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OXIDATIVE DEHYDROGENATION OF ALKYLHETEROAROMATIC COMPOUNDS

1. CATALYSTS CONTAINING VANADIUM AND MOLYBDENUM FOR THE OXIDATIVE DEHYDROGENATION OF ALKYLPYRIDINES

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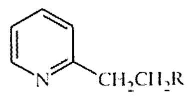
The dehydrogenation of a series of alkylpyridines has been studied on vanadium and molybdenum oxide-containing catalysts in the presence of oxygen of the air and sulfur dioxide gas. A dependence was shown of the catalytic and physicochemical properties of the catalysts indicated on their composition and method of preparation. The optimum catalyst composition and the conditions of carrying out the reaction to provide high activity and selectivity when making vinylpyridines were determined. The relative reactivity of the alkylpyridines investigated on dehydrogenation and further oxidation was determined.

Vinyl pyridines are polymerized readily, they possess high reactivity, are used as monomers in synthetic rubber manufacture, and are important starting materials in numerous organic syntheses [1, 2]. The main methods of obtaining such monomers as 2-methyl-5-vinylpyridine and 2,5-divinylpyridine are the high temperature catalytic dehydrogenation and condensation of picolines with aldehydes [3, 4]. Information on the preparation of vinylpyridines by oxidative dehydrogenation is sparse [5, 6] and little is given in the studies indicated on the conversion of alkylheteroaromatic compounds.

It is known that vanadium and molybdenum catalysts with various promoting additives are used widely in oxidation catalysis.

We previously studied in detail such systems in the oxidative dehydrogenation of alkylaromatic hydrocarbons [7, 8]. It was established that the structure of the surface and the activity and selectivity in reactions depend on the content of active component, the nature of the salts and carriers, and the heat treatment conditions [9, 10]. Study of the route of preparing the vanadium catalyst and the conditions of forming the active surface has enabled efficient catalysts to be created for the dehydrogenation of alkylaromatic hydrocarbons in the presence of hydrogen acceptors [11]. In the present study the results obtained previously are used to optimize the preparation of the catalysts for the oxidative dehydrogenation of alkylpiperidines with the aim of extending the method to the preparation of vinyl substituted heterocyclic compounds.

We have studied the conversion of various alkyl substituted pyridines.



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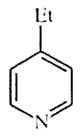

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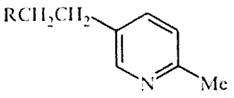

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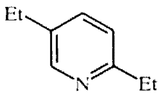

IV

Ia R = H, b R = Me, c R = Et; IIIa R = H, b R = Et

N. D. Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow 117913. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 802-811, June, 1994. Original article submitted April 19, 1994.

TABLE 1. Oxidative Dehydrogenation of 2-Ethylpyridine (Ia) on Binary Vanadium–Magnesium Catalysts with Various Contents of Active Component (480°C, volume rate 1.0-1.5 h^{-1}, molar ratio (Ia):O_2:H_2O = 1:1:12

V_2O_5 content, %	Surface, m^2/g	Volume ratio* V:Mg	Yield, %	
			on (Ia) passed through	on (Ia) decomposed
0	88		6,0	62,0
2,0	123	1 : 31	25,0	68,0
5,0	98		30,0	32,0
7,0			45,0	80,0
9,0	105		50,0	87,0
12,0	100	1 : 10	55,0	88,0
16,0	77	1 : 8	32,0	76,0
25,0	75	1 : 4	28,0	60,0
100,0	11		18,0	40,0

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*Data of XESP.

