was then cooled to room temperature in flowing NH_3. The BET surface area of the Mo_2N prepared in this manner was 237 m^2/g. X-ray diffraction analysis showed lines characteristic of γ-Mo_2N and no evidence of residual MoO_3.

1-Butylalcohol (Aldrich 99.8%), butyraldehyde (Aldrich 99%), butyronitrile (Aldrich 98%), butylamine (Aldrich 99+%), 1-propylalcohol (Aldrich 99+%), 1-pentylalcohol (Aldrich 99+%), and 1-octylalcohol (Aldrich 99+%) were used for the experiment without further purification. Anhydrous ammonia (AIRCO UN1005) was used without purification for both catalyst preparation and reaction. Helium and hydrogen were purified by passage through an Oxysorb (Matheson) trap.

All reactions were carried out in a quartz microreactor heated by a tube furnace. The liquid reactants were supplied by a syringe pump into a flow of helium or hydrogen. To assure complete vaporization of liquid feeds, the portion of the flow manifold located downstream from the point of liquid introduction was maintained at the temperature above 500 K. The flow rate of carrier gas was maintained at 100–110 cm^3/min, and the liquid flow rate was 0.1 cm^3/h. The gaseous alcohol carried by helium or hydrogen was mixed with the ammonia flow before the reactor. The flow rate of ammonia was 10 cm^3/min. The effluent from the reactor was analyzed by an on-line gas chromatograph equipped with a capillary column (Alltech HELIFLEX 13667). Product identification was carried out off-line by gas chromatography/mass spectrometry.

RESULTS AND DISCUSSION

Ammonolysis of Butylalcohol

Figure 1 shows the effluent composition of butylalcohol ammonolysis over Mo_2N as a function of reaction temperatures. The conversion of butylalcohol is very low at 473 K, but increases at 523 K, and reaches 100% at 573 K. The main product at temperatures between 523 and 673 K is butyronitrile, and the selectivity to butyronitrile reaches 99.8% at 573 K. Small amounts of dibutylimine are observed at lower temperatures, whereas progressively larger quantities of hydrocarbons, principally butane and lower molecular alkanes, are observed above 573 K.

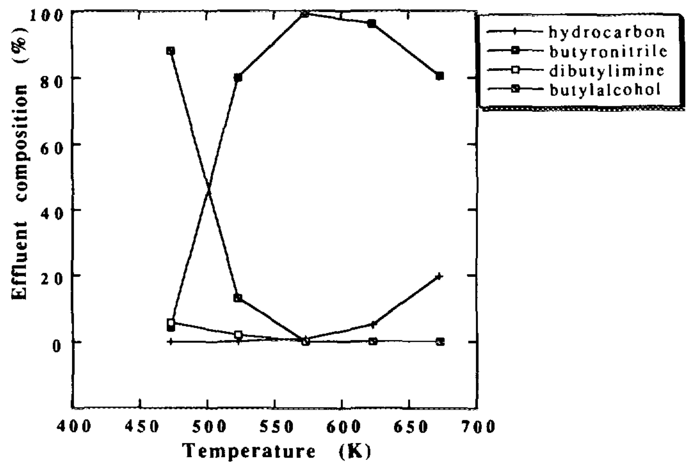

FIG. 1. Product composition versus temperature for butylalcohol ammonolysis. Reaction conditions: $Q_{Butylalcohol}$ = 0.1 cm^3/h, Q_{NH_3} = 10 cm^3/min, and Q_{He} = 100 cm^3/min.

TABLE 1

The Effect of Alkyl Chain Length on Alcohol Conversion and Nitrile Selectivity during Primary Alcohol Ammonolysis over Mo_2N[a]

Alkyl chain length	Alcohol conversion (%)	Nitrile selectivity (%)
2	99	99.2
4	100	99.8
5	100	99.0
8	99	98.0

[a] $T = 573$ K; $Q_{\text{alcohol}} = 0.1$ cm^3/h, $Q_{NH_3} = 10$ cm^3/min, $Q_{He} = 100$ cm^3/min.

A test of catalyst stability was carried out at 573 K. The conversion of butylalcohol and the selectivity to butyronitrile were found to be virtually constant during 30 h of reaction.

