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In situ FTIR study of β-picoline transformations on V–Ti–O catalysts

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ABSTRACT

Surface complexes formed during β-picoline transformations on V–Ti–O catalysts in the temperature range of 120–300 °C were studied using *in situ* FTIR spectroscopy. Two vanadia–titania catalysts with several kinds of vanadia species were used in experiments. FTIR spectra have revealed differences in composition of surface complexes under different coverage, which could be related to different ways of transformations of intermediate pyridine-3-carbaldehyde.

1. Introduction

Vanadia–titania catalysts are active and selective in oxidation of many hydrocarbons including 3-methylpyridine (β-picoline) [1]. Though the model of the mechanism of nicotinic acid formation has been offered [2,3], many details are still unclear, for example the role of vanadia species. It is well known that catalytic behavior of V–Ti–O catalysts strongly depends upon the nature of the surface vanadia species [4–8]. Srinivas et al. [9] supposed that VO_x species were active in β-picoline oxidation. However, the problem was not investigated systematically.

We have used *in situ* infrared spectroscopy as one of the most powerful tools to investigate surface complexes formed during the reaction. The aim of the work is to study the effect of the surface vanadia species on the transformation of β-picoline on vanadia–titania catalysts.

2. Experimental

2.1. Catalyst preparation

Vanadia–titania catalysts were prepared by impregnation of TiO_2 (anatase) by solution of vanadium oxalate followed by drying in air and calcination in air at 450 °C for 4 h (V–Ti). Then the sample was washed with 10% water solution of nitric acid to remove the bulk V_2O_5 phase (V–Ti_m) and calcinated once more at 450 °C for 4 h [3]. Physicochemical characteristics of the samples are given in Table 1.

2.2. FTIR experiments

In situ FTIR spectroscopy experiments were performed in a flow IR cell-reactor with a Bomem MB-102 FTIR spectrometer in the temperature range of 120–300 °C. The catalyst powder (35–50 mg) was pressed into a self-supported 1 cm × 3 cm wafer. The wafer was mounted into a quartz IR cell-reactor with a CaF_2 window and activated in air flow (50 cm^3/min) at 300 °C for 60 min. Then the temperature was decreased to desired one and experiments were carried out. 0.1 or 1 μl of β-picoline (Aldrich Chemical Company Inc., 99%) was injected by microsyringe into air flowing through the reactor cell.

The adsorption of $CDCl_3$ was used to test a basic cites of the catalysts. The wafer of the catalyst was placed in IR cell and evacuated (10^{-2} Torr) at 350 °C for 1 h. $CDCl_3$ was adsorbed onto catalysts from the vapor phase at 20 °C. FTIR spectra were recorded for 2 min after $CDCl_3$ admission.

The background spectra of samples were obtained at each temperature for their further subtraction.

2.3. Ab initio calculations

Non-empirical quantum chemical calculation of the equilibrium geometry and vibrational spectra of possible surface complexes of β-picoline was performed using Gaussian-98 [10] in the density functional theory (DFT) B3LYP approximation. A standard set of basis functions 6–31G (d,p) was used. The original program developed in the laboratory of quantum chemistry of Boreskov

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Table 1
Physicochemical characteristics of the catalysts.

Catalyst	V_2O_5 (% wt)	S_{BET} (m^2/g)	Surface density (at(V)/nm^2)	Phase composition
V–Ti	20.0	53	24.4	V_2O_5, TiO_2 (anatase)
V–Ti_m	7.3	54	8.9	TiO_2, anatase

Institute of Catalysis was used for the frequencies assignment [11].

3. Results and discussion

Fig. 1 shows FTIR spectra of the samples in the range of 4000–2400 cm^{-1} before β-picoline adsorption. The band at ~3650 cm^{-1} due to stretching mode of OH-group is observed in the spectra of both V–Ti and V–Ti_m catalysts. The surface concentration of OH-group in monolayer V–Ti_m catalyst is considerably higher, as the band is considerably more intensive in the spectrum of monolayer catalyst (Fig. 1).

FTIR spectra of surface complexes of β-picoline registered at 120 °C are given in Fig. 2a. The bands of 3-methylpyridinium ions coordinated to Bronsted acid sites 1634 (ν(CC, CN) – 8a, 1612 ν(CC, CN) – 8b, 1551 ν(CC, CN) – 19a and 1475 cm^{-1} ν(CC, CN) – 19b) [3,12] are mainly observed in the spectra of V–Ti_m (spectrum 1) and V–Ti (spectrum 2) catalysts. The bands assigned to stretching modes of CH_3-group (2933 $\nu_{as}(CH_3)$ and 2885 $\nu_s(CH_3)$ cm^{-1}) and CH-groups of pyridinic ring (3125, 3083, 3042 cm^{-1}) are observed in high-frequency range of the spectra.