TABLE 2. Effect of the Heat Treatment Conditions of Vanadium– and Molybdenum–Magnesium Catalysts on the Oxidative Dehydrogenation of 2-Ethylpyridine (Ia) to 2-Vinylpyridine (V) [480°C, volume rate 0.5 h^{-1}, molar ratios (Ia):O_2:H_2O = 1:1:7]

Heat treatment T, °C	Surface m^2/g	Ratio V:Mg (XESP)	Pore volume, cm^3/g	Yield of (V), %	
				on (Ia) passed through	on (Ia) decomposed
		Vanadium–magnesium catalyst			
120	—	—	0,3	12,0	80,0
550	100	1 : 10	0,7	55,0	88,0
850	50	1 : 50	0,4	10,0	79,0
After action of reaction mixture		1 : 15	0,2		
		Molybdenum–magnesium catalyst			
120	—	—	—	14,0	79,0
550	80	—	0,6	54,0	87,0
850	42	—	0,3	12,0	80,0

We have shown that, in the presence of catalysts containing vanadium and molybdenum and oxygen of the air, there were products of oxidative destruction, viz. pyridine, picoline, and pyridine aldehydes (up to 1%), in addition to the main product, vinylpyridines, and unreacted alkylpyridines. Traces of carbon oxides, methane, hydrogen, and nitrogen were detected in the exit gases, and ammonia was found in the aqueous layer. The gas-forming processes were insignificant (less than 3%). Carbon formation on the catalyst surface during an experiment was up to 2%.

Results are given in Table 1 on the dehydrogenation of 2-ethylpyridine (Ia) on binary vanadium–magnesium catalysts with various contents of the active component. The degree of conversion of alkylpyridine changes on increasing the concentration of V_2O_5 in the sample, maximum activity was at 9-12% V_2O_5 content. As was shown in [11] the similar character of the change of activity of vanadium–magnesium catalysts is linked with the formation of active centers of various structure in the carrier matrix. Samples with a V_2O_5 content less than 5% had little activity in the oxidative dehydrogenation of (Ia). As was shown previously in [12], mainly isolated vanadium ions were present in them. The highest activity in the oxidative dehydrogenation (yield of 2-vinylpyridine was ~55%) was possessed by catalysts with a V_2O_5 content of 9-12% where clustering with the formation of associates of 2-3 octahedrally coordinated vanadium ions was observed. In samples with a V_2O_5 contentgreater than 16% a magnesium vanadate phase of regular structure was established in which vanadium ions were

TABLE 3. Effect of the Oxidative Dehydrogenation Conditions on the Conversion of 5-Ethyl-2-methylpyridine (IIIa) into 2-Methyl-5-vinylpyridine (VII)

T, °C	Volume rate	Molar ratio (IIIa):O_2:H_2O	Yield of (VII), wt.%		Carbon formation, as % of (IIIa) passed
			on (IIIa) passed	on (IIIa) decomposed	
460	0,25	1 : 1 : 7	50,0	75,0	5,0
460	0,50	1 : 1 : 7	38,0	68,0	
460	0,50	1 : 1 : 5	44,0	83,0	4,8
460	0,50	1 : 1 : 15	36,0	78,0	
460	0,50	1 : 1 : 20	34,0	75,0	
460	1,00	1 : 1 : 7	42,0	82,0	3,4
460	1,50	1 : 1 : 7	36,0	92,0	2,8
480	0,50	1 : 1 : 7	42,0	82,0	
500	0,50	1 : 1 : 7	49,0	80,0	
520	0,50	1 : 1 : 7	53,0	78,0	5,8

TABLE 4. Oxidative Dehydrogenation of 2,5-Diethylpyridine (IV) to the Ethylvinylpyridines (VIIIa, b) and Divinylpyridine (IX) (volume rate 0.25 h^{-1})

T, °C	Molar ratios (IV):O_2:H_2O	Yield, wt.%		
		on (IV) passed through		on (IV) decomposed (total unsaturated)
		(VIIIa, b)	IX	
480	1 : 1 : 10	18,0	5,6	89,0
380	1 : 2 : 10	20,0	10,0	88,0
420	1 : 2 : 10	20,5	17,0	88,0
460	1 : 2 : 10	21,7	25,0	87,0
480	1 : 2 : 10	12,0	37,0	88,0
480	1 : 2,5 : 10	11,5	36,0	86,0
480	1 : 3 : 10	11,0	35,0	84,0
500	1 : 2 : 10	10,0	36,0	82,0
520	1 : 3: 10	10,0	35,0	83,0
520	1 : 4 : 10	10,5	34,0	81,0

