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Ammoxidation of methylpyrazine over V–Ti oxide system

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Abstract

The catalytic properties of vanadium–titanium oxide system in ammoxidation of methylpyrazine have been studied. Catalytic activity increases monotonically and yield of selective products passes a wide maximum in the range of V_2O_5 content from 10 to 75 wt.% with increase in the V/Ti relation. The active centers of binary catalysts include V^{5+} cations with distorted octahedral coordination strongly bounded with titania apparently owing to formation of V–O–Ti bonds. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ammoxidation; Methylpyrazine; V–Ti–O system

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1. Introduction

Vanadium–titanium catalysts are highly effective in selective oxidation of different organic compounds [1,2]. Activity of these catalysts has been associated with the presence of surface vanadium species of various composition and structure — isolated monomeric, polymeric with distorted or unregulated structure, possessing terminal V=O bonds with specific orientation, and so on. While even for the best known reaction of *o*-xylene oxidation this question remains open.

In parallel with the partial oxidation reactions, vanadium–titanium catalysts are successfully employed in ammoxidation of substituted aromatics [3] and *N*-heterocycles, especially picolines [4–6], to the corresponding nitriles. The latter are valuable intermediates in the organic synthesis of various dyestuffs, pesticides and pharmaceuticals. Studies on the V–Ti–O system in the ammoxidation of heterocycles containing two nitrogen atoms, however, are few and they deal with the description of discrete samples in methylpyrazine (MP) ammoxidation only [7,8].

This work presents the results of systematic investigation of catalytic properties of vanadium–titanium oxide system in MP ammoxidation as well as the state and local environment of vanadium cations.

2. Experimental

We have studied binary catalysts with vanadium content 5, 10, 20, 30, 50 and 75 wt.% expressed as V_2O_5, and individual vanadium and titanium oxides. The samples were prepared according to the procedure given in [9].

Catalytic activity was determined in flow and circulating flow setups with a chromatographic analysis of reagents [10]. Experiments were carried out in the temperature interval 250–400°C, the inlet reaction mixture was (vol.%): 1 MP, 8 O_2, 17 NH_3, 17 H_2O, the rest being N_2.

^{51}V NMR measurements were performed on a Bruker MSL-400 spectrometer (ν_0=105.2 MHz for ^{51}V resonance) using spin-echo and one pulse se-

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quences for wide line and magic-angle spinning (MAS) techniques. MAS spectra were recorded at the rotation frequencies of 6–15 kHz using 4 mm (outer diameter) rotor. All chemical shieldings were referred with respect to $VOCl_3$ as an external standard. Computer simulations of ^{51}V statistic and MAS NMR spectra were made as described in [11].

3. Results and discussion

The reaction products obtained are amidopyrazine (AP), cyanopyrazine (CP), pyrazine (P) and carbon oxides (CO_x). Chromatography shows that there are no nitrogen oxides (NO_x) among the reaction products.

Transformations of MP into reaction products can be ascribed as follows:

$$C_5H_6N_2 \xrightarrow{NH_3,\,O_2} C_5H_5N_3O + 2H_2O \tag{1}$$

$$C_5H_6N_2 \xrightarrow{NH_3,\,O_2} C_5H_3N_3 + 3H_2O \tag{2}$$

$$C_5H_6N_2 \xrightarrow{O_2} C_4H_4N_2 + CO_x + H_2O \tag{3}$$

$$C_5H_6N_2 \xrightarrow{O_2} 5CO_x + 3H_2O + N_2 \tag{4}$$

Here Eqs. (1) and (2) represents ammoxidation, Eq. (3) represents oxidative dealkylation and Eq. (4) for complete oxidation of MP.

