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Pyridinealdehydes preparation by vapour phase oxidation of 2- and 3-pyridenemethanols and of their *N*-oxides on a V–Mo oxide catalyst[α]

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Abstract

The vapour phase oxidation of 2- and 3-pyridinemethanols and their respective *N*-oxides, reported here for the first time, over V-Mo and MnO_2 catalysts yielded corresponding pyridine carboxaldehydes at 400°C. V-Mo showed a high activity in comparison with the MnO_2 catalyst. A possible mechanism is also discussed.

Keywords: Vanadium-molybdenum/alumina, pyridine carbinol oxidation, manganese dioxide, oxidation catalysts.

INTRODUCTION

Pyridine carboxaldehydes are highly useful intermediates in the production of pharmaceuticals and pesticides, especially as antidotes such as 2-PAM iodide/chloride, obidoxime, etc. One of the known routes for the synthesis of these carboxaldehydes is the selective liquid-phase oxidation of the corresponding pyridinemethanols. For instance, using MnO_2 catalyst, the 2- and 3-pyridinemethanols and their respective *N*-oxides have been oxidized to their corresponding carboxaldehydes in 68, 67, 62 and 51% yields, respectively [1]. Micovic and Mihailovic [2] using lead tetracetate, obtained pyridine carboxaldehydes with yields of 65–70% from pyridinemethanols and with selenium dioxide catalyst, Jerchel and Heck [3] reported 60–65% yield. All these catalysts have proven to be fairly active for the production of their respective compounds. However, these reactions suffer from certain disadvantages like large catalyst volume, non-regenerability of the catalyst and the fact that large batches can not be handled effectively. Though it is known that the vapour

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phase oxidation of 2- and 3-picolines to the corresponding carboxaldehydes have been reported for a number of catalysts, the yields reported are always around 40% [4–8]. To our knowledge, there are no literature data on the partial oxidation of 2- and 3-pyridinemethanols and their *N*-oxides to the respective aldehydes with air in the vapour phase by any catalytic system. Therefore, in this paper we present a method for the production of these aldehydes in the gas phase that is attractive by virtue of its simplicity, selectivity and ease of product isolation in comparison to the conventional liquid-phase oxidation.

EXPERIMENTAL

In the present work, the reactants, 2- and 3-pyridinemethanols and their *N*-oxides are prepared as reported in the literature [2,9,10]. The catalysts were prepared by impregnating the α-Al_2O_3 support with a solution containing AnalaR ammonium heptamolybdate, ammonium metavanadate and oxalic acid. For an optimum catalyst the amount of active component V–Mo–O (V/Mo = 3.7/1) is 10 wt.-%. A fixed bed reactor fitted with the usual feeding and controlling facilities and operating under normal atmospheric pressure was used to determine the activities of the catalysts at 375 °C and the products were analysed by gas chromatography. An amount of 10–15 g of catalyst was used with an optimized molar feeding ratio of Py–CH_2OH/Py–CH_2OH–N-oxide:air: H_2O = 1:18:80. The surface areas of catalysts are in the range of 6–9 m^2g^{-1}.

RESULTS AND DISCUSSION

Table 1 presents the product distribution obtained with V–Mo and MnO_2 samples after about one hour run under constant experimental conditions. The

TABLE 1

Catalytic vapour phase oxidation of 2- and 3-pyridinemethanols and their *N*-oxides

Catalyst	Reactant	Conversion of reactant (%)	Aldehyde (%)	Acid (%)	Pyridine (%)	Pyridoin (%)	$CO+CO_2=CO_x$
V-Mo	2-Py-CH_2OH	85.0	80.0	4.0	8.0	2.0	2.5
	3-Py-CH_2OH	60.0	75.0	10.0	2.0	1.0	2.0
	2-Py-*N*-oxide	75.0	78.0	3.0	6.0	1.0	2.0
	3-Py-*N*-oxide	50.0	76.0	8.0	3.0	Trace	3.5
MnO_2	2-Py-CH_2OH	40.0	70.0	3.5	4.5	2.5	5.0
	3-Py-CH_2OH	20.0	68.0	7.5	2.0	1.0	4.0
	2-Py-*N*-oxide	30.0	72.0	2.0	3.0	Trace	2.0
	3-Py-*N*-oxide	30.0	65.0	3.5	1.5	1.0	3.0

oxidation of 2-pyridinemethanol produced 2-pyridine aldehyde as a major product, 2-picolinic acid, pyridine in small amounts, pyridoin and hydrogen cyanide in trace amounts along with oxides of carbon. In the case of 3-picololylalcohol, nicotinaldehyde was the major product along with notable amounts of nicotinic acid. Trace amounts of pyridine are also seen, as well as carbon monoxide and carbon dioxide. It is generally difficult to oxidize the alcoholic groups to their aldehydes selectively without consecutively oxidizing them to acids. Hence, the corresponding acids were seen in the by-products. In addition, the relative thermal decarboxylation of both acids is reflected in the amount of pyridine formation during these oxidations. The presence of pyridoin can be attributed as per the mechanism described by Battacharyya et al. [11]. The *N*-oxides of the corresponding alcohols followed a similar pattern of oxidations as their respective pyridinemethanols.