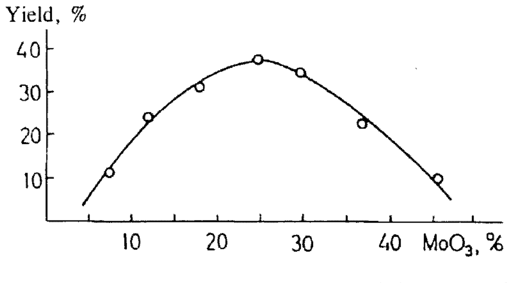

Fig. 1. Dependence of the yield of 2-vinylpyridine (V) with respect to the 2-ethylpyridine (Ia) passed through on the content of the active component in binary molybdenum–magnesium catalysts (480°C, volume rate 0.5 h^{-1}, molar ratios (Ia):O_2:H_2O = 1:1:7).

found mainly in tetrahedral coordination. These ions were reduced with difficulty and had low reactivity in the oxidative reduction of alkylpyridines. At a V_2O_5 content greater than 30% the free V_2O_5 phase grew as well. Such samples also had low activity in the reaction being investigated.

With binary molybdenum–magnesium catalysts the greatest activity in the oxidative dehydrogenation of compound (Ia) was possessed by samples containing 25-30% MoO_3 (Fig. 1). These were characterized by electronic diffusion reflection

TABLE 5. Oxidative Dehydrogenation of 5-Butyl-2-methylpyridine (IIIb) to 5-Butenyl-2-methylpyridine (X) [volume rate 0.5 h^{-1}, molar ratios (IIIb):O_2:H_2O = 1:1:7]

T, °C	Yield of (X), wt.%	
	on (IIIa) passed through	on (IIIb) decomposed
460	38,0	85,0
480	40,5	80,0
500	42,0	72,0
520	44,5	70,0

TABLE 6. Oxidative Dehydrogenation of 4-Ethylpyridine (II) to 4-Vinylpyridine on Vanadium–Magnesium Catalyst in the Presence of Sulfur Dioxide (volume rate 1.0 h^{-1})

T, °C	Molar ratios (II):SO_2:H_2O	Yield of (VI), wt.%	
		on (II) passed through	on (II) decomposed
460	1 : 0,3 : 7	61,0	95,2
480	1 : 0,35 : 8	65,0	94,0
490	1 : 0,35 : 8	66,4	93,5
500	1 : 0,35 : 8	68,0	92,5
560	1 : 0,35 : 8	58,0	89,0
580	1 : 0,35 : 8	56,0	85,0
480	1 : 0,4 : 7	65,0	94,0
480	1 : 0,8 : 7[*]	30,0	
480	1 : 1,2 : 7[*2]	35,0	
480	1 : 0,35 : 5	50,0	92,0
480	1 : 0,35 : 10	64,0	95,0
480	1 : 0,35 : 15	63,5	94,6
480	1 : 0,35 : 20	58,0	92,3

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[*] Content of sulfur dioxide in contact phase was 23%.

[*2] Content of sulfur dioxide in contact phase was 35%.

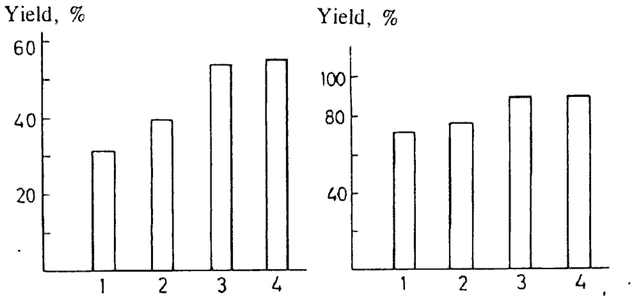

Fig. 2. Catalytic properties of binary and modified samples in the oxidative dehydrogenation of 2-ethylpyridine (Ia) to 2-vinylpyridine (V): 1) 25% MoO_3/MgO catalyst; 2) 9% V_2O_5/MgO catalyst; 3) 25% MoO_3/MgO catalyst modified; 4) 9% V_2O_5/MgO modified [480°C, volume rate 0.5 h^{-1}, molar ratios (Ia):O_2:H_2O = 1:1:7].

