OXIDATIVE AMMONOLYSIS OF 3-PICOLINE ON MIXED OXIDE CATALYSTS*

B. V. Suvorov, A. D. Kagarlitskii, T. A. Afanas'eva, O. B. Lebedeva, A. I. Loiko, and V. A. Serazetdinova

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 6, pp. 1024–1027, 1969

UDC 547.821.41

The oxidative ammonolysis of 3-picoline has been studied on the following catalysts: V_2O_5 on corundum, V_2O_5 with the addition of 1% of H_2WO_4 on corundum, $V_2O_5 + MoO_3 + P_2O_5$ (1 : 0.35 : 0.35) on silica gel, $V_2O_5 + Al_2O_3$, and a melt of $V_2O_5 + TiO_2$ (1 : 0.22). Mixed catalysts of vanadium and titanium oxides exhibited the highest activity and selectivity. With the passage of 25–45 moles of oxygen (in the form of air), 5–10 moles of ammonia, and 50–70 moles of water per mole of 3-picoline at a temperature of 390–410° C, the amount of nicotinonitrile formed on these catalysts amounted to 85–90% of the theoretically possible amount.

Although a large number of catalysts based on vanadium oxides and mixtures of them with oxides of molybdenum, tin, titanium, iron, and other transition metals has been recommended for the oxidative ammonolysis of 3-picoline (I) to nicotinonitrile (II) [2–8], only fused tin vanadate [6, 7] and catalysts prepared by the precipitation of vanadium pentoxide on active alumina [5] possess satisfactory activity and selectivity in this reaction. The aim of the present work was to seek new effective catalysts for the oxidative ammonolysis of I.

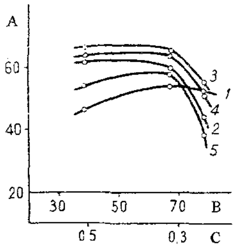

Fig. 1. Yield of II as a function of the amount of air and the time of contact in the oxidative ammonolysis of I on K-63 catalyst: A) yield, %; B) oxygen in moles per mole of I; C) time of contact in sec: 1) 330° C; 2) 345° C; 3) 360° C; 4) 375° C; 5) 390° C.

Among the catalysts that we tested were several prepared by fusing vanadium oxide on corundum. The results of some of the experiments with the catalyst K-63 (vanadium pentoxide without additives on corundum) are given in Figs. 1 and 2. The highest yield of II, about 68% of the theoretically possible amount calculated on the raw material taken, was obtained with a feed of 36 g of I, 1700–3400 *l* of air, 60–65 g of ammonia, and 1000–1200 g of steam per liter of catalyst per hour with a contact time of 0.25–0.50 sec and a reaction temperature of 360° C. A lowering of the concentration of ammonia in the reaction zone, and a decrease in the time of contact or the temperature reduced the yield of II. Simultaneously the amount of unchanged alkylpyridine increased. When the parameters of the process that have been mentioned were increased or when the feed of steam was decreased, side reactions involving far-reaching oxidation increased. As a result of this, the conversion of the raw material into C_1 products—hydrogen cyanide and oxides of carbon—rose and the yield of II fell correspondingly. Nicotinaldehyde (III), ammonium nicotinate (IV), and nicotinamide (V) were present in small amount in the catalyzates of almost all the experiments.

Among the modifications of the catalysts described that were tested, the most effective proved to be K-63A—vanadium pentoxide with the addition of 1% of tungstic acid on a MK support containing 1.0% of titanium dioxide. While providing the possibility of the preparation of IIa with a yield of 66–68%, this catalyst exhibited a comparatively high productivity. At a molar ratio of I to ammonia to oxygen (in the form of air) to steam of 1 : 9 : 37 : 70 and a temperature of 420° C, the yield of II here amounted to 60–65 g per liter of catalyst per hour. As can be seen from Figs. 3–5, the general features of the process studied remain as before.

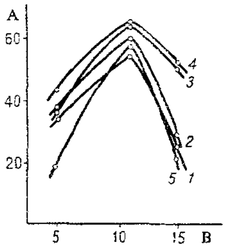

Fig. 2. Catalyst K-36. Yield of II as a function of the amount of ammonia: A) yield, %; B) ammonia in moles per mole of I; 1) 330° C; 2) 345° C; 3) 360° C; 4) 375° C; 5) 390° C.

