Applied Catalysis A: General 466 (2013) 45–50

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Oxidative and non-oxidative degradation of C_1–C_3 carboxylic acids over V_2O_5/TiO_2 and MoVTeNb oxides: A comparative study

Vladimir I. Sobolev[a,*], Konstantin Yu. Koltunov[a,b,**]

[a] Boreskov Institute of Catalysis, Russian Academy of Science, Pr. Akademika Lavrentieva, 5, Novosibirsk 630090, Russia
[b] Novosibirsk State University, Pirogova, 2, Novosibirsk 630090, Russia

ARTICLE INFO

Article history:
Received 2 April 2013
Received in revised form 3 June 2013
Accepted 17 June 2013
Available online 25 June 2013

Keywords:
V_2O_5/TiO_2
Mo–V–Te–Nb mixed oxides
Formic acid
Acetic acid
Propionic acid
Degradation
Oxidative degradation

ABSTRACT

Carboxylic acids are valuable chemical products, which can be produced efficiently by catalytic oxidation of various organic compounds using vanadium-based catalysts. Degradation resistance of carboxylic acids under applied reaction conditions is an important factor influencing selectivity of such reactions. This paper addresses the oxidative and non-oxidative gas phase degradation of formic, acetic and propionic acids over V_2O_5/TiO_2 and MoVTeNb mixed oxides. Formic acid has been found to undergo mainly acid catalyzed decarbonylation, regardless the presence or absence of oxygen in the feed. Both acetic and propionic acids underwent oxidation (in aerobic conditions) through one-carbon degradation steps until CO and CO_2 were produced. The mechanistic aspects of these transformations are discussed. The key intermediacy of 2-(hydro)peroxy carboxylic acids is suggested, based on the nature of primary reaction products. The catalytic activity of MoVTeNb mixed oxides toward oxidative and non-oxidative degradation of acetic and propionic acids appeared notably lower compared to that of V_2O_5/TiO_2. This may be linked to the enhanced efficiency of the former catalyst in selective oxidation of organic substrates to carboxylic acids.

1. Introduction

Carboxylic acids are important bulk chemicals. In principle, they can be obtained by catalytic aerobic oxidation of various organic compounds, such as aldehydes, alcohols, hydrocarbons and others. It is relevant in this connection that vanadium-based catalysts proved to be extraordinary efficient in large variety of oxidation reactions, including production of carboxylic acids [1]. For example, formaldehyde is readily oxidized to formic acid over V_2O_5/TiO_2 [2]. Ethanol oxidation gives acetic acid in high yields when the same catalyst is used [3–5]. The incorporation of special additives and promoters can stabilize a certain crystal structure of vanadium oxide, which determines the catalytic activity [6,7]. Thus, three-component MoVNb oxides supported on TiO_2 as well as bulk four-component MoVTeNb mixed oxides [8,9] have shown the best selectivity and productivity in ethanol (as well ethane and ethylene) oxidation to acetic acid [10–12]. Furthermore, butenes, 2-butanone and 2-butanol underwent oxidative scission in the presence of V_2O_5/TiO_2 to give again acetic acid [13–15].

Unfortunately, the concerned synthetic approach to carboxylic acids often suffers from overoxidation to CO_x, which is usually regarded as nonselective oxidation of starting materials or intermediate compounds. However, insufficient resistance of a target carboxylic acid should also be taken into account as an important factor influencing selectivity of these reactions. The catalytic decomposition of a number of aliphatic carboxylic acids upon various reaction conditions has been extensively studied [16,17]. In particular, it was shown recently that aqueous formic, acetic and propionic acids underwent degradation over a technical 6 wt% V_2O_5/TiO_2 catalyst [18]. This offered an incentive to a systematic study on behavior of carboxylic acids in the presence of various vanadia catalysts. In this paper, we focused our investigation on activity of typical (but distinct) representatives of widely used vanadium catalysts, such as V_2O_5/TiO_2 and MoVTeNb mixed oxides, toward degradation of formic, acetic and propionic acids under oxidative and non-oxidative conditions. The catalytic activity of TiO_2 support was also tested for the purpose of comparison (see also Ref. [17]).

