

Investigation of the reaction mechanism of methylpyrazine ammoxidation on vanadia–titania catalyst by FTIR *in situ*

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Received 10 April 2006; received in revised form 12 January 2007; accepted 12 January 2007

Available online 20 January 2007

Abstract

The mechanism of methylpyrazine ammoxidation on a vanadia–titania catalyst has been studied by *in situ* FTIR spectroscopy. The structure of surface intermediates has been identified and the sequence of their transformation in the temperature range of 150–230 °C has been ascertained. The interaction of methylpyrazine with catalyst surface includes a consecutive transformation of coordinatively bound methylpyrazine into oxygenated surface compounds, *viz.*, an aldehyde-like complex and an asymmetrical carboxylate. The main reaction product, amidopyrazine, is formed through the interaction of the surface oxyintermediates with adsorbed ammonia species.

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Keywords: Ammoxidation of methylpyrazine; V–Ti–O catalyst; *In situ* FTIR spectroscopy

1. Introduction

Vanadia–titania system is known as effective catalyst for selective oxidation and ammoxidation of aromatic as well as heteroaromatic hydrocarbons [1–5]. The catalytic action of vanadia–titania systems, the structure and reactivity of supported vanadium species are considered in numerous fundamental studies (e.g., review papers [6–8]).

Recently, we have found [9] that vanadia–titania catalysts containing 10–70 wt.% of V₂O₅ are active in ammoxidation of methylpyrazine (MP) at temperatures below 320 °C. These catalysts comprise two phases: V₂O₅ and anatase doped with vanadium. The latter is an active phase of these catalysts, whereas bulk V₂O₅ makes only a small contribution to the catalytic properties. The active sites were shown to include V⁵⁺ cations with distorted octahedral oxygen environment strongly bound with titania due to formation of V–O–Ti bonds.

Unlike another oxide catalysts [10–12], in this particular case the main selective product is amidopyrazine rather than cyanopyrazine. At that, cyanopyrazine was detected in a much smaller amount due to its hydrolysis to amidopyrazine [9].

There are few literature data on the reaction mechanism of methylpyrazine ammoxidation over oxide catalysts. The interaction of methylpyrazine with the surface of individual vanadia and molybdena supported on MgO was studied by IR spectroscopy in [13,14]. A coordinatively bound methylpyrazine was found to form under methylpyrazine adsorption at 80–110 °C, further heating of the samples at 300–400 °C in the presence of gaseous oxygen resulted in the formation of an aldehyde-like complex. The TPD–TPR–MS study of methylpyrazine ammoxidation over Sb–V–Mn–O catalyst [15] showed the nitrogen-containing reaction product (cyanopyrazine) to form through the interaction of adsorbed methylpyrazine with adsorbed rather than gaseous NH₃.

The goal of the present study is to elucidate the mechanism of methylpyrazine ammoxidation over vanadia–titania catalysts. We applied *in situ* IR spectroscopy to characterize the structure of surface complexes formed during the individual adsorption and co-adsorption of the reaction mixture components in the range of 150–230 °C.

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2. Experimental

2.1. Catalyst

Vanadia–titania catalyst 20 V₂O₅–80TiO₂ (wt.%) was prepared by a spray drying of an aqueous suspension of titanium dioxide (anatase) and vanadyl oxalate followed by calcination of the obtained powder in air at 450 °C during 5 h [9]. Then, the sample was washed with diluted nitric acid (1.2 M) to remove the excess of the free V₂O₅ phase. The absence of the free V₂O₅ phase was controlled by both the original method of differential dissolution [16] and ⁵¹V NMR techniques [9]. The content of vanadium in the washed sample was 11% (calculated as wt.% of V₂O₅), and the BET surface area was 36 m²/g. It follows that coverage with vanadium surface species was about twice a monolayer (8 Vat/nm² [17]).