Formation of 3-methylpyridinium ions is accompanied by decrease of the intensity of the band at ~3650 cm^{-1} due to ν(OH) mode (Fig. 2b). Though intensities of the bands assigned to 3-methylpyridinium ions are equal for both catalysts, changes of intensity of the band ν(OH) differ. For V–Ti_m catalyst noticeably more decrease of the intensity of the band is observed (Fig. 2b, spectra 1 and 2). Such differences could be due to participation of OH-groups in formation of another surface species. In fact, rather weak bands of β-picoline coordinatively bounded to Lewis acid sites (1583 (CC, CN) – 8b and 1427 cm^{-1} (CC, CN) – 19b) are also present in the spectra of both catalysts (Fig. 2a, spectra 1, 2 and the inset). The bands of the complex with Lewis sites are more intensive in the spectrum of the V–Ti_m catalyst (Fig. 2a, spectra 1, 2 and the inset). We believe that part of hydroxyl groups has basic nature and is substituted by molecules of β-picoline during its adsorption with formation of coordinatively bounded surface complexes. The higher concentration of the complex with Lewis sites on the surface of monolayer catalyst as compared with two-phase one is associated with the larger amount of basic OH-groups. The analogous effect was observed previously in the case of β-picoline adsorption on TiO_2 [3].The increase of basic sites amount for monolayer catalyst was verified by $CDCl_3$ adsorption (Fig. 3). $CDCl_3$ adsorption on V–Ti_m catalyst results in appearance of band at 2254 cm^{-1} due to ν(CD) mode in the FTIR spectrum. In the case of V–Ti catalyst ν(CD) band is shifted to high frequency region. It signifies that the basic cites of monolayer catalyst are stronger. Note also that the

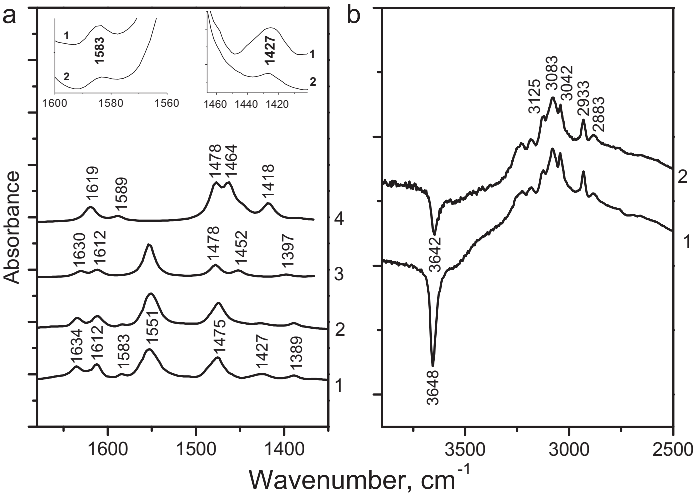

Fig. 2. Experimental and calculated FTIR spectra of surface complexes of β-picoline in the spectral range 1670–1350 cm^{-1} (a) and 3900–2500 cm^{-1} (b) 1 – experimental spectrum V–Ti_m, 2 – experimental spectrum V–Ti, 3 – theoretical spectrum of 3-methylpyridinium ion, 4-theoretical spectrum of complex with BF_3 (calculated spectra were scaled by the factor of 0.9690, for experimental spectra the background spectra have been subtracted).

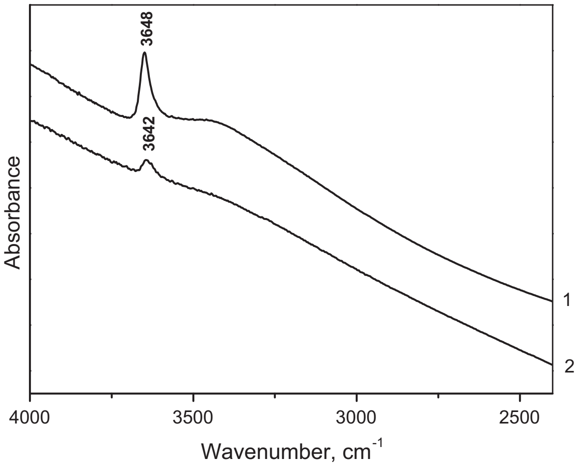

Fig. 1. FTIR spectra of V–Ti_m (1) and V–Ti (2) catalysts before injection of β-picoline in the spectral range 4000–2400 cm^{-1}.