2. Experimental

A 20 wt% V_2O_5/TiO_2 sample ($S_{BET} = 111\ m^2\ g^{-1}$) designated as V_2O_5/TiO_2 was obtained by impregnating TiO_2 (anatase; specific surface area, 350 $m^2\ g^{-1}$; Alfa Aesar, Germany) with an aqueous solution of vanadyl oxalate prepared using >99.6% V_2O_5 (Reakhim,

---

* Corresponding author. Tel.: +7 383 326 9765; fax: +7 383 330 8056.
** Corresponding author at: Boreskov Institute of Catalysis, Russian Academy of Science, Pr. Akademika Lavrentieva, 5, Novosibirsk 630090, Russia.
Tel.: +7 383 326 9765; fax: +7 383 330 8056.
E-mail addresses: visobo@catalysis.ru (V.I. Sobolev), koltunov@catalysis.ru (K.Yu. Koltunov).

0926-860X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2013.06.018

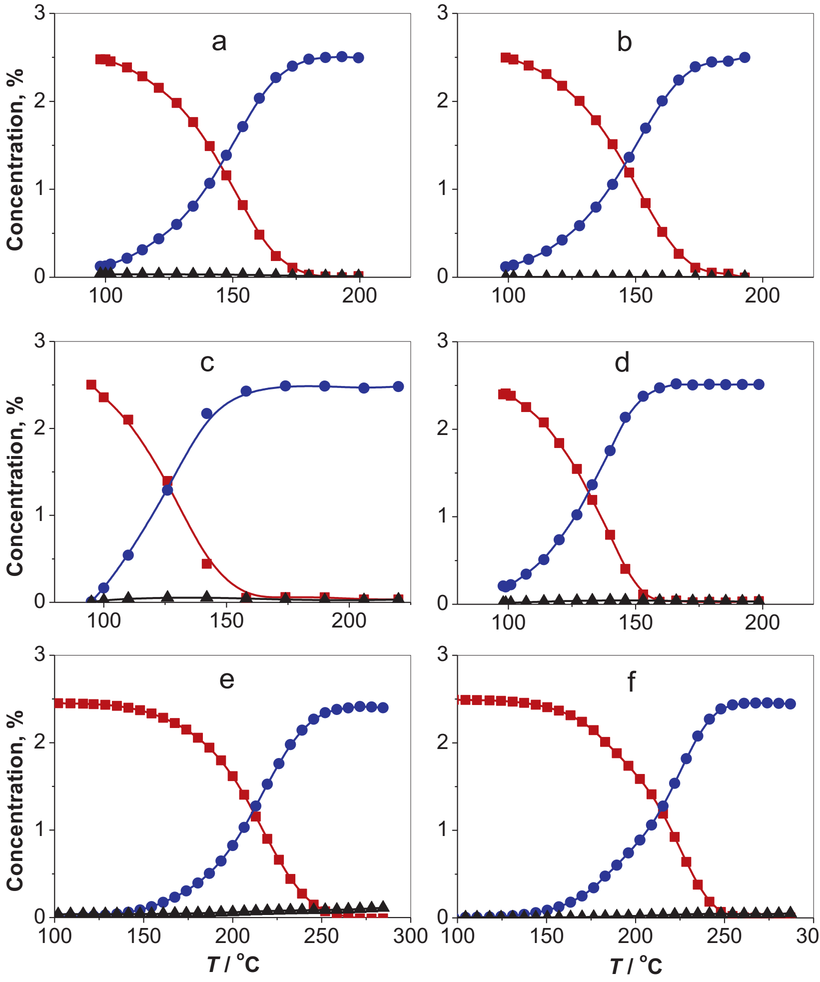


Fig. 1. Formic acid degradation over TiO_2 (a and b); V_2O_5/TiO_2 (c and d) and MoVTeNb (e and f) as a function of temperature: concentration of formic acid (■), CO (●) and CO_2 (▲). Feed compositions: 2.5 vol% HCOOH, 20.0 vol% O_2 and He balance (a, c, e); 2.5 vol% HCOOH and He balance (b, d, f); GHSV = 3600 h^{-1}.