2.2. In situ FTIR study

The adsorption of the reaction mixture components was studied in a static IR cell [18] using IFS-113 Bruker and FTIR-8300 Shimadzu spectrometers (the region of 1000–2000 cm⁻¹ with the spectral resolution 4 cm⁻¹). The catalyst sample was pressed into a self-supported wafer (1 cm × 3 cm in size and ca. 50 mg in weight) and mounted in the IR cell. The sample was pre-treated in atmosphere of air at 450 °C for 30 min, then cooled to room temperature, and evacuated to *P* = 0.1 Torr. The adsorption was carried out at 150 °C. The components (pure MP (*P* = 1 Torr) or mixtures, MP + NH₃ (1:15, *P* = 15 Torr), MP + O₂ (1:10, *P* = 10 Torr), MP + O₂ + NH₃ (1:10:15, *P* = 25 Torr)) were syringe injected by pulses into the IR cell loaded with the catalyst. Then, the temperature was elevated to 230 °C. The intermediate spectra were recorded at 25 °C intervals after achieving the stationary coverage with surface complexes. The background IR spectra of the catalyst were subtracted at each temperature.

3. Results and discussion

IR spectra were used to identify the surface compounds (SC) formed upon adsorption of the components of methylpyrazine ammoxidation reaction mixture in the range of 150–230 °C. The assignment of the absorption bands, the structure, and the temperature range of the SC detection are shown in Table 1.

When methylpyrazine is adsorbed on vanadia–titania catalyst at 150 °C (Fig. 1a, spectrum A), the absorption bands (a.b.) are initially observed at 1166, 1253, 1296, 1404, 1474, 1524, and 1587 cm⁻¹. These bands, being close to the bands of liquid methylpyrazine [19], are characteristic of some transition metal complexes with coordinated methylpyrazine [20–24]. The observed shift of the a.b. of the heteroaromatic ring towards higher frequencies indicates coordination between the heterocyclic compound and the surface Lewis acid sites (L.a.s.). Coordinate bond is formed through the lone-pair donation from one nitrogen atom to vacant d-orbitals of a metal ion, i.e. V⁵⁺. So, the surface complex of coordinatively bound methylpyrazine SC1 is formed.

A longer (over 75 min) adsorption at 150 °C gives rise to a new broad a.b. at 1700 cm⁻¹ (Fig. 1a, spectrum B), which is characteristic of ν(C=O) in aldehydes [25,26]. In addition, the band at 1404 cm⁻¹ is broadened and a low intense band at 1587 cm⁻¹ is split to give two rather intense a.b. at 1579 and 1610 cm⁻¹. The cymbate increase in the intensity of these new bands (at 1700, 1579, and 1610 cm⁻¹) with time allows them to be assigned to a surface aldehyde-like compound SC2. While the ν(C=O) band is shifted only slightly with respect to its position in the spectrum of the free aldehyde [25,26], one can observe a noticeable shifting of the C–C and C–N ring vibrations (Table 1). Thus, it is reasonable to suppose that complex SC2 is bound to the L.a.s. by the nitrogen atom, while a hydrogen bond is formed between oxygen of the CHO-group and the surface Brønsted acid sites.

The elevation of the adsorption temperature over 150 °C leads to a further increase in intensity of a.b. at 1579 and 1610 cm⁻¹ and to the appearance of absorption at 1725–1735 cm⁻¹ and two bands at 1386 and 1263 cm⁻¹ (Fig. 1, spectra C–E). Several a.b. (at 1700 and 1730 cm⁻¹) at the vibration region of the C=O bond may be assigned to the different compounds. With reference to the position of ν(C=O) in pyrazinecarboxylic acid [27] and in surface esters of carboxylic acids [28], the appearance of a.b. at 1730, 1386 and 1263 cm⁻¹ may indicate the formation of a new surface compound SC3. This compound seems to be an asymmetrical carboxylate with the free C=O group. In turn, when pyrazinecarboxylic acid is adsorbed on vanadia–titania catalysts at 175 °C (Fig. 1a, spectrum F), some shift of the position of ν(C=O) towards lower frequencies is observed. Apparently, this is due to the interaction of lone-pair electrons of oxygen atom of the carbonyl group with L.a.s. This fact is an added reason for ascribing the new a.b. at 1730, 1386 and 1263 cm⁻¹ to the asymmetrical carboxylate with the free C=O group. A change in the position of a.b. of the pyrazine ring indicates, as in the case of SC1 and SC2, the coordination of SC3 to the L.a.s. by the nitrogen atom. The use of the experimental static cell with not evacuated gas phase made impossible to follow the transformation of SC2 into SC3 correctly. However, an increase in the intensity of a.b. of SC3 with time may be an argument for such a transformation.

