New Class of Catalysts for the Ammoxidation of Propane to Acrylonitrile over Nickel–Molybdenum Mixed Nitrides

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Nickel–molybdenum mixed nitride catalysts were first reported for the ammoxidation of propane to acrylonitrile. It was found that the mixed nitrides exhibited high activity and selectivity to acrylonitrile. The mixed nitride catalyst with 1.0 of Ni/Mo atomic ratios showed the best catalytic properties for propane ammoxidation. The highest yield of acrylonitrile was 28.5% at the propane conversion of 68.4% at 773 K.

Direct conversion of alkanes to produce high value products for the chemical industry constitutes an arduous and stimulating scientific and technological challenge. Among the most significant industrial applications in this field is the production of acrylonitrile (ACN) through the propane ammoxidation process. The acrylonitrile, as one kind of the most important chemical intermediates, is used extensively in the manufacture of fibers, polymers, such as styrene–acrylonitrile (SAN) and acrylonitrile–butadiene–styrene (ABS), and other valuable chemicals.

Many catalysts have been tested for the ammoxidation of propane to acrylonitrile, and the most effective ones fall into two main classes:[1] they are either VMo_xM_y mixed oxides (M is most often Bi or Te) or VSb_xM_y mixed oxides (M are elements used as a promoter such as W, Te, Nb, Sn, Bi, Al, and Ti). The highest acrylonitrile yields to date (about 60%)[2–4] have already been obtained on laboratory scale from propane using a Mo–V–Nb–Te–O_x catalyst among VMo_xM_y mixed oxides. V–Sb mixed oxides also have been reported to yield 34–40% ACN.[5,6] In addition, several other mixed oxides, such as Bi–Mo,[7] P–V,[8] and Fe–Sb,[9] are also active in the conversion of propane to acrylonitrile. However, the yield of ACN does not exceed 20%.[10] With the exception of the above mixed oxides, a few other catalytic materials are used in the propane ammoxidation to acrylonitrile. Recently, the vanadium–aluminum oxynitrides have been first reported for the propane ammoxidation process by Florea et al.,[11] and the catalysts yield up to 30% ACN,[12] which present the opportunity for the mixed metal oxynitrides or nitrides used in the ammoxidation of propane to acrylonitrile.

This paper is the first to report that the Ni–Mo mixed nitride catalysts were used in the process of propane ammoxidation to acrylonitrile.

The Ni–Mo oxides were used as precursors for Ni–Mo nitride catalysts. The precursors were prepared by the co-precipitation from a solution of nickel nitrate to which a solution of ammonium molybdate tetrahydrate was added stepwise. Temperatures of co-precipitation were 323 K. The mixed oxide precursors with various Ni/Mo ratios and the pure $NiMoO_4$ precursor were obtained by varying pH values of the solution during precipitation and aging periods. The Ni–Mo mixed oxides were obtained at a pH of 5.5 and pure $NiMoO_4$ was obtained at a pH of 7.5. The obtained hot precipitate was filtered, washed with hot distilled water, and dried in an oven at 383 K (12 h). The resulting solid was ground by hand and heated at 573 K for 2 h, then ground and calcined in air again at 773 K for 2 h. The materials were used in the subsequent synthesis of Ni–Mo bimetallic nitrides.

The Ni–Mo mixed nitride catalysts and pure Ni_3Mo_3N catalyst were prepared by temperature-programmed reaction of the precursors obtained above with ammonia using a fixed-bed microreactor, a quartz tube with an inner diameter of 15 mm. Typically, about 3 g of precursor particles with 20–60 mesh was heated under flowing ammonia gas (400 mL/min). The temperature was increased from room temperature to 573 K in 28 min, and from 573 to 973 K in 360 min; finally, the temperature was maintained at 973 K for 120 min. The nitrided Ni–Mo samples were cooled to room temperature in flowing ammonia gas and then passivated in a stream of 1% O_2/N_2 (v/v) for 12 h. Pure Mo_2N catalyst was also prepared by temperature-programmed reaction of MoO_3 and NH_3.

Activity tests were carried out in a laboratory stainless steel fixed-bed reactor operating at atmospheric pressure. One g of catalyst was loaded, shaped in particles having size ranging from 20 to 40 mesh. The following reaction conditions were used: the feed composition 2 mol % propane, 15% ammonia, 15% oxygen, remainder helium; the total flow rate of 14.5 mL/min. The reactor outlet was kept at 443 K. Feed and products were analyzed on-line using a gas chromatograph (SP-2100), equipped with FID detector and a methaniser. A Porapak Q column, 60–80 mesh (2 m × 3 mm), was used for the seperation of CO, CO_2, C_2H_4, C_3H_6, C_3H_8, acetonitrile, acrolein, and acrylonitrile.

The precursors and the Ni–Mo mixed nitrides were analyzed by the X-ray diffraction (XRD), using a Shimadzu XRD-6000 diffractometer with a Cu Kα radiation source for phase identification.