The effect of alkyl chain length of the reactant alcohol on the alcohol conversion and the selectivity to nitrile was examined by using *n*-propylalcohol, 1-pentylalcohol, and 1-octylalcohol. The results are shown in Table 1. At 573 K, the conversion of the alcohol is 100% in all cases, and the selectivity to nitrile is virtually 100%. It is, therefore, apparent that alkyl chain length has no effect on either the conversion or the selectivity of alcohol ammonolysis over Mo_2N at 573 K. The observed ammonolysis activity and nitrile selectivity of Mo_2N are superior to those reported previously for other catalysts (*3–7*).

A series of experiments were carried out in an effort to elucidate the reaction pathway by which butyronitrile is formed from butylalcohol. Since the reaction of aldehydes with ammonia is known to occur without a catalyst at room temperature (*10*), an experiment was performed to determine whether butyraldehyde would be formed by butylalcohol dehydrogenation. Figure 2 shows the effluent composition of butylalcohol dehydrogenation versus reaction temperature. Butyraldehyde is observed already at 473 K, and the selectivity to this product reaches a maximum value of 30% at 548 K. Figure 2 also shows that the formation of hydrocarbon products increases monotonically with increasing temperature. It is also interesting to observe that a small amount of butyronitrile is formed at temperatures above 600 K, presumably via the removal of nitrogen from the catalyst surface (see below).

To confirm that butyraldehyde is a reaction intermediate, the ammonolysis of butyraldehyde was carried out at several reaction temperatures. As shown in Fig. 3,

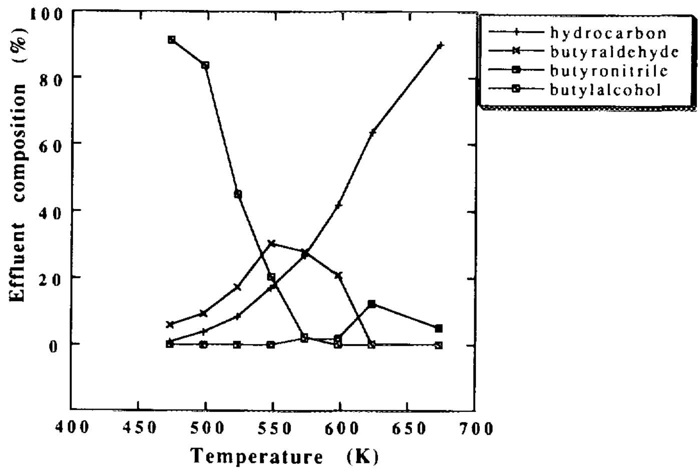

FIG. 2. Product composition versus temperature for butylalcohol dehydrogenation. Reaction conditions: $Q_{\text{Butylalcohol}} = 0.1$ cm^3/h and $Q_{He} = 100$ cm^3/min.

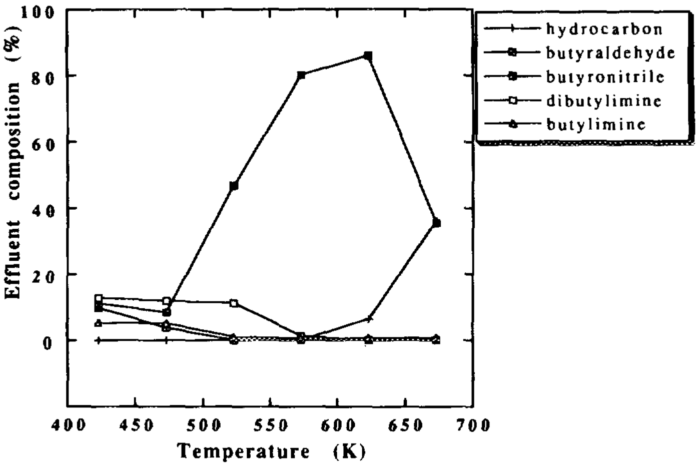

FIG. 3. Product composition versus temperature for butyraldehyde ammonolysis. Reaction conditions: $Q_{\text{Butyraldehyde}}$ = 0.1 cm³/h, Q_{NH_3} = 10 cm³/min, and Q_{He} = 100 cm³/min.

butyronitrile is the main product in this reaction, too. Comparison of Figs. 1 and 3 shows that the conversion of butyraldehyde is considerably higher than that of butylalcohol, strongly supporting the idea that butyraldehyde is an intermediate in the ammonolysis of butylalcohol. At temperatures below 573 K, butylimine and dibutylimine were detected as products of butyraldehyde ammonolysis. The formation of butylimine is ascribed to the reaction of ammonia with butyraldehyde, whereas dibutylimine is believed to be formed by the reaction of butylimine and butyraldehyde. Above 573 K, hydrocarbons are formed increasing proportion. The rise in the proportion of hydrocarbon products with increasing temperature observed during the ammonolysis of butyraldehyde and butylalcohol are comparable.