Selectivities to AP, CP, P and CO_x were calculated as:

$$S_{AP}\,(\%) = \left[\frac{A_{AP}}{A^0_{MP} - A_{MP}}\right] \times 100 \tag{5}$$

$$S_{CP}\,(\%) = \left[\frac{A_{CP}}{A^0_{MP} - A_{MP}}\right] \times 100 \tag{6}$$

$$S_{P}\,(\%) = \frac{4}{5}\left[\frac{A_{P}}{A^0_{MP} - A_{MP}}\right] \times 100 \tag{7}$$

$$S_{CO_x}\,(\%) = \frac{1}{5}\left[\frac{A_{CO_x}}{A^0_{MP} - A_{MP}}\right] \times 100 \tag{8}$$

Here A^0_{MP} is the inlet MP content (mol/l) and A_{MP}, A_{AP}, A_{CP}, A_P and A_{CO_x} are the outlet methylpyrazine, amidopyrazine, cyanopyrazine, pyrazine and carbon oxides content (mol/l), respectively.

For all of the binary vanadium–titanium catalysts the main selective product is AP unlike vanadium–antimonium catalysts described previously [10], where CP is the main one. P and CO_x are by-products with the relationship between their selectivities close to four at all temperatures examined and regardless of the catalysts composition. According to reaction (3) and Eqs. (7) and (8) as well as analysis carried out in [10], relationship of this kind results from the proceeding of oxidative dealkylation of MP and its selective derivations — AP and CP without destruction of the heteroaromatic ring.

The selectivities to reaction products versus MP conversion at 270°C are plotted in Fig. 1 for the sample of composition 20 V_2O_5–80 TiO_2 (wt.%). The selectivities to sum AP and CP is high (88–90%) at the conversion ranging between 10 and 70%. Extrapolation of selectivity dependencies to zeroth MP conversion enables to estimate the proportion of reaction products formed from MP by the parallel route. Further increase of the conversion results in a decrease of the selectivities to AP and CP with the latter is less sharp. At the same time selectivities to by-products — P and CO_x increases. This is indicative of the overoxidation of selective product.

High temperature hydration of CP was examined as a possibility for the formation of AP by the consecutive route. Under the conditions close to those of ammoxidation of MP (temperature, contact time and composition of inlet reaction mixture) CP converts into AP

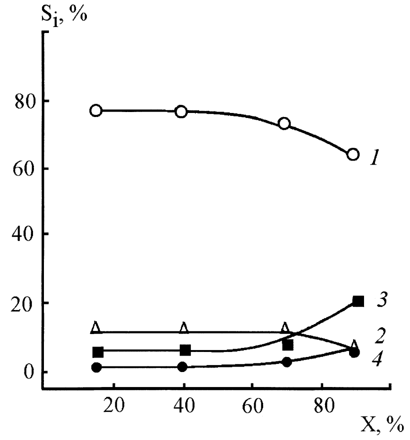
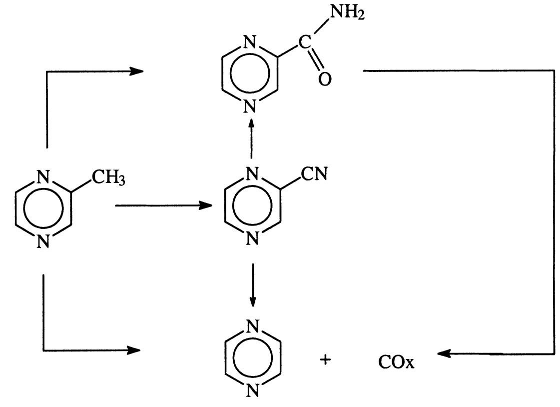


Fig. 1. Selectivities to (1) amidopyrazine, (2) cyanopyrazine, (3) pyrazine and (4) carbon oxides versus MP conversion at 270°C.



Scheme 1.