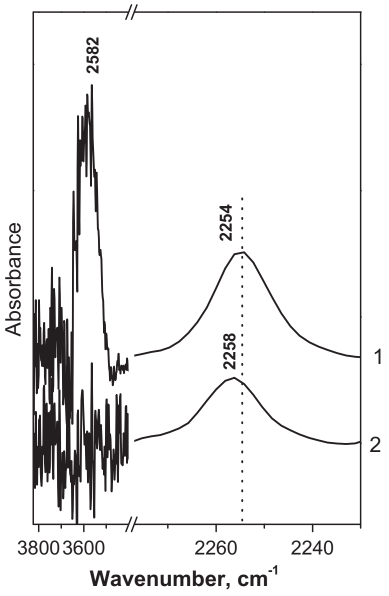

Fig. 3. FTIR spectra of V–Ti_m (1) and V–Ti (2) catalysts after $CDCl_3$ adsorption (the background spectra have been subtracted).

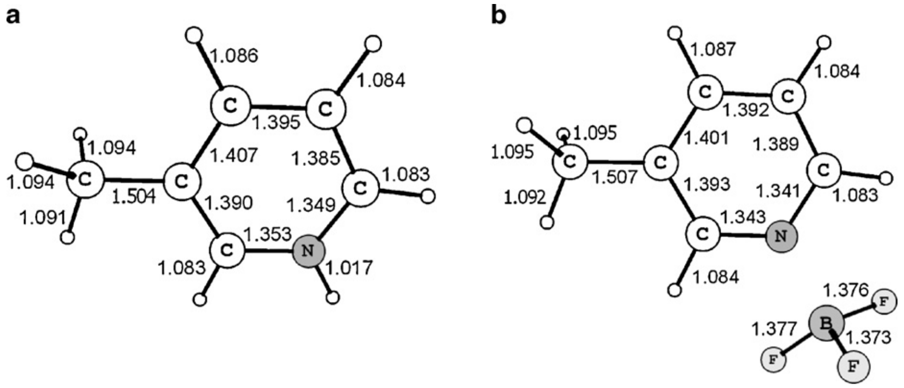

Fig. 4. Theoretical models of 3-methylpyridium ion (a) and β-picoline complex with BF_3 (b).

intensity of the band and therefore concentration of basic cites is about twofold higher in the case of monolayer catalyst. Besides, only in the case of monolayer catalyst $CDCl_3$ adsorption results in low frequency shift of ν(OH) vibration (from 3648 to 3582 cm^{-1}). Thus enhanced basicity of monolayer catalyst is at least partially related to basic hydroxyls.

Theoretical spectra of 3-methylpyridinium ion and the complex with the BF_3 which is the model of catalyst's Lewis acid sites have also been calculated (Fig. 2, spectra 3 and 4). Fig. 4 shows theoretical models and their main geometrical parameters. One can see that theoretical and experimental spectra are in good agreement (Fig. 2a).

The increase of adsorption temperature results in significant changes in IR spectra (Fig. 5a and b). In the case of two-phase V–Ti catalyst the intensity of bands assigned to CH_3-group stretching vibrations decreases upon heating from 120 to 260 °C while the intensity and the position of ν(CH) bands of the pyridine ring do not change (Fig. 5a, spectra 1–4). Hence, it could be assumed that oxidation of CH_3-group proceeds and the ring is still intact. In the temperature range of 160–180 °C the bands at 1720 and 1660 cm^{-1} due to ν(C=O) mode of aldehyde-like surface complexes are observed. Further increase of the temperature leads to appearing of strong bands of surface nicotinates at 1562 cm^{-1} (ν_{as}(COO)) and at 1412 cm^{-1} (ν_s(COO)). At actual reaction temperatures (260–280 °C) the broad bands at 1770–1750 and 1700–1650 cm^{-1} due to ν(C=O) modes of gaseous and molecular adsorbed nicotinic acid respectively appeared. Similar transformations were observed in earlier experiments using two-phase V–Ti–O catalyst with less specific surface area ($S \sim 25\ m^2/g$) [13].