To further investigate the role of butyraldehyde as an intermediate in the formation of butyronitrile, butyraldehyde was passed over the catalyst without ammonia at 573 K. The results of these experiments are shown in Fig. 4. The principal product

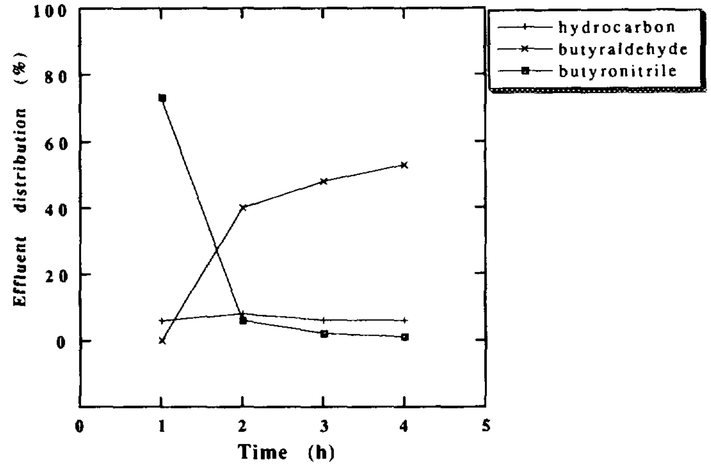

FIG. 4. Product composition versus time for the reaction of butyraldehyde over Mo_2N at 573 K. Reaction conditions: $Q_{\text{Butyraldehyde}}$ = 0.1 cm³/h and Q_{He} = 100 cm³/min.

formed initially is butyronitrile. The formation of this product drops off rapidly after 1 h of reaction, and goes to zero after 4 h. Paralleling the fall in the formation of butyronitrile, there is a rise in the formation of hydrocarbons. The nitrogen appearing in butyronitrile derives from Mo_2N. The amount of nitrogen removed from the catalyst in 4 h corresponds to 24% of all the nitrogen in Mo_2N, or 76% of surface nitrogen on Mo_2N.

Dehydrogenation of Butylamine

Figure 5 shows the effects of temperature on the dehydrogenation of butylamine over Mo_2N. The conversion of butylamine is approximately 10% at 373 K, but increases to 100% above 523 K. Butyronitrile is the principal product between 473 and 623 K, and the selectivity to this product reaches a maximum value of 99% at 573 K. The amount of hydrocarbon formed, mainly *n*-butane, increases above 623 K. Dibutylamine is detected below 523 K, but no butyl imine. The activity and selectivity observed for Mo_2N is considerably higher than that reported for MgO or other oxide catalysts (*8*).

Supplementary experiments using butylamine and butyronitrile as reactants were carried out to determine the pathways by which hydrocarbons and dibutylimine are formed. In the absence of hydrogen, butyronitrile was found to be very stable up to 675 K, with only a few percent conversion to hydrocarbons occurring above 600 K. These experiments demonstrate that butyronitrile is a relatively stable product. When the carrier gas is hydrogen, Fig. 6 shows that butyronitrile readily undergoes reaction to form hydrocarbons, as well as smaller amounts of dibutylimine, and butylamine. The reaction of butylamine in the presence of H_2 produces a variety of products, as shown in Fig. 7. At low temperatures the principal products are butyronitrile, dibutylimine, and dibutylamine, but progressively larger amounts of hydrocarbons are formed as the temperature is increased above 525 K.