spectroscopy (EDRS) by the presence of octahedrally coordinated Mo^{6+} ions (300-320 nm) [13], and bands at 425, 670, 820, and 995 cm^{-1} in the IR spectra corresponding to the stretching vibrations of MoO_3. Samples containing 40-50% MoO_3 had low activity in the oxidative dehydrogenation of an alkylpyridine. Absorption bands were recorded in the EDRS spectra corre-

TABLE 7. Comparison of the Oxidative Dehydrogenation of Alkylpyridines in the Presence of Oxygen of the Air and of Sulfur Dioxide (480°C, volume rate 1.0 h^{-1}, molar ratios of alkylpyridine:O_2:H_2O = 1:1:7, and alkylpyridine:SO_2:H_2O = 1:0.4:8)

Starting material	Acceptor	Yield of corresponding vinylpyridine, wt.%	
		on alkylpyridine passed through	on alkylpyridine decomposed
5-Ethyl-2-methylpyridine	O_2	42,0	82,0
	SO_2	67,0	92,0
4-Ethylpyridine	O_2	65,0	90,0
	SO_2	66,0	95,0

sponding to tetrahedrally coordinated Mo^{6+} (260-290 nm). In them, according to data of X-ray analysis of phases (XPA), reflections were recorded at 3.35, 3.12, and 1.93 Å and IR absorption bands at 812, 886, 912, and 950 cm^{-1} corresponding to a magnesium molybdate $MgMoO_4$ phase.

The effect of the conditions of the heat treatment on the structural and catalytic properties of samples is characterized by the data of Table 2. Investigation of the oxidative dehydrogenation of 2-ethylpyridine on vanadium–magnesium and molybdenum samples subjected to various heat treatments shows that the most active samples were obtained by heat treatment at 550°C. It is known that on dehydrogenation of the surface (200-550°C) partial reduction occurs of octahedrally coordinated V^{5+} ions to V^{4+} [10] and Mo^{6+} to Mo_{tet}^{5+} (absorption bands at 500-540 nm in the EDRS spectra [13]. Under these conditions the reaction of ions of the active component with magnesium oxide is probably limited to the predominant formation of vanadates and molybdates of magnesium of irregular structure. These samples are reduced readily and display high activity in the oxidative dehydrogenation of alkylpyridines. X-Ray phase and thermogravimetric analysis and IR spectral data showed that magnesium molybdates and vanadates of regular structure with tetrahedrally coordinated ions are formed as a result of calcining molybdenum–magnesium and vanadium–magnesium samples at 650-850°C. Such samples have low activity in oxidative dehydrogenation. Data of XESP (Table 2) show that depletion (5-6 fold) of vanadium ions from the catalyst surface occurs on calcining. This may indicate the formation of magnesium vanadates in the bulk of the catalyst [9].

The heat treatment is also vitally important for forming the texture of samples. Under optimum activation conditions (550°C) catalysts are formed with the following structural characteristics: specific surface 100-120 m^2/g, pore volume 0.7-0.6 cm^3/g, predominant pore radius 200-500 Å. The content of V_2O_5 on the surface (from data of XESP) is 2-2.5 times greater than in the bulk of such samples. On increasing the activation temperature to 750-850°C complete dehydrogenation of the surface occurs accompanied by enlargement of the pores, reduction of the surface 2-2.5 fold, and a significant drop in the activity of samples.

It is known that the catalytic properties of binary vanadium–magnesium catalysts may be improved significantly by introducing modifiers ($KHSO_4$, $MgSO_4$, ZnO, CdO) [9]. We showed that Cs_2O, V_2O_5, and Nb_2O_5 have a similar effect on molybdenum–magnesium catalyst (Fig. 2). According to EDRS the modification provides stabilization of octahedrally coordinated vanadium and molybdenum ions at the higher oxidation states V^{5+} and V^{4+}, Mo^{6+} and Mo^{5+}). These samples contain V_{oct}^{5+} and Mo_{oct}^{6+} ions after carrying out an oxidative dehydrogenation reaction and reduction in a stream of hydrogen.

