

BRIEF  
COMMUNICATIONS

## Binary Oxide Systems in Catalytic Synthesis of 2-Methylpyrazine from 1,2-Propylene Glycol and Ethylenediamine

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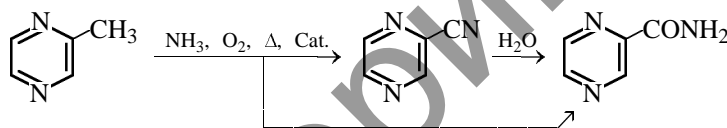
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**Abstract**—A series of binary catalysts based on oxides of zinc and variable-valence metals were tested in synthesis of 2-methylpyrazine by catalytic dehydrocyclization of 1,2-propylene glycol with ethylenediamine.

The growing incidence of tubercular diseases calls for improving the synthesis processes and increasing the production of tuberculostatic means. One of the most important antitubercular preparations is Pyrazinamide.

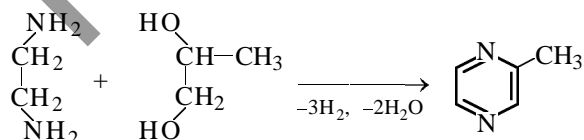
Its active agent, which is also the starting compound for preparing low-toxic bacteriostatics [1], is pyrazine-2-carboxamide, prepared by oxidative ammonolysis of 2-methylpyrazine (MP) [2].



By now, fairly selective catalysts have been developed for oxidative ammonolysis of MP, allowing preparation, depending on reaction conditions, of either 2-cyanopyrazine [3] or 2-pyrazinamide [4] in yields of 80% and higher; however, there are no commercially acceptable procedures for synthesis of the starting compound.

The existing routes to MP, involving synthesis and subsequent dehydrogenation of 2-methylpiperazine [5] or reaction of propylene oxide with ethylenediamine at elevated pressure [6], are of no promise for commercial production of MP.

One of efficient routes to MP can be catalytic dehydrocyclization of ethylenediamine with 1,2-propylene glycol.



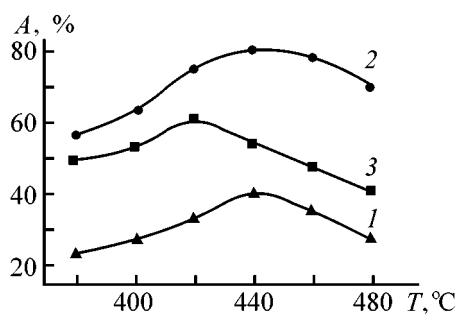
At present, the most frequently used cyclizing and dehydrogenating catalysts for this reaction are those

based on oxides of Zn [7–9], Cu, or Cr(III) [10]; in their presence, the yield of MP reaches 60–70%. The best results are obtained with catalysts prepared by mixing the components to a pasty state, with subsequent extrusion and drying [8].

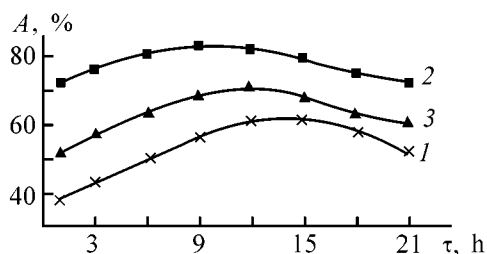
In this study, we tested MoO<sub>3</sub>-modified zinc oxide catalysts prepared by such a procedure. The dependence of the MP yield on the catalyst composition and reaction temperature is illustrated by Fig. 1. We found that the catalyst containing ZnO and MoO<sub>3</sub> in 1 : 0.3 molar ratio ensures a yield of the target product as high as 75–80% in the temperature range 420–460°C.

However, we found that the catalysts prepared by extrusion are rapidly coked and require frequent regeneration, which results in the loss of mechanical strength and, finally, in decreased yield of the target product. The service life of such catalysts does not exceed 10 h.

To prolong the service life of the zinc–molybdenum catalysts and enhance their mechanical strength, the catalysts were prepared by pelletizing with sub-



**Fig. 1.** MP yield *A* vs. temperature *T*. Catalyst ZnO–MoO<sub>3</sub> prepared by extrusion; ZnO:MoO<sub>3</sub> ratio: (1) 1:0.2, (2) 1:0.3, and (3) 1:0.4.



**Fig. 2.** Effect of the granulometric composition of the 1:0.3 ZnO–MoO<sub>3</sub> catalyst on the MP yield *A* at 460°C. ( $\tau$ ) Time of catalyst operation. Grain size, mm: (1) 0–1, (2) 1–2, and (3) 2–3.

sequent calcination. The results obtained with pelletized catalysts were similar to those obtained with the catalysts prepared by extrusion (see table). Although the mechanical strength increased considerably, the service life between regenerations decreased to 6 h, probably owing to a decrease in the specific surface area in the course of pelletizing.