Since vanadium oxide catalysts promoted with alumina [9–10] and also various compositions based on oxides of vanadium, molybdenum, and phosphorus [18] are active in the oxidative ammonolysis of the xylenes and α-olefins, it appeared desirable to investigate their behavior in the oxidative ammonolysis of I. The

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*Part LXIII of the series "Oxidation of organic compounds;" for part LXII, see [1].

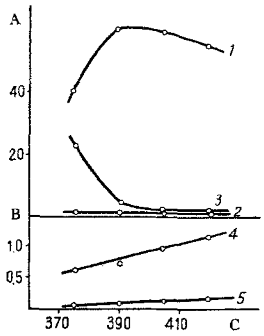

Fig. 3. Yield of the products of the oxidative ammonolysis of I as a function of the temperature of the reaction of K-63A catalyst: A) yield of II, V, and unchanged I, %; B) yield of CO_2 and NH_4CN in moles per mole of I; C) reaction temperature: 1) II; 2) V; 3) I; 4) CO_2; 5) NH_4CN.

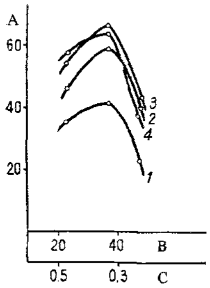

Fig. 4. Catalyst K-63A. Yield of II as a function of the amount of air and time of contact: A) yield, %; B) oxygen in moles per mole of I; C) time of contact in sec; 1) 375° C; 2) 390° C; 3) 405° C; 4) 420° C.

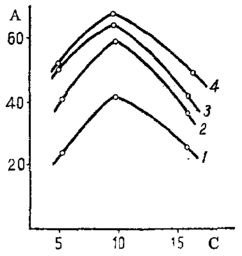

Fig. 5. Catalyst K-63A. Yield of II as a function of the amount of ammonia: A) yield, %; B) ammonia in moles per mole of I; 1) 375° C; 2) 390° C; 3) 405° C; 4) 420° C.

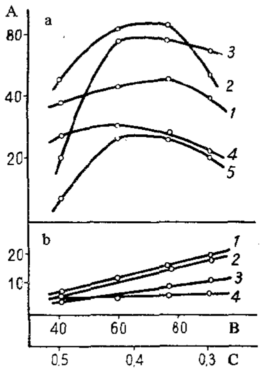

Fig. 6. Oxidative ammonolysis of I on a V_2O_5–MoO_3–P_2O_5 catalyst: A) yield, %; B) oxygen in moles per mole of I; C) contact time in sec; a) II; b) V. Rate of feed of I, 33 g; of ammonia, 51 g; and of steam, 840 g per liter of catalyst per hour; 1) 330° C; 2) 345° C; 3) 360° C; 4) 375° C; 5) 390° C.

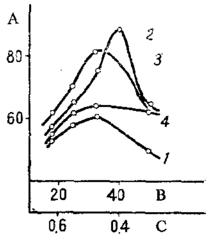

Fig. 7. Yield of II as a function of the amount of air and the time of contact in the oxidative ammonolysis of I on a fused vanadium–titanium oxide catalyst: A) yield, %; B) oxygen in moles per mole of I; C) time of contact in sec. Rate of feed of I, 60 g; of ammonia, 85 g; of air, 1600–4800 *l*; and of steam, 760 g per liter of catalyst per hour, τ, 0.27–0.6 sec; 1) 375° C; 2) 390° C; 3) 405° C; 4) 420° C.

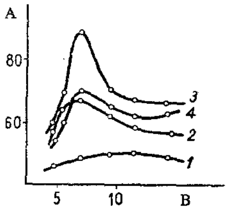

Fig. 8. Fused vanadium-titanium catalyst. Yield of II as a function of the amount of ammonia: A) yield, %; B) ammonia in moles per mole of I; 1) 375° C; 2) 390° C; 3) 405° C; 4) 420° C.

first of the catalysts mentioned did not justify this hope, since on it II was obtained with a yield of not more than 50%. A catalyst prepared by precipitating a mixture of the higher oxides of vanadium, molybdenum, and phosphorus taken in a ratio of 1 : 0.35 : 0.35 on silica gel proved more interesting in this respect. On this, in addition to II, considerable amounts of V were obtained. It follows from Fig. 6 that under the optimum conditions the total yield of these reaction products amounted to 70–75%. However, it must be mentioned that this catalyst is capable of working at a comparatively low temperature, in the 345–360° C range.