The spectra obtained at the co-adsorption of methylpyrazine and dioxygen are shown in Fig. 1b. These spectra resemble the spectra observed for the individual adsorption of methylpyrazine; however, there is a redistribution of intensity of the a.b. at 1700 and 1730 cm⁻¹ attributed to ν(C=O) of the surface aldehyde and the carboxylate, accordingly. In addition, in the presence of oxygen, in place of the a.b. at 1263 and 1296 cm⁻¹ we have fixed one broad a.b. at 1294 cm⁻¹. Thus, the same three surface complexes are formed both at adsorption of methylpyrazine and at co-adsorption of methylpyrazine and oxygen, viz., coordinatively bound methylpyrazine (SC1), surface aldehyde (SC2) and carboxylate (SC3).

Note that toluene, when being adsorbed on the monolayer vanadium–titanium oxide catalysts at 150 to 300 °C, also interacts with oxygen of the catalyst to produce oxyintermediates such as surface benzaldehyde and benzoate [29,30]. Subsequent treatment with oxygen at low temperature (≤150 °C) was shown

Table 1
IR-spectroscopy data for the surface complexes (SC) formed during adsorption of the components of the methylpyrazine ammoxidation reaction mixture over vanadia–titania catalyst

Sign	Structure ^a	SC	Assignment	C ₅ H ₆ N ₂ (liquid) [19]	C ₅ H ₄ N ₂ O ₂ (solid) [27]	C ₅ H ₅ N ₃ O (solid) [31]	T (°C) ^b
SC1		1166	Ring	1155			150
		1253	$\nu(\text{CX})$	1250			
		1296	$\delta(\text{CH})$	1303			
			$\delta_s(\text{CH}_3)$	1376			
		1404	$\nu(\text{CC}, \text{CN})$	1399			
			$\delta_{\text{as}}(\text{CH}_3)$	1446			
		1474	$\nu(\text{CC}, \text{CN})$	1476			
SC2		1166	Ring				150–230
		1255	$\nu(\text{CX})$				
		1296	$\delta(\text{CH})$				
		1409	$\nu(\text{CC}, \text{CN})$				
		1476	$\nu(\text{CC}, \text{CN})$				
		1524	$\nu(\text{CC})$				
		1579	$\nu(\text{CC})$				
1610	$\nu(\text{CC})$						
1700	$\nu(\text{C=O})$						
SC3		1166	Ring		1150		175–230
			Ring		1170		
		1263	$\nu(\text{CX})$		1220		
		1386	$\nu(\text{C-O})$		1310		
		1476	$\nu(\text{CC}, \text{CN})$		1390		
		1524	$\nu(\text{CC}, \text{CN})$				
		1579	$\nu(\text{CC})$		1530		
1610	$\nu(\text{CC})$						
1730	$\nu(\text{C=O})$		1720				
SC4		1156	Ring			1175	150–230
		1320	$\delta(\text{CH})$			1316	
		1390	$\nu(\text{C-NH}_2)$			1385	
		1410	$\nu(\text{CC}, \text{CN})$			1443	
		1452	$\nu(\text{CC})$			1530	
		1577	$\nu(\text{CC})$			1589	
		1605	$\delta(\text{NH}_2)$			1610	
1665	$\nu(\text{C=O})$			1710			

^a Vⁿ⁺ is an oxidized vanadium cation ($n=5$); V^{m+} is a reduced vanadium cation ($m=3-4$).

^b T is the temperature range in which the respective SC are detected.

to have only a slight effect. A more complicated picture was observed at elevated temperature (about 300 °C), *viz.*, along with the presence of at least two types of carboxylates, there were a.b. characteristic of cyclic anhydrides [29].