Russia) and >97% oxalic acid (Reakhim, Russia), followed by drying in air at 110 °C for 24 h and calcination in an air flow (50 mL min^{-1}) for 4 h at 400 °C. The resulting catalyst was characterized by XRD analysis, IR and Raman spectroscopy, temperature-programmed reduction with hydrogen, and differential dissolution [2]. Vanadium in V_2O_5/TiO_2 is represented by both V_2O_5 bulk phase (mixture of amorphous and crystalline V_2O_5) and monolayer polymeric VO_x species [2].

The procedure for preparing and classifying the sample of mixed MoVTeNb oxides, designated here as MoVTeNb, was described elsewhere [19]. A sample of nominal composition $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ (obtained by spray drying at 190 °C) was calcined in He flow at 600 °C to ensure the formation of the targeted active phase. After calcination, specific surface area of the sample was 7.3 m^2 g^{-1}; the molar ratio Te/Mo decreased from 0.23 to 0.16. Thus, the final chemical composition of the sample was $Mo_1V_{0.3}Te_{0.12}Nb_{0.12}O_x$ [19]. The catalytic properties of MoVNbTe are related to the presence of two crystalline phases: orthorhombic M1 and hexagonal M2, which act as a bifunctional catalyst. The M2 phase consists of a well crystallized MoVTe oxide, and M1 is composed of MoVNbTe crystals with a minor Te content [8,9,19].

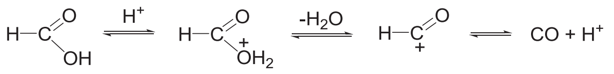
The temperature programmed gas-phase reactions were performed in a quartz tube flow reactor with an internal diameter of 6 mm using shaped catalyst granules (d = 0.25–0.5 mm; 1 mL, ca. 500 mg). The reactive gas mixture (60 mL min^{-1}) was fed into the reactor filled with the catalyst; the reactor was operated under atmospheric pressure. The reaction temperature (±1 °C) was measured inside the reactor using a thermocouple inserted into the catalyst bed. The heating rate was 2 K min^{-1}. During the catalytic runs, gas samples were analyzed periodically by integrated online gas chromatography (GC, gas chromatograph Tsvet-500; 30 m × 0.32 mm monolithic poly(divinylbenzene) capillary column; 170 °C) with a flame-ionization detector for determination of organics. For determination of CO and CO_2, they were preliminarily separated on a 1.5 m × 3 mm steel column filled with Porapak Q at 20 °C followed by methanation.

Prior to the kinetic measurements, the catalysts were activated in the reactor at 400 °C in a flow of O_2/He (1:3) for 1 h. The reactor was then cooled to 100 °C and the feed was switched at this temperature to the reactive gas mixture for 20–30 min in order to reach steady state initial conditions.

3. Results and discussion

3.1. *Reactivity of formic acid*

At first, temperature-dependent behavior of formic acid in aerobic and anaerobic conditions was studied. The catalytic performance of TiO_2, V_2O_5/TiO_2 and MoVTeNb samples in a single-pass flow reactor system is summarized in Fig. 1. As it can be seen, CO is the main product of the formic acid degradation for each catalyst regardless of the presence or absence of oxygen. Moreover, oxygen does not influence the rate of these reactions (see Supporting information, Fig. 1S). It is evident that formic acid undergoes



Scheme 1. Mechanism of the acid-catalyzed decarbonylation of formic acid.

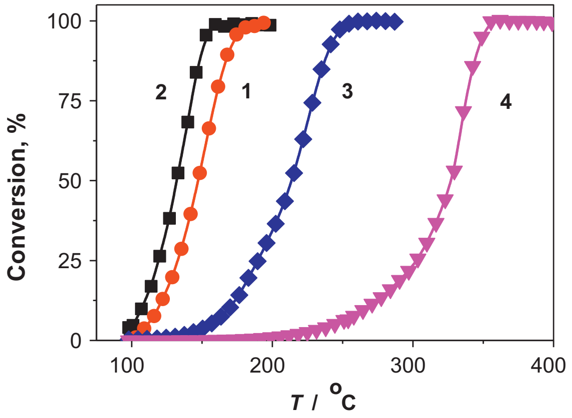


Fig. 2. Formic acid conversion over TiO_2 (1); V_2O_5/TiO_2 (2), MoVTeNb (3) and without catalyst (4) as a function of temperature. Feed composition: 2.5 vol% HCOOH and He balance, GHSV = 3600 h^{-1}.