The effects of air exposure of the catalyst on its activity and selectivity were also examined. Table 2 shows that at 573 K, air exposure of Mo_2N had no effect on the activity of this catalyst for butylamine dehydrogenation, and only slightly decreased the selectivity to butyronitrile. For comparison, Table 1 also lists the activity and selectivity of MoO_3. It is apparent that under identical reaction conditions, MoO_3 is less

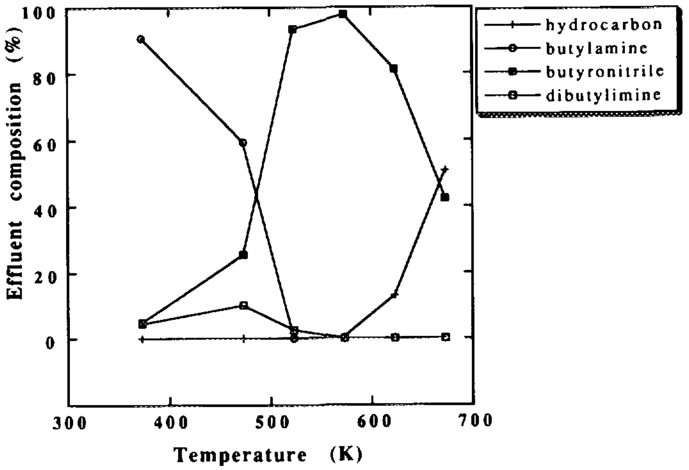

FIG. 5. Product composition versus temperature for butylamine dehydrogenation. Reaction conditions: $Q_{\text{Butylamine}} = 0.1\ \text{cm}^3/\text{h}$ and $Q_{\text{He}} = 100\ \text{cm}^3/\text{min}$.

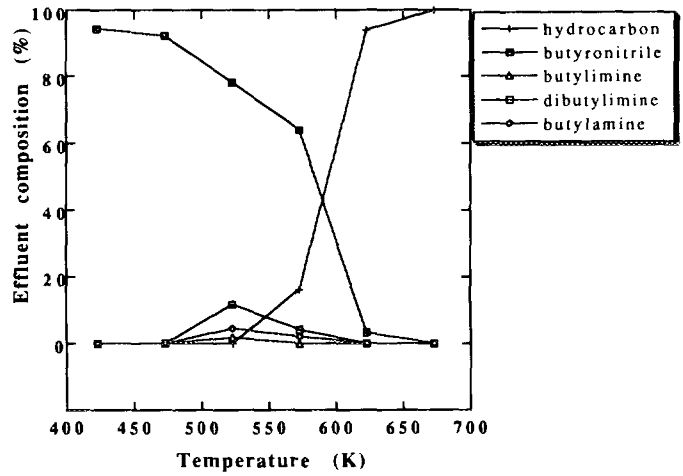

FIG. 6. Product composition versus temperature for butyronitrile hydrogenation. Reaction conditions: $Q_{\text{Butyronitrile}} = 0.1$ cm^3/h and $Q_{H_2} = 100$ cm^3/min.

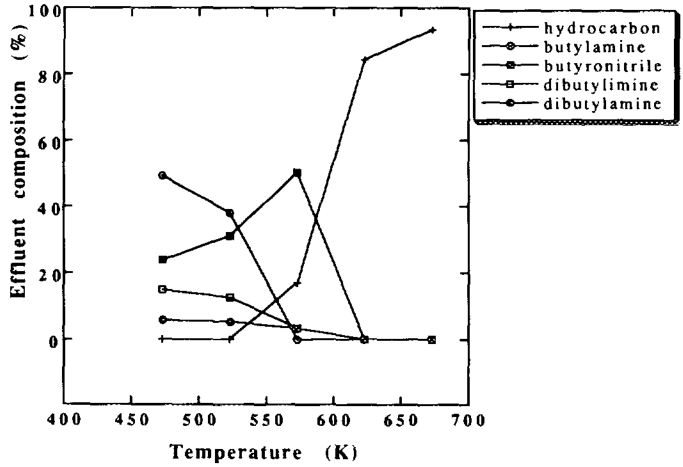

FIG. 7. Product composition versus temperature for butylamine hydrogenolysis. Reaction conditions: $Q_{\text{Butylamine}} = 0.1$ cm^3/h and $Q_{H_2} = 100$ cm^3/min.

TABLE 2

Comparison of Butylamine Conversion and Product Distribution for Butylamine Dehydrogenation over Mo-Based Catalysts[a]

		Product distribution (%)		
Catalyst	Conversion (%)	Butyro-nitrile	Dibutyl-amine	Other
Mo_2N	100	99	1	0
Mo_2N[b]	100	95	4	1
MoO_3	59	32	65	3

[a] $T = 573$ K; $Q_{\text{Butylamine}} = 0.1$ cm^3/h, $Q_{\text{He}} = 100$ cm^3/min.
[b] Air exposed.

active than Mo_2N for butylamine dehydrogenation. Consistent with this, the selectivity to dibutylimine is considerably higher over MoO_3 than over Mo_2N and, correspondingly, the selectivity to butyronitrile is much less.