At the co-adsorption of methylpyrazine and ammonia at 150 °C, a.b. of complex SC1 and an intense a.b. at 1440 cm⁻¹ related to $\delta_{\text{as}} \text{NH}_4^+$ [25] are only observed in the spectrum (Fig. 2a, spectrum A). Note that the adsorption of ammonia on vanadia–titania catalysts has been the object of a number of papers [32–35]. It was found that ammonia is adsorbed both as NH₄⁺ and molecular ammonia coordinatively bound with L.a.s. The bands characteristic of the coordinatively bound ammonia at 1590–1620 cm⁻¹ (δ_{as}) and 1200–1280 cm⁻¹ (δ_s) [25] are overlapped with a.b. of SC1. A longer (75 min) adsorption at a higher temperature results in a considerable decrease in the intensity of a.b. at 1440 cm⁻¹, shifting and splitting the bands at 1404 cm⁻¹ (to 1386 and 1410 cm⁻¹) and 1587 cm⁻¹ (to 1577 and 1605 cm⁻¹), and the appearance of a new intense

a.b. at 1665 cm⁻¹ (Fig. 2a, spectra B and C–E). In the temperature range of 200–230 °C, the spectra (Fig. 2a, spectra D and E) are close to the spectrum of amidopyrazine (Table 1). However, in the present case, the band related to stretching vibrations of C=O in amide group is shifted to the low-frequency region (from 1710 to 1665 cm⁻¹) and a.b. of the ring are shifted to the high-frequency region. All the above indicates that the surface amidopyrazine-like complex SC4 is formed, wherein the amidopyrazine-to-surface bonding by oxygen of the amide group and additional coordination by the nitrogen atom of the ring occurs. Such is indeed the case, when amidopyrazine is being adsorbed on vanadia–titania catalysts at 175 °C (Fig. 2a, spectrum F). The similar transformations are described for amidopyrazine complexes with salts of transition metals [36,37].

Hence, one can conclude that when methylpyrazine and ammonia are co-adsorbed, the surface complex SC1 interacts with oxygen of the catalyst and adsorbed ammonia to produce surface amidopyrazine SC4. The latter is coordinatively bound

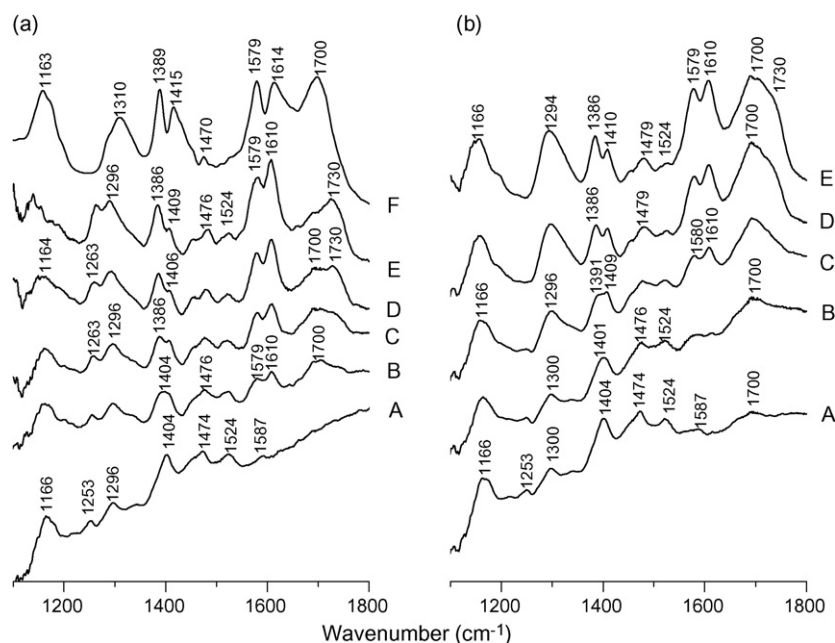


Fig. 1. FTIR spectra of the surface species after exposure of vanadia–titania catalyst in (a) methylpyrazine at different temperatures: 150 °C (A), 150 °C after 75 min exposure (B), 175 °C (C), 200 °C (D), and 230 °C (E). The spectrum obtained at adsorption of pyrazinecarboxylic acid at 175 °C (F); (b) methylpyrazine + dioxygen mixture at different temperatures: 150 °C (A), 150 °C after 75 min exposure (B), 175 °C (C), 200 °C (D), and 230 °C (E). Except for spectra A, B and F, exposure time at the given temperature was 30 min.

with L.a.s. by nitrogen of the ring and carbonylic oxygen of the amide group.