In our case, the oxidation of 2-pyridinemethanol gave 85% conversion with a selectivity of 80% aldehyde showing the novel ability when V/Mo was used as a catalyst. Comparing our results obtained with V–Mo catalyst with that of liquid phase oxidation of these compounds over MnO_2 in the literature, a striking difference in deactivation and selectivity can be noted for V–Mo system. In addition, from this observation some important differences can be noted between the vapour- and liquid-phase mode of oxidation reactions of these pyridine carbinols. The catalysts in liquid-phase mode of oxidation, MnO_2 and SeO_2, can not be regenerated. In contrast, the investigated V–Mo catalytic system gets oxidized back simultaneously by air in the feed, thus helping a continuous production of aldehyde with high activity and life. Furthermore, in comparison the MnO_2 catalyst, which proved to be a valuable oxidizing agent in liquid-phase oxidation of 2- and 3-pyridine methanol and their *N*-oxides, gave a poor performance in vapour-phase mode of operation. Also pyridine methanols are much more selective in vapour-phase formation of pyridine aldehydes than the picoline vapour-phase oxidations [4–8]. Another factor is that 2-pyridinemethanol conversion is higher than 3-pyridine methanol conversion, as seen in Table 1. This is analogous to the reactivity differences reported for the three isomeric picoline oxidations [12].

It is known that the strength of the $V=O$ bond has been the controlling factor for the catalytic activity in partial oxidation reactions of V-based catalysts. The promotive action of MoO_3 on V_2O_5 for this mild oxidation of pyridinemethanols may be due to the weakening of the $V=O$ bond [13]. It is generally accepted that in a selective oxidation reaction, the catalysts give up lattice oxygen to take part in the oxidation reaction, and the reduced catalysts can absorb oxygen from the gas phase and transform it to lattice oxygen [14]. When 2- and 3-pyridinemethanols and their *N*-oxides are oxidized, the mechanistic information concerning the intermediates formed and their conversion to selective products is complex, because of the simultaneous presence of many parallel and/or consecutive pathways leading to intermediates and prod-

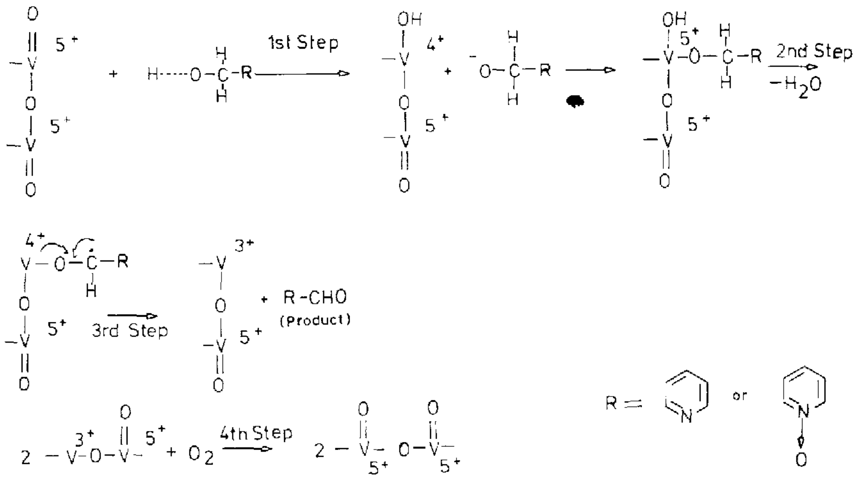

Fig. 1. Mechanism for oxidation of pyridenemethanols over V_2O_5 catalyst. R = Pyridine or Pyridine-*N*-oxide.

ucts. The main product aldehyde may be formed by the reaction steps assumed in Fig. 1. The overall mechanism involves the oxidative dehydrogenation of alcohol and replenishment of the resulting lattice vacancies by vapour-phase oxygen. The application of the present vapour-phase oxidation to other systems of pyridinemethanols is currently under active investigations.

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