The general nature of the regular changes in activity of the vanadium–magnesium and molybdenum–magnesium catalysts as a function of catalyst composition and heat treatment, both for the oxidative dehydrogenation of ethylbenzene to styrene [9-11] and for the oxidative dehydrogenation of alkylpyridines studied by us, suggest that octahedrally coordinated vanadium and molybdenum ions are probably responsible for the oxidative dehydrogenation.

The vanadium–magnesium and molybdenum–magnesium catalysts are close in efficiency to one another in the oxidative dehydrogenation of alkylpyridines. However it must be noted that it is necessary to introduce a large quantity of the active component for the preparation of the molybdenum catalysts. On working with molybdenum–magnesium catalysts in extended cycles some drop in activity was observed, probably due to carrying away of the active phase as the oxide MoO_3, which makes this catalyst less attractive than the vanadium–magnesium catalyst.

Oxidative dehydrogenation of alkylpyridines (II), (IIIa), and (IIIb) was carried out on a vanadium–magnesium catalyst of composition 10% V_2O_5, 2% modifying additive, and 88% MgO.

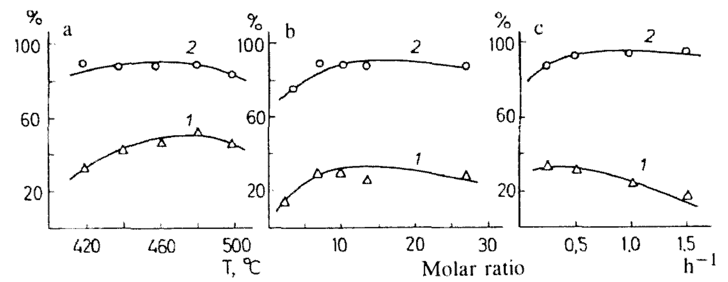

Fig. 3. Effect of a) reaction temperature, b) dilution with water vapor, and c) volume rate on the yield of 4-vinylpyridine (VI) with respect to 4-ethylpyridine 1) passed and 2) decomposed during dehydrogenation on modified vanadium–magnesium catalyst [molar ratio (II):O_2 = 1:1].

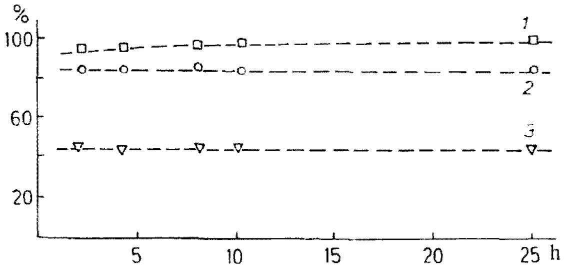

Fig. 4. Results of the extended testing of a catalyst in the oxidative dehydrogenation of 5-ethyl-2-methylpyridine (IIIa) to 2-methyl-5-vinylpyridine (VII): 1) yield of catalysate; 2) yield of 2-methyl-5-vinylpyridine (VII) on (IIIa) decomposed; 3) on (IIIa) passed [460°C, volume rate 0.5 h^{-1}, molar ratios (IIIa):O_2:H_2O = 1:1:7]

The results of the dehydrogenation of 4-ethylpyridine (II) are given in Fig. 3. The maximum conversion (53%) to 4-vinylpyridine (VI) was achieved at 480°C, a volume rate of 0.5 h^{-1}, and molar ratios of (II):O_2:H_2O = 1:1:7-9. We observed a high selectivity in practically all the conditions investigated. Only at low dilution of the reaction mixture with water vapor (ratio 1:1:3.5) did a significant reduction in selectivity occur due to the formation of a large quantity of picolines and pyridine (up to 14%).

The dehydrogenation of 5-ethyl-2-methylpyridine (IIIa) over a wide range of reaction conditions is given in Table 3. With a reduction in the volume rate from 1.5 to 0.25 h^{-1} the degree of conversion into 2-methyl-5-vinylpyridine (VII) was increased initially, then maintained at a constant level, and later began to fall due to the increase of side reactions (decomposition and further oxidation). Selectivity was reduced with the fall in volume rate, carbon deposition being increased concomitantly. At 460°C and a volume rate of 1.5 h^{-1} the selectivity was 92% and at a rate of 0.25 h^{-1} it had fallen to 75% while carbon formation was increased approximately 1.5 times.