The spectra obtained at the co-adsorption of methylpyrazine, ammonia and dioxygen are shown in Fig. 2b. They resemble the spectra observed for the adsorption from the above discussed oxygen-free mixture, but the most intense band related to C=O vibration of the amide group (1670 cm^{-1}) appears in the spectrum even at 150 °C.

To elucidate the role of oxygen-containing complexes SC2 and SC3 in the formation of amidopyrazine, the ammonia adsorption was studied with the sample pretreated in a mixture of methylpyrazine and oxygen at 175 °C. After adsorption of ammonia at 150 °C, the temperature was then elevated up to 230 °C. The results are illustrated in Fig. 3a.

The absorption bands characteristic of SC2 (at 1166, 1300, 1409, 1476, 1579, 1610, and 1700 cm^{-1}) and SC3 (at 1166,

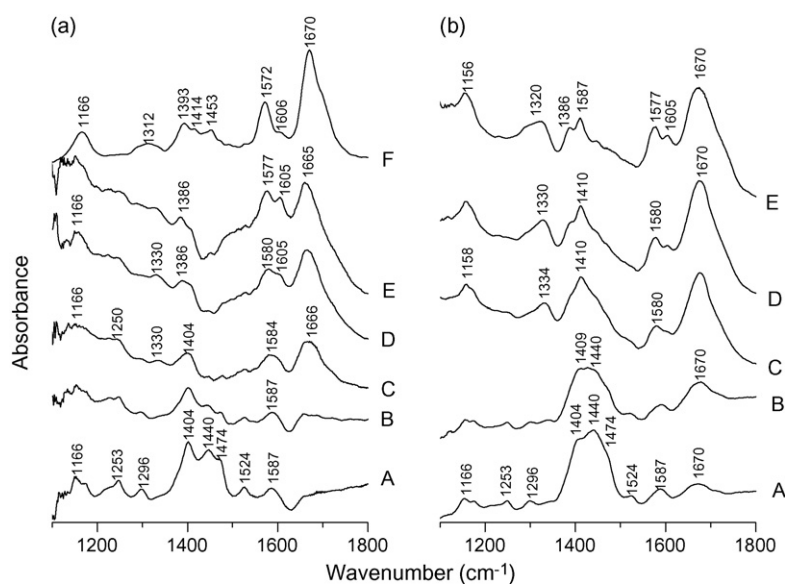


Fig. 2. FTIR spectra of the surface species after exposure of vanadia–titania catalyst in (a) methylpyrazine + ammonia mixture at different temperatures: 150 °C (A), 150 °C after 75 min exposure (B), 175 °C (C), 200 °C (D), and 230 °C (E). The spectrum obtained at adsorption of amidopyrazine at 175 °C (F); (b) methylpyrazine + ammonia + dioxygen at different temperatures: 150 °C (A), 150 °C after 75 min exposure (B), 175 °C (C), 200 °C (D), and 230 °C (E). Except for spectra A, B and F, exposure time at the given temperature was 30 min.