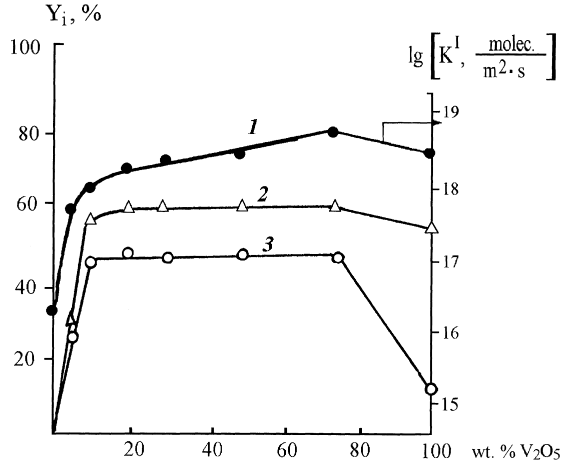


Fig. 2. First-order rate constant of the overall MP conversion (1) at 300°C, maximum yield of the sum amido- and cyanopyrazine (2) and maximum yield of AP (3) versus composition of vanadium–titanium oxide system.

with high selectivity. Thus, it may be concluded that AP is formed immediately from MP and CP under its hydration.

The experimental data obtained permit us to describe MP ammoxidation over V–Ti oxide catalysts by consecutive-parallel network:

Scheme 1 differs from that the one given earlier for oxide V–Sb [10] as well as PMo and mixed PMoV heteropoly acids and their salts [12]. With V–Ti–O catalysts, besides the formation of the new selective product, AP, the process is free of heteroaromatic ring destruction, i.e., reaction (4) does not proceed unless carbon oxides are formed during the oxidative dealkylation both MP and selective products — AP and CP. Similarly, notice that side-reaction in ammoxidation of 2-picoline over V–Ti–O catalysts is its dealkylation [6,13].

The main selective product with individual V_2O_5 is CP, AP is formed in less quantity. At the temperature examined relation between correspondent selectivities (S_{CP}/S_{AP}) changes in the range from 2/1 to 3/1. Carbon oxides ($S_{CO_2} > S_{CO}$) are formed not only under oxidative dealkylation, but at full destruction of MP and heteroaromatic products.

Individual TiO_2 (anatase) practically conducts the process of destruction of MP to P and CO_x only. Judging from the relationship between their selectivities ($S_P/S_{CO_x} \approx 4$), oxidative dealkylation proceeds in the main.

In order to compare the catalytic properties of vanadium–titanium oxide system, the first-order rate constant of the overall MP conversion and maximum yield of AP and AP+CP obtained under experimental conditions were used. Fig. 2 presents these data.

TiO_2 (anatase) reveals a low selectivity and activity in the MP ammoxidation. Introduction of vanadium results in significant increase of activity and production of selective products — AP and CP. Furthermore, activity increases monotonically with subsequent growth of vanadium content up to 75 wt.%. Maximum yield to AP+CP, ~60%, was observed for the catalysts containing 10–75 wt.% V_2O_5. V_2O_5 is somewhat less active and is especially selective to AP.

From XRD data [14], in V–Ti–O system, the only individual vanadium and titanium oxide phases are fixed. No mixed V–Ti–O phase was revealed. However, the catalytic properties of the samples differ essentially from those of individual oxides involved. This is indicative of interaction between V_2O_5 and TiO_2 in the binary system to form new centers which are active in MP ammoxidation. Observed course of the dependencies of the activity and yield to selective products with the increasing of V/Ti relation in the samples can be due to the presence of active centers with identical nature, but different content.

Investigation by the differential dissolution (DD) technique of the interaction of vanadium and titanium in the samples before [14] and after [15] use in MP ammoxidation has shown that vanadium exists in two

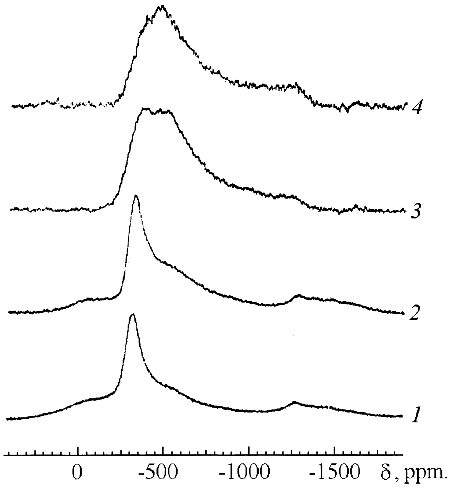


Fig. 3. ^{51}V NMR spectra of the catalysts containing 30 (1), 20 (20), 10 (3) and 5 wt.% V_2O_5.

forms: free vanadium as V_2O_5 and strongly bounded with TiO_2 as doped anatase. Increase of vanadium content in the samples is accompanied by growth of the quantity of both these forms. In this case the amount of V_2O_5 phase increases, while that of doped anatase phase decreases.