An increase of temperature to 500-520°C gave an increase in the extent of conversion with a simultaneous drop in selectivity and a rise in carbon deposition on the catalyst. On increasing the dilution of the reaction mixture with water vapor (molar ratios 1:1:15-20) the yields of catalyzate and of product (VII) fell sharply, gas formation was increased, as was the content of CO_2, H_2, and volatile pyridines such as γ-picoline, 2,5-lutidine, and 3-vinylpyridine.

The testing of vanadium–magnesium catalyst in extended experiments on the dehydrogenation of compound (IIIa) is shown in Fig. 4. No drop in catalyst activity was observed after 25 h operation under optimum conditions.

When dehydrogenating 2,5-diethylpyridine (IV) the ratio of dehydrogenation products of one ethyl group, the ethylvinylpyridines (VIIIa, b), and of two ethyl groups, the divinylpyridine (IX), depends both on the temperature and on the dilution with oxygen from the air (Table 4). An increase in temperature from 380 to 480°C afford an increase in the total content of unsaturated compounds in the catalyzate (49%) and increased the yield of divinylpyridine to 37%. A further increase of temperature to 520°C leads to some fall in the yield of ethylvinylpyridines (VIIIa, b) and a significant drop in selectivity (76-78%) due to destructive oxidation and an increase in carbon deposition on the catalyst surface.

With an increase in the dilution with oxygen of the air (molar ratios 1:2-2.5:10) the content of unsaturated pyridines is increased. At ratios of 1:3:10 it is somewhat reduced with a simultaneous reduction in reaction selectivity due probably to the increase in products of further oxidation (CO_2 and pyridine aldehydes). It must be noted that at high dilution by oxygen of the air (molar ratio 1:4:10) the conversion into 2,5-divinylpyridine depends less on temperature.

On dehydrogenating 5-butyl-2-methylpyridine (IIIb), in addition to 5-butenyl-2-methylpyridine (X), a wider selection of side products was observed, viz. pyridine, picolines, 5-ethyl-2-methylpyridine, 5-ethylpyridine, 2-methyl-5-vinylpyridine, and 5-vinylpyridine. Butane, butylene, ethane, and methane were observed in the exit gases. No oxygen-containing compounds were detected. At 460-480°C and molar ratios of (IIIb):O_2:H_2O = 1:1:7 the yield of methylbutenylpyridines was 38-40% at a selectivity of 80-85% (Table 5). An increase in temperature even to 500-520°C caused a sharp reduction in selectivity to 70-72%, probably due to carbon formation and a significant increase in the further oxidation of the starting material.

Comparison of the relative ability of converting these compounds by oxidative dehydrogenation into the corresponding vinyl derivatives at both low (20%) and at high (47-60%) conversions enabled us to arrange them in the following series: (Ia) > (II) > (IV) (as total unsaturated) > (IIIa) > (IIIb). The reverse sequence was observed for the further oxidation: (IIIb) > (IIIa) > (IV) > (II) > (Ia).

It is therefore possible to conclude on the basis of the results of investigating the conversion of a series of alkylpyridines during oxidative dehydrogenation that the optimal conditions providing high yields of vinylpyridines are a temperature of 460-480°C, a volume rate of 0.5-1.0 h^{-1}, molar ratios of alkylpyridine:oxygen of the air:water vapor of 1:1:7-10 for monoalkylpyridine derivatives and 1:2-2.5:7-10 for 2,5-diethylpyridine.

It is known that the use of a milder oxidizing agent than oxygen as hydrogen acceptor may assist an increase in conversion and selectivity during oxidative dehydrogenation [14]. Results are given in Table 6 of the oxidative dehydrogenation of compound (II) in the presence of sulfur dioxide. The optimum conditions for carrying out this process, providing high activity and selectivity when obtaining product (VI), are a temperature of 480-490°C, a volume rate of 1.0 h^{-1}, and molar ratios of (II):sulfur dioxide:H_2O = 1:0.35-0.40:8-10. The yield of (VI) was 66-68% at a selectivity of 92-94%, which was retained practically constant for more than 15 h continuous operation.