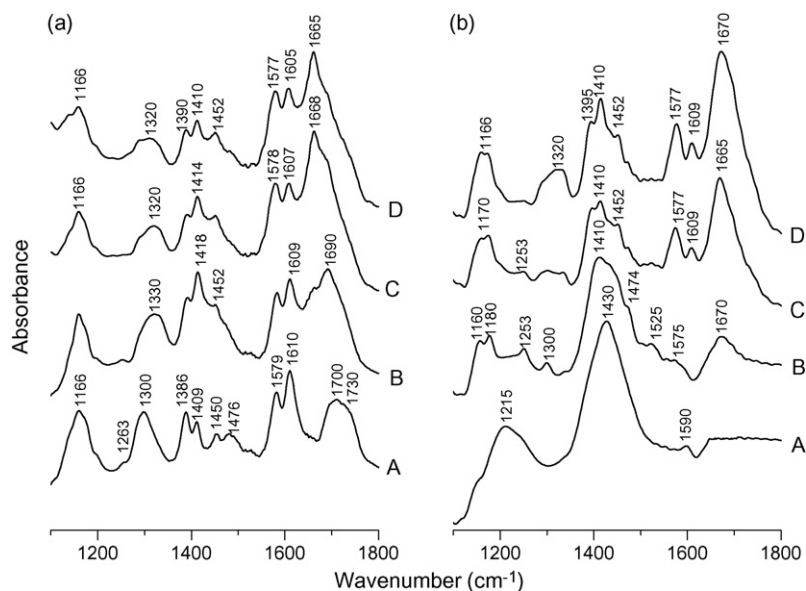


Fig. 3. FTIR spectra of the surface species after exposure of vanadia–titania catalyst in (a) methylpyrazine + dioxygen at 175 °C (A) and that with the consecutive injection of ammonia at temperatures: 175 °C (B), 200 °C (C), and 230 °C (D); (b) ammonia at 150 °C (A) and that with the consecutive injection of methylpyrazine at 150 °C (B) and 230 °C (C), and that with the consecutive injection of dioxygen at 230 °C (D). Exposure time at the given temperature was 30 min.

1263, 1386, 1476, 1579, 1610, and 1730 cm^{-1}) are observed in the spectrum obtained at the co-adsorption of methylpyrazine and dioxygen (Fig. 3a, spectrum A). When ammonia is additionally fed to the IR-cell, an a.b. appears at 1690 cm^{-1} along with two intense a.b. at 1418 and 1330 cm^{-1} , which are assigned to the $\delta_{\text{as}} \text{NH}_4^+$ and $\delta_{\text{s}} \text{NH}_3$ (Fig. 3, spectrum B). As the temperature rises, the a.b. at 1690 cm^{-1} is monotonically shifted to the low-frequency region (down to 1665 cm^{-1}) and increased in intensity (Fig. 3, spectra C and D). The bands at 1700–1730 cm^{-1} characteristic of SC2 and SC3 and a.b. related to adsorbed ammonia species decrease in intensity. Moreover, a shift of a.b. at 1579 and 1610 cm^{-1} to lower frequency and a redistribution of their intensities are observed. The data obtained we suggest to indicate the interaction of SC2 and SC3 with adsorbed ammonia to form surface amidopyrazine SC4.

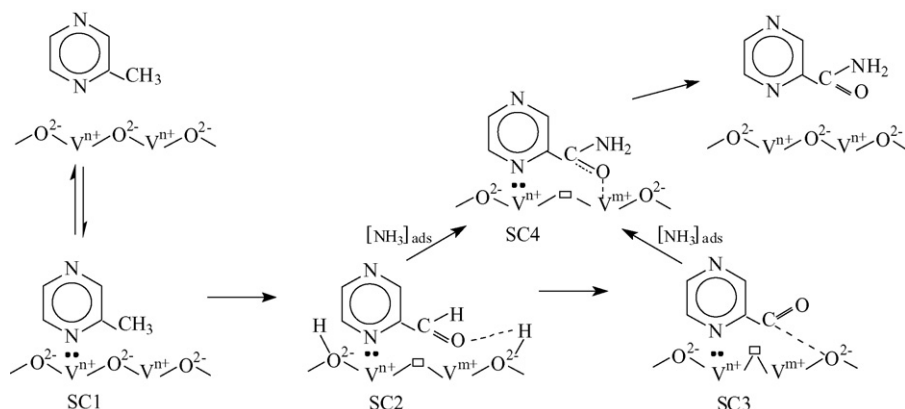
Alternatively, Fig. 3b presents the spectra obtained at the consecutive adsorption of the methylpyrazine and dioxygen mixture on an ammonia covered surface. First, ammonia was adsorbed at room temperature with subsequent evacuation of IR cell, and then the temperature was increased up to 150 °C, whereupon methylpyrazine was adsorbed. The spectrum of adsorbed ammonia (Fig. 3b, spectrum A) consists of intense broad a.b. at 1215 and 1430 cm^{-1} as well as low intense a.b. at 1590, corresponding to the formation of surface NH_4^+ cations and coordinatively bound with L.a.s. molecular ammonia [25]. Subsequent adsorption of methylpyrazine at 150 °C (Fig. 3b, spectrum B) is accompanied by the appearance of the a.b. at 1160, 1180, 1253, 1300, 1410, 1474, 1525 cm^{-1} typical of ring vibrations in SC1 and SC2 complexes as well as the a.b. at 1670 cm^{-1} characteristic of C=O vibration. Temperature elevation up to 230 °C (Fig. 3b, spectrum C) results in the further reduction of intense a.b. of adsorbed ammonia species. At the same time, a.b. at 1166, 1320, 1395, 1410, 1452, 1577, 1609, and 1665 cm^{-1} ascribed to SC4 are observed. At the consecutive adsorption