To characterize the local environment of vanadium in the catalysts, we have used NMR ^{51}V spectroscopy. Fig. 3 shows ^{51}V spectra of the binary samples after treating in the reaction of MP ammoxidation.

The spectrum of the sample containing 30 wt.% V_2O_5 is typical to V^{5+} in distorted octahedral coordination peculiar to bulk V_2O_5 [16]. In the spectrum of the sample containing 20 wt.% V_2O_5 a slight shoulder at about −500 ppm appears additionally. Intensity of this shoulder increases with vanadium content. Comparison of the NMR ^{51}V and DD data permits to assume that the shoulder at about −500 ppm could be attributed to vanadium strongly bounded with anatase.

Based on DD data we have prepared a sample consisting of the only phase — TiO_2 with strongly bound vanadium involved. To remove V_2O_5 phase the catalyst sample (20 V_2O_5–80 TiO_2 (wt.%)) was repeatedly washed in diluted HNO_3 at ambient temperature and then in H_2O until pH=7 of the solution was achieved. After this procedure sample was dried and calcined in air at 300°C.

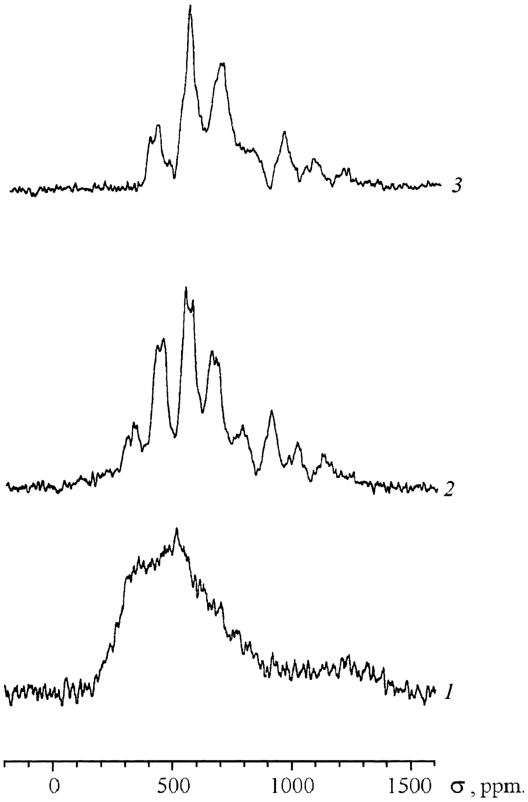


Fig. 4. Static ^{51}V (1) and MAS NMR spectra recorded at different spinning rate — 12.2 (2) and 14.1 kHz (3) of the “washed” sample.

Fig. 4 shows both ^{51}V static and MAS NMR spectra. Simultaneous analysis of ^{51}V static and MAS spectra recorded at different spinning rate was made according to the method described in [11]. Automatic fitting of the quadrupole and chemical shielding anisotropy (CSA) tensor parameters permitted us to extract all NMR parameters with a reasonable accuracy. Table 1 lists these parameters.