facile acid-catalyzed decarbonylation to give CO in agreement with generally accepted reaction mechanism (Scheme 1) [20–22]. Fig. 2 combines temperature dependent profiles for the formic acid decomposition catalyzed by TiO_2, V_2O_5/TiO_2 and MoVTeNb in the absence of oxygen. The catalytic activity of V_2O_5/TiO_2 is somewhat higher compared to that of TiO_2, whereas MoVTeNb is notably less active. Very similar results were obtained also for aerobic conditions (see Supporting information, Fig. 2S). Obviously, the catalytic activity in the formic acid degradation reflects the acidity of the catalysts upon the reaction conditions [21,23].

According to the literature, formic acid showed comparatively higher resistance in the presence of technical V_2O_5/TiO_2 [18]. This, however, was most likely due to a high content of water (16.5 vol%) in the feed [18]. Indeed, the suppression effect of water vapor on decarbonylation of formic acid over V_2O_5/TiO_2 was unambiguously shown by kinetic and in situ FT-IR studies [24]. It seems reasonable that water as a stronger base (compared to formic acid) competes efficiently for adsorption in the acid sites and therefore prevents the acid-catalyzed reaction.

A negligible evolution of CO_2 during degradation of formic acid over V_2O_5/TiO_2 and MoVTeNb (Fig. 1) can be attributed to a reversible production of formates and their partial cleavage on the catalyst surface [21,24].

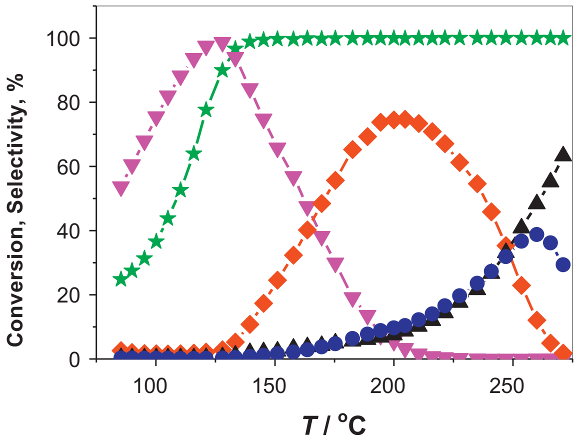


Fig. 3. Ethanol oxidation over V_2O_5/TiO_2: conversion of ethanol (★), selectivities to acetaldehyde (▼), acetic acid (♦), CO (●) and CO_2 (▲). Feed composition: 2 vol% EtOH, 18 vol% O_2 and He balance, GHSV = 3600 h^{-1}.

3.2. Reactivity of acetic acid

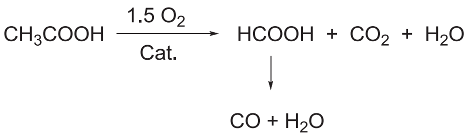
Initially, we have checked the activity of V_2O_5/TiO_2 sample in ethanol oxidation to acetic acid (Fig. 3) [5]. In particular, Fig. 3 shows temperature-dependent selectivities to acetic acid, CO and CO_2 at complete ethanol conversion, which is achieved to 140 °C. It is apparent that carbon oxides are produced starting from the very beginning of the acetic acid generation. Noteworthy is the ratio of CO and CO_2, which is about 1:1 being quite constant right up to 250 °C. Moreover, in a separate experiment, we observed that CO is not oxidized to CO_2 over V_2O_5/TiO_2 up to 300 °C. Therefore, one may propose direct oxidation of acetic acid to carbon oxides similar to that for oxidation of aqueous acetic acid over V_2O_5/TiO_2 [18]. Indeed, further experiments on the acetic acid resistance (at conditions applied to ethanol oxidation) supported such an assumption. Fig. 4 shows temperature-dependent behavior of acetic acid in aerobic and anaerobic conditions in the presence of TiO_2, V_2O_5/TiO_2 and MoVTeNb. According to the data in Fig. 4, MoVTeNb ensures best resistance of acetic acid, which is stable right up to 250 °C under aerobic conditions and practically does not react in the absence of oxygen. This can be part of the reason for the extraordinary catalytic efficiency of MoVTeNb in ethanol oxidation to acetic acid [11]. In contrast, V_2O_5/TiO_2 is notably more active toward undesirable oxidation of acetic acid, which is in agreement with the diminished efficiency of this catalyst in the acetic acid production [3–5].