Figure 1 shows the X-ray diffraction patterns of the precursors with various Ni/Mo ratios. The crystalline phases of the precursors were mainly composed of MoO_3, verified by the peaks at $2\theta = 23.7$, 25.8, and 27.4° (JCPDS Card 85-2405) and $NiMoO_4$, verified by the peaks at $2\theta = 28.8$, 32.6, and 43.9° (JCPDS Card 33-0948). Figure 2 shows X-ray diffraction patterns for the Ni–Mo nitride catalysts with different Ni/Mo atomic ratios prepared under the above established conditions. As shown in Figure 2, the diffraction peaks of MoO_3 and $NiMoO_4$ disappeared after the precursors were nitrided. The crystalline phases of the prepared catalysts were mainly composed of Mo_2N and Ni_3Mo_3N. The XRD peaks of Mo_2N were detected at $2\theta = 26.0$, 37.8, 43.9, and 63.3°;[13,14] the diffraction peaks at $2\theta = 40.9$, 45.5, and 72.8° could be ascribed to Ni_3Mo_3N.[13]

The results of propane ammoxidation over the prepared catalysts at 773 K are listed in Table 1. The pure Mo_2N or Ni_3Mo_3N catalyst did not show high activity for propane ammoxidation

Table 1. Catalytic properties of studied catalysts for the ammoxidation of propane at 773 K[a]

Ni/Mo atomic ratio	BET surface area /$m^2\,g^{-1}$	Conv. /%C_3H_8	Selectivity/%				Yield /%ACN
			CO_x	C_3H_6	AcCN[b]	ACN	
Mo_2N	60	6.5	46.5	32.0	1.9	16.6	1.1
0.2	74	52.2	55.7	9.4	4.3	29.0	15.1
0.6	76	55.3	34.1	6.2	15.1	42.5	23.5
1.0	80	68.4	44.3	5.7	7.4	41.6	28.5
1.2	99	64.2	35.6	6.5	12.3	43.7	28.1
1.5	102	61.0	40.4	8.0	7.4	42.2	25.7
Ni_3Mo_3N	57	24.5	25.8	41.0	4.7	27.4	6.7

[a]Catalyst amount: 1 g; $C_3H_8/NH_3/O_2/He = 1/7.5/7.5/34$ (mol). [b]AcCN: acetonitrile.
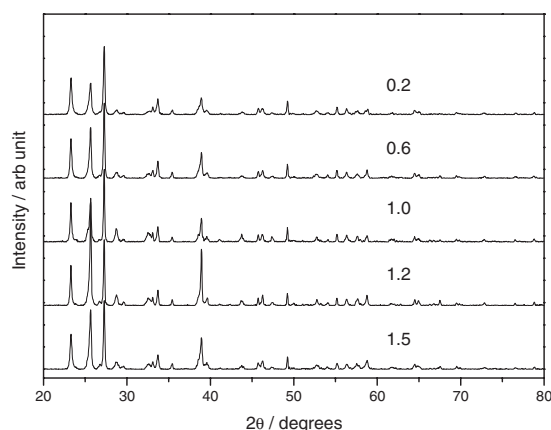
Figure 1. XRD patterns of the precursors with different Ni/Mo ratios.
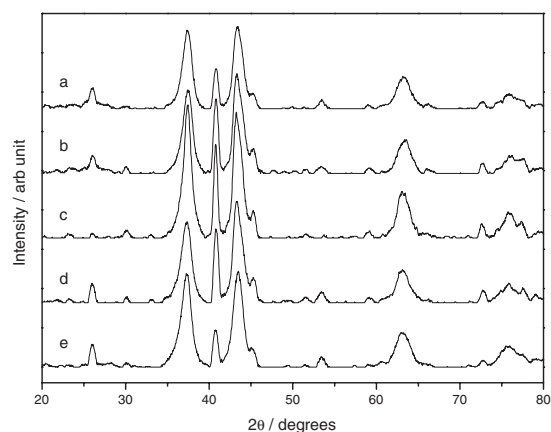
Figure 2. XRD patterns of the Ni–Mo mixed nitrides with various Ni/Mo ratios (a)0.2, (b)0.6, (c)1.0, (d)1.2, and (e)1.5.

and high selectivity to acrylonitrile, while the mixed nitrides of Ni and Mo were very active and selective for the ammoxidation of propane to acrylonitrile. In the case of the Ni–Mo mixed nitrides, the conversion of propane and the selectivity to acrylonitrile passed through a maxiumum with increasing Ni/Mo ratios. The yield of acrylonitrile reached a maximum of 28.5% when the atomic ratio of Ni/Mo was between 1 and 1.2. As shown in Table 1, the Ni–Mo mixed nitrides have large surface area compared to pure Mo_2N and Ni_3Mo_3N, but the activities of the nitride catalysts were not in total proportion to their surface area, which suggests that besides the surface area of the catalysts, other factors, such as synergetic effect, also seem to play an important role in the process of propane ammoxidation. The Ni–Mo mixed nitrides show a high activity and selectivity for propane ammoxidation, while the selectivity to acrylonitrile gradually decreases with time on stream. Thus, it is necessary to further investigate the stability of the nitride catalysts for propane ammoxidation.

In summary, the Ni–Mo mixed nitrides are a novel catalyst system for the ammoxidation of propane to acrylonitrile. The application of the Ni–Mo mixed nitride catalysts in the propane ammoxidation affords an opportunity for a new application of transition metal nitrides and oxynitrides.

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