of dioxygen (Fig. 3b, spectrum D), intensity of the a.b. related to adsorbed ammonia species and SC4 changes solely, *viz.*, the intensity of the former decreases, while the intensity of the latter increases.

At 230 °C, the spectra obtained at both the simultaneous and consecutive (methylpyrazine and dioxygen, then ammonia, as well as ammonia, then methylpyrazine, and then dioxygen) adsorption of the reaction components are similar (see Fig. 2b, spectrum E against Fig. 3a, spectrum D and Fig. 3b, spectrum D). This fact seems to be an evidence of the formation of identical surface compounds, *i.e.*, coordinated amidopyrazine SC4. Note, it has been demonstrated with the ammoxidation of toluene [29,30,38] and xylene isomers [39] over monolayer vanadia supported on TiO_2 [29,30] and Al_2O_3 [38,39], that the formation of related nitriles, like the amide from methylpyrazine in the present case, also occurs upon the interaction of adsorbed ammonia with the oxygen-containing surface intermediates (aldehyde and carboxylate).

The data obtained allow the following pathway to be suggested for the selective transformation of methylpyrazine to amidopyrazine as the main reaction product (Scheme 1):

Methylpyrazine interacts with the L.a.s. of the vanadia–titania catalyst by donating a pair of *n*-electrons from nitrogen of the heteroaromatic ring to form a coordinatively bound complex SC1. The coordination of methylpyrazine favours the activation of the C–H bonds of the substituting group. Its subsequent interaction with oxygen of the catalyst results in the transformation of SC1 to an aldehyde-like surface complex SC2 and an asymmetrical carboxylate SC3. The oxygen-containing complexes SC2 and SC3 are coordinatively bound to the L.a.s. by the nitrogen atom. In the presence of ammonia, these complexes interact with adsorbed ammonia species to form surface amidopyrazine SC4. The latter is coordinatively bound through nitrogen of the ring and oxygen of the –CONH₂ group to the surface L.a.s.



Scheme 1. The main features of the mechanism of the methylpyrazine ammoxidation to amidopyrazine over vanadia–titania catalyst. Details of the evolution O_2 as well as adsorbed NH_3 and H atoms are not shown.

Complex SC3 is a surface pyrazinecarboxylate. Surface carboxylates stabilized on vanadium cations are known as weakly bound intermediates and escape in the form of related acids to the gas phase [40]. However, the methylpyrazine oxidation in the temperature range 250–300 °C gives only the destruction products, *viz.*, pyrazine and carbon oxides. This reaction does not produce pyrazinecarboxylic acid, even though surface carboxylate SC3 exists on the catalyst surface. The reason for this seems to be a low thermostability of pyrazinecarboxylic acid, which is decarboxylated at 225 °C [41].

4. Conclusions

The interaction of methylpyrazine with the surface of vanadia–titania catalyst at 150–230 °C includes a consecutive transformation of coordinatively bound methylpyrazine into oxygenated surface compounds, *viz.*, an aldehyde-like complex and an asymmetrical carboxylate, which are also coordinatively bound through the nitrogen atom to the surface Lewis acid sites. The same surface complexes are formed at co-adsorption of methylpyrazine and dioxygen. In the presence of ammonia, the oxyintermediates interact with adsorbed ammonia species to form surface amidopyrazine. Note that amidopyrazine is the main product of methylpyrazine ammoxidation reaction at 250–270 °C. The surface amidopyrazine is coordinatively bound through nitrogen of the ring and oxygen of the –CONH₂ group with Lewis acid sites.

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