MP yield at various compositions of binary catalysts. Feed space velocity 120 h<sup>-1</sup>

Catalyst*	MP yield, %, at indicated temperature, °C					
	380	400	420	440	460	480
ZnO:MoO <sub>3</sub> :						
1:0.2	23	27	34	42	37	30
1:0.3	58	63	74	82	79	67
1:0.4	53	57	62	55	50	44
ZnO:V <sub>2</sub> O <sub>5</sub> :						
1:0.2	22	31	40	45	37	31
1:0.3	30	46	58	50	43	35
1:0.4	27	39	49	47	38	34
ZnO:WO <sub>3</sub> :						
1:0.1	29	38	42	51	55	50
1:0.2	27	33	38	43	52	50

\* Molar ratio of the components is given.

Data in the table also show that we failed to improve the properties of zinc oxide catalysts by their modification with vanadium and tungsten oxides.

The results obtained in dehydrocyclization of 1,2-propylene glycol with ethylenediamine in the presence of ZnO–MoO<sub>3</sub> catalyst of the composition ZnO:MoO<sub>3</sub> = 1.0:0.3, prepared by granulation, deserve attention. The service life of this catalyst between regenerations, 20 h, is twice that of the catalyst prepared by extrusion. It should be noted that the optimal selectivity of this catalyst noticeably depends on the grain size (Fig. 2).

## EXPERIMENTAL

Extrudates were prepared according to [11]. To obtain catalysts as pellets, the oxides were thoroughly mixed to uniform state and pressed at 100 atm (catalyst with WO<sub>3</sub>, at 500 atm) in plunger dies with cell size of 4 × 4 mm. Pellets were dried at 105°C for 2 h, promoted with 1% MnSO<sub>4</sub> and 3% H<sub>3</sub>PO<sub>4</sub> solutions [11], and again dried under the same conditions, with subsequent calcination in a muffle furnace at 650°C for 1 h.

For granulation, we used ZnO and MoO<sub>3</sub> with particle size of 10–40 and 40–60 μm, respectively. The oxides were mixed to uniform state and pelletized in a cup granulator by spraying a 5% NaOH solution in amount of 5–20% of the mixture weight. The resulting pellets were dried successively at 50–80 (2 h) and 100–150°C (2 h). The dried grains were sieved to obtain 0–1-, 1–2-, and 2–3-mm fractions and promoted similarly to the pellets prepared by pressing. Then the grains were dried for 2 h at 250°C.

The catalyst (extrudates, pellets, or grains) was charged in an amount of 150 cm<sup>3</sup> into a straight-flow reactor with a stainless steel tube (400 mm long, 20 mm i.d.), into which an equimolar mixture of ethylenediamine and 1,2-propylene glycol, diluted with 40 vol % water and preheated in a steam heater to 280–300°C, was fed at a space velocity of 120 h<sup>-1</sup>. The reaction temperature was adjusted within 420–470°C; the reaction products were cooled in the trapping system.

MP was isolated from the reaction mixture as an azeotrope with water {bp 97°C (737 mm Hg), MP content 45% [12]}, from which the target product was recovered by extraction with chloroform or diethyl ether.

The reaction course was monitored by GLC (Chrom-5 chromatograph, flame-ionization detector, 2500 × 3-mm glass column, stationary phase 5% SE-30 on Chromaton N-AW-HMDS, column temperature 100°C, vaporizer temperature 180°C, detector temperature 190°C, carrier gas argon, flow rate 20 ml min<sup>-1</sup>).

The constants of the isolated MP after distillation (bp 135°C,  $n_D^{20}$  1.4967,  $d_4^{20}$  1.030) were consistent with published data [13].

The mass spectrum of MP, taken on an MKh-1300 spectrometer ( $m/z$  94, 67, 26, 39, 40, 53, 38, 42, 28, 41) confirms the structure of the synthesized MP [14].

### CONCLUSIONS

(1) New zinc oxide catalysts modified with Mo, V, and W oxides were developed and tested in synthesis of 2-methylpyrazine from 1,2-propylene glycol and ethylenediamine.

(2) The selectivity of the mixed oxide catalyst ZnO–MoO<sub>3</sub> (molar ratio 1 : 0.3) with respect to 2-methylpyrazine is as high as 75–82% under the optimal conditions (420–460°C).

(3) The Zn–Mo–O catalyst produced by granulation has a considerably longer service life between regenerations than the catalysts prepared by pelletizing and extrusion.

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