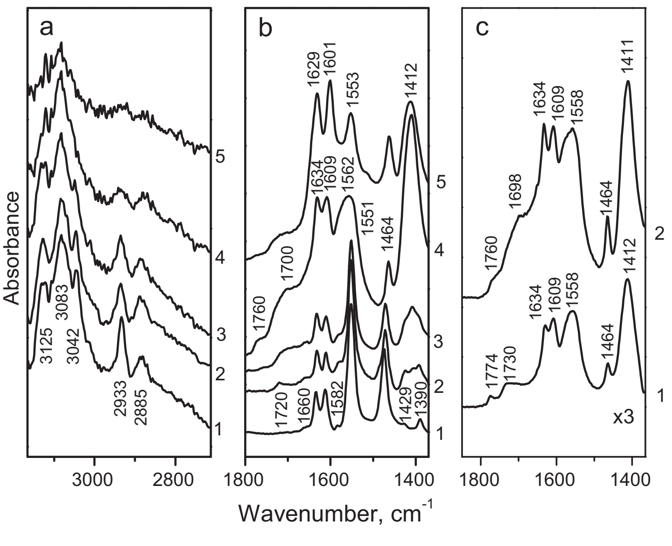

Fig. 5. FTIR spectra of β-picoline transformations at 120–300 °C on V–Ti catalyst. (a and b) FTIR spectra for adsorption 0.2 μl of β-picoline on V–Ti at 120 (1), 160 (2), 200 (3), 260 (4) and 300 °C (5), (c) FTIR spectra after injection 0.2 (1) and 1 (2) μl of β-picoline at 260 °C (the background spectra have been subtracted).

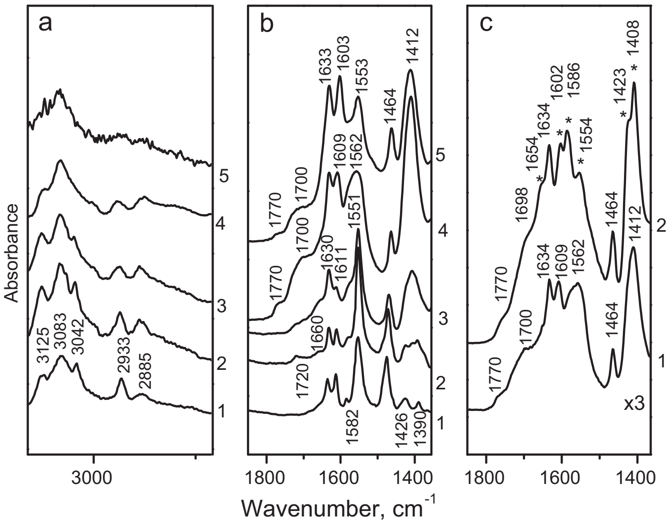

Fig. 6. FTIR spectra of β-picoline transformations at 120–300 °C on V–Ti_m catalyst. (a and b) FTIR spectra for adsorption 0.2 μl β-picoline at 120 (1), 160 (2), 200 (3), 260 (4) and 300 °C (5), (c) FTIR spectra after injection 0.2 (1) and 1 (2) μl of β-picoline at 260 °C (the background spectra have been subtracted). The bands due to side-product are marked by asterisk.

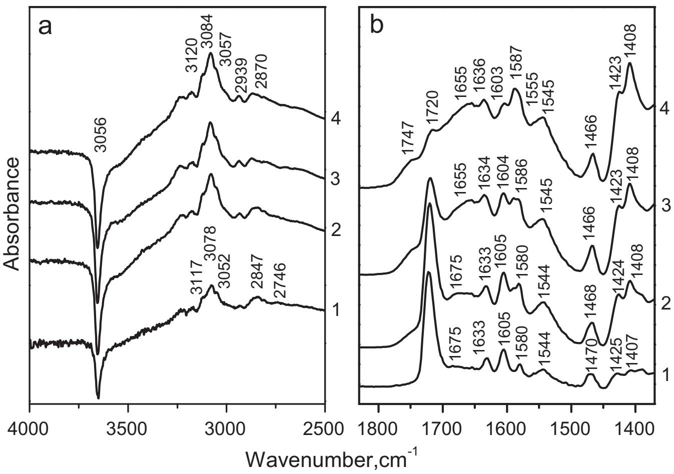

Fig. 7. FTIR spectra of pyridine-3-carbaldehyde adsorbed on V–Ti_m catalyst at 160 °C: 1 min (1), 10 min (2), 15 min (3), 20 min after injection (4).