In the oxidative ammonolysis of the alkylbenzenes, a fused titanium vanadate catalyst exhibited exceptionally high activity [9, 11, 12]. It has been reported that it is also effective in the oxidative ammonolysis of I [6]. In view of this, a fused vanadium–titanium oxide catalyst was studied in this reaction in more detail. The reaction temperature, the contact time, and the feeds of raw material, air, ammonia, and steam were varied within wide limits. As was to be expected, the qualitative composition of the catalyzate and also the general nature of the influence of the individual components of the initial reaction mixture and the other parameters of the process scarcely changed in this case (Figs. 7 and 8). At the same time, the use of the vanadium–titanium oxide catalyst permitted extremely substantial increases in the selectivity of the reaction and in the yield of II. As a rule, on this catalyst, III, IV and V were obtained in an amount of not more than 5%. At a feed of 25–45 moles of oxygen (in the form of air), 5–10 moles of ammonia, and 50–70 moles of steam per mole of I and a temperature of 390–410° C, the yield of II exceeded 70% and in a number of experiments it reached 85–90%. Under these conditions the productivity of the process amounted to 55–60 g of II per liter of catalyst per hour. The activity of the catalyst had not decreased after its use for almost 500 hr. In addition, it proved extremely resistant to sintering.

EXPERIMENTAL

The starting material used was I, bp 139–141° C, n_D^{24} 1.5043, d_4^{25} 0.9515, containing 97.5–98% of the main substance and about 0.9% of 2,6-lutidine, 0.8% of 2-picoline, and 0.7% of pyridine.

The experiments were carried out on a continuous apparatus which has been described previously [13]. The reaction products were trapped in scrubbers of the air-lift type fed with water.

The K-63 and K-63A catalysts were prepared* by a method proposed in USSR patents [14, 15]. The method of preparing the mixed catalyst of oxides of vanadium, molybdenum, and phosphorus has also been described in the literature [16, 17]. The coprecipitated aluminum–vanadium oxide catalyst was prepared by the method described previously [18]. The components were taken in a ratio of 1 : 1 (by weight), and the temperature of calcining was 750° C. The vanadium-titanium catalyst was obtained by fusing vanadium pentoxide and titanium dioxide taken in a weight ratio of 1 : 0.22.

The products of the reaction were analyzed polarographically on a type PO-5122 oscillographic polarograph. To determine V, 10 ml of the scrubber liquid was extracted with benzene (4 × 5 ml) in order to eliminate I, II, and III. The aqueous residue was diluted with water to 25 ml. Samples with a volume of 1–2 ml were placed in a 25-ml measuring flask and made up to the mark with 0.1 N potassium hydroxide solution. The concentration of V was calculated from the measured limiting current (I_a) with $E_{1/2}$ = 1.80 V from a calibration graph. To determine the II, 10 ml of the reaction liquid was treated with 5 ml of 0.1 N potassium permanganate solution in the presence of 1 ml of a 10% solution of magnesium sulfate in order to oxidize the III. A sample with a volume of 1–2 ml was placed in a 25-ml measuring flask and made up to the mark with 0.1 N potassium hydroxide solution. The limiting current of the wave with $E_{1/2}$ = 1.80 V is the sum of the currents of II and V (I_{H+a}). The content of II was calculated from the difference $I_{H+a} - I_a$ using a calibration graph. The presence of ammonia and IV did not interfere with the determination of the products mentioned above [7].

The oxides of carbon were determined by gas chromatography.

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*The authors thank I. I. Ioffe, B. L. Moldavskii, A. G. Lyubarskii, Yu. D. Kernos, E. M. Kaganova, and A. F. Grigorova for samples of the catalysts mentioned which were kindly provided for testing in the present work.

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8 January 1968

Institute of Chemical Sciences
AS Kazakh SSR, Alma-Ata