On increasing the temperature to 560-580°C the yield fell with a simultaneous significant fall in selectivity. On increasing the ratio of (II):sulfur dioxide to 1:1.2 the quantity of unreacted sulfur dioxide in the contact phase grew sharply which may hinder the purification of the reaction products and be unfavorable ecologically. Sulfur dioxide was absent from the exit gases at the optimum reactant ratio, since it is used completely.

Comparison of the data on the oxidative dehydrogenation of 4-ethylpyridine and 5-ethyl-2-methylpyridine in the presence of sulfur dioxide or oxygen indicates that the dehydrogenation proceeds with a higher selectivity and higher yields of vinylpyridines in sulfur dioxide (Table 7).

The investigations carried out show that the oxidative dehydrogenation of alkylpyridines may be effected with high results on these vanadium–magnesium and molybdenum–magnesium catalysts in the presence of oxygen of the air and of sulfur dioxide. This method possesses several advantages over the usual dehydrogenation and over multistage organic syntheses since higher conversion and selectivity are achieved. The energy and resource saving are also distinct advantages since the oxidative dehydrogenation process is conducted at relatively low temperatures using small quantities of low temperature water vapor. The catalysts developed enable oxidative dehydrogenation to be carried out over extended cycles without regeneration.

EXPERIMENTAL

Catalysts were prepared by mixing the carrier MgO (S_{sp} 100 m^2/g) with an aqueous solution of the calculated quantity of ammonium vanadate or molybdate. The content of active component calculated as V_2O_5 was 0-25 wt.% and as MoO_3 0-50 wt.%. The molybdenum–magnesium composite was also prepared by precipitation from a mixture of aqueous solutions of ammonium molybdate and magnesium nitrate at 60°C and pH 8.5 with subsequent introduction of the MgO carrier with specific surface 19 m^2/g to the mixture of hydroxides. The mass obtained was shaped with a press. Granules were dried in the air and then in a drying chamber at 120°C. The dried catalyst was subjected to heat treatment in a reactor in a stream of air at a rate of temperature increase of 100°C/h to 550-850°C and maintained at this temperature for 3-4 h.

The oxides of vanadium, cesium, or niobium were used as modifying additives for the molybdenum–magnesium catalyst and $KHSO_4$, $MgSO_4$, ZnO, or CdO (no more than 2% in total) for the vanadium–magnesium catalyst.

The size of the specific surface of samples was determined by the low temperature nitrogen adsorption method of Brunauer–Emmet–Teller (BET). X-Ray analysis of phases was effected on a DRON-3 diffractometer using an X-ray tube with copper radiation. Diffusion reflection spectra were recorded on a SF-4A spectrophotometer in the range 240-1000 nm using $BaSO_4$ as standard at room temperature. Porosity was determined on a Carlo Erba porosimeter. The IR spectra were recorded on a UR 20 spectrometer.

Quartz flow-type reactors with a stationary layer of catalyst (volume 40 ml) were used for studying catalytic properties. To improve the isothermicity at the catalyst the layer was diluted twice by volume with broken quartz at a ratio of 1:2 by volume.

The oxidative dehydrogenation reaction was investigated over a wide range of parameters: temperature 360-560°C, volume rate 0.25-1.5 h^{-1}, molar ratios of alkylpyridine:acceptor:water vapor = 1:0.3-4:3.5-20. The duration of experiments the catalyst was regenerated at the reaction temperature for 5-10 min with a mixture of water vapor and air then with air for 30 min.

Liquids and gaseous products were analyzed by GLC. The column (2 m × 3 mm) was packed with polyethyleneglycol 2000 on NaCl, previously treated with 1% KOH solution. Analysis temperature was 90°C, carrier gas helium. Correction coefficients for calculating the chromatograms were determined by analysis of artificially prepared mixtures of alkyl- and vinylpyridines in various weight ratios.

The amount of carbon deposition on the catalyst was determined after oxidation to CO_2 or by a thermogravimetric method. The yield of vinyl derivatives on passed through and decomposed starting material was calculated from the analytical results and the data of the material balance for each analysis.

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