It is significant that the main products of the acetic acid oxidation are CO and CO_2 in about 1:1 ratio on both V_2O_5/TiO_2 and MoVTeNb catalysts (Fig. 4). The equimolar generation of carbon oxides can be explained by intermediate producing of formic acid, which then undergoes decarbonylation (Scheme 2). In our experiments we did not observe the intermediate formic acid, although it was produced with 5–20% selectivity at 175–275 °C upon oxidation of aqueous acetic acid over V_2O_5/TiO_2 [18]. This discrepancy is explained by relatively facile decarbonylation of formic acid in our case, providing low content of water in the feed (see above).

Unlike the vanadium-containing catalysts, TiO_2 alone evokes another type of reactivity of acetic acid. Under anaerobic conditions acetic acid converts into equimolar mixture of acetone and CO_2 (Fig. 4b). This is in accordance with the literature data. Similar reaction is known as a synthetic approach to obtain acetone via thermolysis of acetates [25]. Moreover, the analogous conversion of acetic acid was carried out catalytically over various metal oxides, including TiO_2 [17,26,27]. When oxygen is present in the feed, the produced acetone undergoes oxidation, especially at temperatures above 250 °C (Fig. 4a). In addition to this reaction pathway, direct oxidation of acetic acid to CO_2 and CO (i.e. HCOOH) also takes place. As a final result, a mixture of CO and CO_2 (predominant product) is formed (Scheme 3).

Notably that acetone is almost not generated on V_2O_5/TiO_2 (Fig. 4c and d). This is due to an exhaustive coverage of the support by vanadium oxide (see Section 2 and Ref. [2]).

Fig. 5 combines temperature dependent profiles for the acetic acid degradation under oxidation conditions catalyzed by TiO_2,



Scheme 2. Oxidative degradation of acetic acid over V_2O_5/TiO_2 and MoVTeNb mixed oxides.

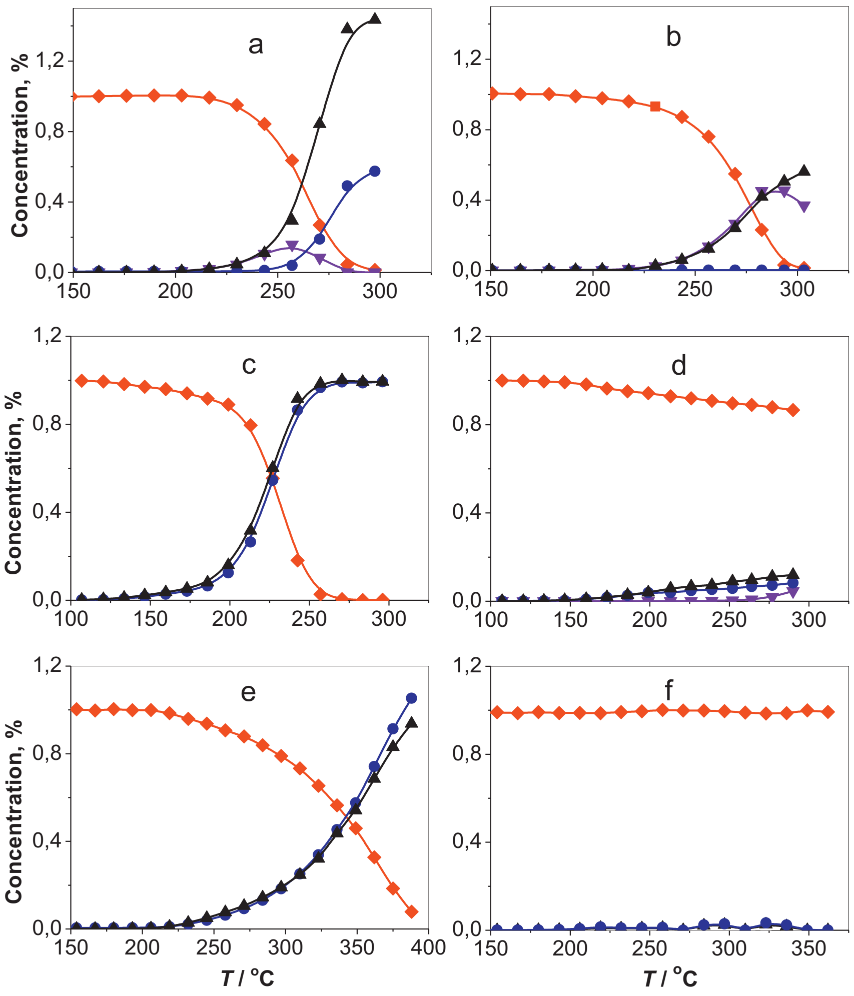
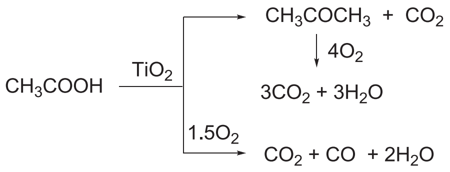