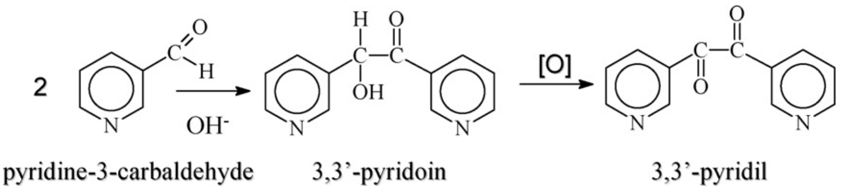

Fig. 8. The scheme of supposed alternative way of pyridine-3-carbaldehyde transformation; OH^- is the nucleophile and [O] is the oxidizing agent.

In the temperature range of 260–300 °C bands corresponding to modes of $\nu_{as}(COO)$, $\nu_s(COO)$, $\nu(C{=}O)$ and of $\nu(CH)$, $\nu(CC)$ of heterocyclic ring decrease and new bands at 1629, 1601 and 1553 cm^{-1} due to $\nu_{as}(COO)$ mode of carboxylates appeared (Fig. 5a and b, spectrum 5). We suggest that these carboxylates are intermediates in deep oxidation of β-picoline [15].

In the case of monolayer V–Ti_m catalyst spectra registered at actual reaction temperatures (260–280 °C) depend significantly on the amount of β-picoline adsorbed (Fig. 6c). At low coverage with surface complexes spectra registered are very similar to spectra collected on two-phase catalyst at the same conditions (Fig. 6a and b, spectra 1–5). Thus, identical sequence of surface species transformation is observed. At the high coverage with surface complexes besides the bands of nicotinate and nicotinic acid the additional bands at 1654, 1602, 1586, 1554, 1423 and 1408 cm^{-1} probably due to ν(CC, CN) of pyridinic ring are present in the spectra registered at 260 °C (Fig. 6c, spectrum 2).

Similar bands were also observed in FTIR spectra of pyridine-3-carbaldehyde adsorbed on the same catalyst even at 160 °C (Fig. 7). After 1 min exposure the bands of molecular absorbed pyridine-3-carbaldehyde 3125, 3083, 3042 ν(CH) ring, 2847 ν(CH) aldehyde, 1720, 1675 ($\nu(C{=}O)$), 1633, 1605, 1580, 1544, 1470 and 1425 cm^{-1} (ν(CC, CN)) are mainly observed. The increase of exposure time results in decrease of the intensity of adsorbed pyridine-3-carbaldehyde bands and bands at 1655, 1636, 1603, 1587, 1555, 1466, 1423 and 1408 cm^{-1} appear and their intensity grows. Thus it could be supposed that appearance of new bands is due to proceeding of alternative way of pyridine-3-carbaldehyde transformation, for example pyridoin condensation and further oxidation of 3,3′-pyridoin (Fig. 8). As the part of OH-groups on the surface of catalyst V–Ti_m is basic, they could play a role of nucleophile in pyridoin condensation. Products of pyridoin condensation were observed earlier in studies of oxidation of picolines on vanadium catalysts in fixed and fluidized beds [14]. Thus the appearance of additional bands in the spectra during adsorbed β-picoline transformation on monolayer catalyst is explained by formation of pyridine-3-carbaldehyde as intermediate product. Contrary to monolayer catalyst, surface coverage does not effect on mechanism of surface complexes transformation in the case of two-phase catalyst (Fig. 5c) because of minor amount of basic hydroxyls (Fig. 1).

4. Conclusions

Adsorption of β-picoline both on monolayer and on two-phase vanadia–titania catalysts results in formation of the same surface species and similar sequence of their transformations. H-bonded 3-methylpyridinium ion is the main form of β-picoline adsorption. Nicotinic acid forms through consecutive transformation of the complex into aldehyde-like and nicotinate complexes. In the case of two-phase catalyst the composition of surface complexes and the sequence of their transformation do not depend on surface coverage.

Contrariwise surface coverage strongly effects on mechanism of surface complexes transformation in the case of monolayer catalyst. At high coverage condensation of pyridine-3-carbaldehyde probably occurs with formation of pyridoin and products of its oxidation. This fact is probably due to higher amount of basic hydroxyls on the surface of monolayer catalyst as compared with two-phase catalyst.

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