It is evident from data obtained that NMR parameters are different from those for bulk V_2O_5 mainly by the large value of quadrupole coupling constant (C_Q) and asymmetry parameter (η_Q). At the same time CSA tensor principal components are practically the same as were reported previously for V_2O_5 single crystal and powders [16]. So, data obtained indicate that the local environment of vanadium strongly bound with TiO_2 is very close to that for bulk V_2O_5 — distorted octahedron. The large value of C_Q is caused by the significant electric field gradient tensor at vanadium nucleus position. It may be due to considerable distortion of the second and higher coordination spheres of

Table 1
^{51}V NMR parameters strongly bonded TiO_2 V^{5+} species in V–Ti–O catalyst of the composition 20 V_2O_5–80 TiO_2 (wt.%) and literature data for bulk V_2O_5 [16][a]

Sample	C_Q (MHr)	η_Q	η_σ	σ_{iso} (ppm)	σ_1 (ppm)	σ_2 (ppm)	σ_3 (ppm)
V–Ti–O	14.711	0.589	0.0177	611.3	280.5	292.0	1261.3
V_2O_5	0.811	0.04	0.15	609	252	340	1229

[a] C_Q, η_Q: quadrupole tensor parameters; η_σ, σ_{iso}, σ_1, σ_2, σ_3: chemical shielding anisotropy tensor parameters.

V^{5+} ions possibly resulting from interaction of vanadium with support to form the V–O–Ti bonds significantly different from V–O–V ones, e.g. at V^{5+} ions incorporation into the anatase lattice [17] or with formation of the regular surface stacking of V_2O_5 and TiO_2 crystallites [18]. Our calorimetric data on high temperature reduction by CO and O_2 adsorption obtained earlier [19] may serve as experimental verification of mixed bonds formation. It has been shown that binary vanadium–titanium catalysts significantly differ in bond energy, homogeneity of surface oxygen and mobility of the bulk from those of individual V_2O_5 and TiO_2.

Catalytic properties of two-phase and monophase samples (doped anatase) were compared to elucidate the role of these phases. Catalytic data obtained are presented in Table 2.

Selectivities for both samples are seen to be closely allied at the temperature studied, however, activity of the “washed” sample is higher. Apparently, the excess of V_2O_5 blocks part of the active sites. Similar proposal was made in [5] for ammoxidation of 3-picoline. Contribution of bulk vanadia in catalytic properties of the binary catalysts is small probably due to its low specific surface (S=4 m^2/g). Values of activation energy of the overall MP conversion are presented in Table 3.

Table 3
Activation energy of overall MP conversion

Content of V_2O_5 (wt.%)	E_a (kcal/mol)
0	19.0
5	19.0
10	16.0
20	16.0
20[a]	16.3
30	16.5
50	16.5
75	16.5
100	25.0

[a] “Washed” sample.

One can see that values of activation energy with binary samples containing $\geq$10 wt.% V_2O_5 are practically the same, and differ significantly from that characteristic for bulk V_2O_5. This result may also be indicative of a small contribution of V_2O_5 in the catalytic properties.

Thus, from the data obtained we conclude that anatase doped with vanadium is the active phase in MP ammoxidation. The active sites of binary catalysts

Table 2
Catalytic properties of V–Ti–O catalysts in MP ammoxidation

Sample	S_{sp} (m^2/g)	T_r (°C)	τ (s)	X (%)	Selectivity (%)				$W\times10^9$ (mol/m^2 s)
					CO_x	P	CP	AP	
1[a]	35	280	1.60	57.0	0.8	3.9	16.9	75.2	6.5
		300	0.86	57.3	0.9	4.5	22.3	72.5	10.3
		320	0.62	61.3	3.3	9.0	30.2	57.4	17.1
2[b]	36	280	1.42	56.2	1.0	4.3	16.3	74.4	7.9
		300	0.86	62.2	1.3	5.2	31.2	71.3	14.7
		320	0.58	62.5	4.0	9.9	28.7	56.5	26.1

[a] Two-phase sample of the composition 20 V_2O_5–80 TiO_2 (wt.%).
[b] Monophase “washed” sample.

include V^{5+} cations with distorted octahedral coordination strongly bound with titania apparently owing to the formation of V–O–Ti bonds. The higher the amount of these sites in the vanadium content of the samples, the higher is their activity.

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