Reaction Pathways

The reactions pathways for the formation of butyronitrile via butylalcohol ammonolysis and butylamine dehydrogenation are closely related and, therefore, are dis-

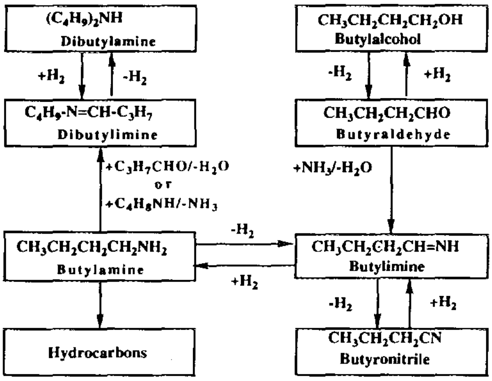

FIG. 8. Proposed reaction pathways for the ammonolysis of butylalcohol and the dehydrogenation of butylamine.

cussed together. As shown in Fig. 8, the ammonolysis of butylalcohol is initiated by the dehydrogenation of the alcohol to form butyraldehyde. This product then reacts with NH_3 to form butylimine and water. The butylimine undergoes dehydrogenation to form butyronitrile. The dehydrogenation of butylamine to butyronitrile proceeds in a stepwise fashion, producing butylimine as a intermediate product. The appearance of dibutylimine in both reaction systems can be attributed to the reaction of butylimine with either butyraldehyde or butylamine. Small amounts of dibutylamine are formed by hydrogenation of dibutylimine. The formation of hydrocarbons at higher temperatures is the direct result of hydrogenolysis of either butylalcohol or butylamine. The presence of ammonia in the gas phase inhibits this process, as has been shown by the recent work of Lee *et al.* (*11*).

CONCLUSION

Mo_2N is an active and selective catalyst for the ammonolysis of butylalcohol to butyronitrile. At 573 K, 100% conversion of the alcohol is attained together with a nitrile selectivity of 99.8%. Similar activities and selectivities are observed for the ammonolysis of *n*-propyl-, 1-pentyl-, and 1-octylalcohols. The ammonolysis of butylalcohol begins with the dehydrogenation of the alcohol to form butyraldehyde. This product then reacts readily with ammonia to form butylimine, which, in turn, forms butyronitrile by dehydrogenation. Mo_2N is also highly active and selective for the dehydrogenation of butylamine to butyronitrile. At 573 K, 100% of the butylamine is converted and the selectivity to butyronitrile is 99%. Butyrolnitrile is formed from butylamine by stepwise dehydrogenation.

ACKNOWLEDGMENT

This work was supported by the Office of Basic Energy Sciences, Material Sciences Division of the U.S. Department of Energy, under contract DE-AC03-76SF00098.

REFERENCES

1. Johnson, R. W., and Fritz, E., "Fatty Acids in Industry." Dekker, New York, 1989.
2. Pattison, E. S., "Fatty Acids and Their Industrial Applications." Dekker, New York, 1968.
3. U.S. Patent 3,278,598 to Atlas Chemical Ind., K. H. Markiewitz (July 18, 1963).
4. U.S. Patent 4,152,353 to Dow Chemical Co., C. E. Haberman (May 1, 1979).
5. Bashkirov, A. N., Zakirov, N. S., Abdurakhmanov, E. A., Kliger, G. A., Muradov, K., and Snagovskii, Y. S., *Neftekhimiya* **27,** 818 (1987).
6. Korchagova, E. K., Dziluma, E., Slavinskaya, V. A., and Avots, A., *Zh. Prikl. Khim.* (*Leningrad*) **55,** 2784 (1982).
7. Card, R. J., and Schmitt, J. L., *J. Org. Chem* **46,** 754 (1981).
8. Tanabe, K., Misono, M., Ono, Y., and Hattori, H., "New Solid Acids and Bases." Elsevier, New York, 1989.
9. Volpe, L., and Boudart, M., *J. Solid State Chem.* **59,** 332 (1985).
10. "Organikum." VED Deutscher Verlag der Wissenschaften, Berlin, 1977.
11. Lee, K. S., Abe, H., Reimer, J. A., and Bell, A. T., *J. Catal.*, **139,** 34 (1993).