Fig. 4. Acetic acid degradation over TiO_2 (a and b); V_2O_5/TiO_2 (c and d) and MoVTeNb (e and f) as a function of temperature: concentration of acetic acid (♦), CO (●), CO_2 (▲), and acetone (▼). Feed compositions: 1 vol% CH_3COOH, 20 vol% O_2 and He balance (a, c, e); 1 vol% CH_3COOH and He balance (b, d, f); GHSV = 3600 h^{-1}.



Scheme 3. Oxidative degradation of acetic acid over TiO_2.

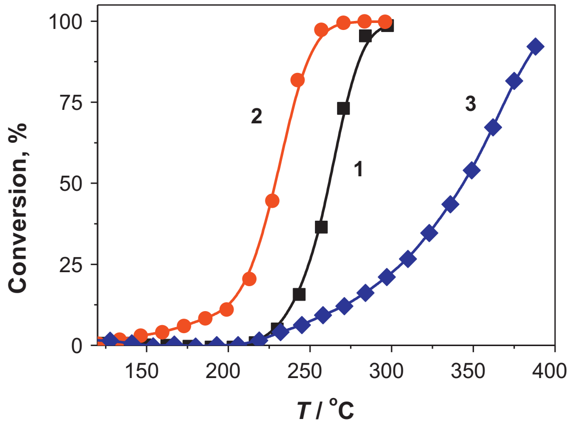


Fig. 5. Acetic acid conversion over TiO_2 (1); V_2O_5/TiO_2 (2) and MoVTeNb (3) as a function of temperature. Feed composition: 1 vol% CH_3COOH, 20 vol% O_2 and He balance, GHSV = 3600 h^{-1}.

V_2O_5/TiO_2 and MoVTeNb. Surprisingly, TiO_2 support revealed significant catalytic activity, which is even higher than that of MoVTeNb.

3.3. Reactivity of propionic acid

According to the literature, aqueous propionic acid is oxidized over V_2O_5/TiO_2; the main products are acetic acid, formic acid and carbon oxides [18]. We have studied reactivity of propionic acid on V_2O_5/TiO_2 and MoVTeNb in the presence and absence of oxygen (Fig. 6). Likewise acetic acid, it is notably more reactive on V_2O_5/TiO_2 than on MoVTeNb (Fig. 6). In general, propionic acid is found less resistant than acetic acid (see, for comparison, Fig. 7).

Noteworthy is the formation of diethyl ketone on V_2O_5/TiO_2 at temperatures above 300 °C under anaerobic conditions (Fig. 6b). This reaction was shown earlier to occur on TiO_2 surface [17] and is analogous to acetone production from acetic acid (see above).

Under oxidation conditions propionic acid converts to a set of products (Fig. 6a and c). Among the primary products appeared to be acetaldehyde, CO_2 and acetic acid, which are observed from the beginning of the reaction. However, the early appearance of acetic acid may be related to immediate oxidation of acetaldehyde. Finally, a mixture of CO and CO_2 is formed at temperatures above 250 and 380 °C for V_2O_5/TiO_2 and MoVTeNb, respectively.

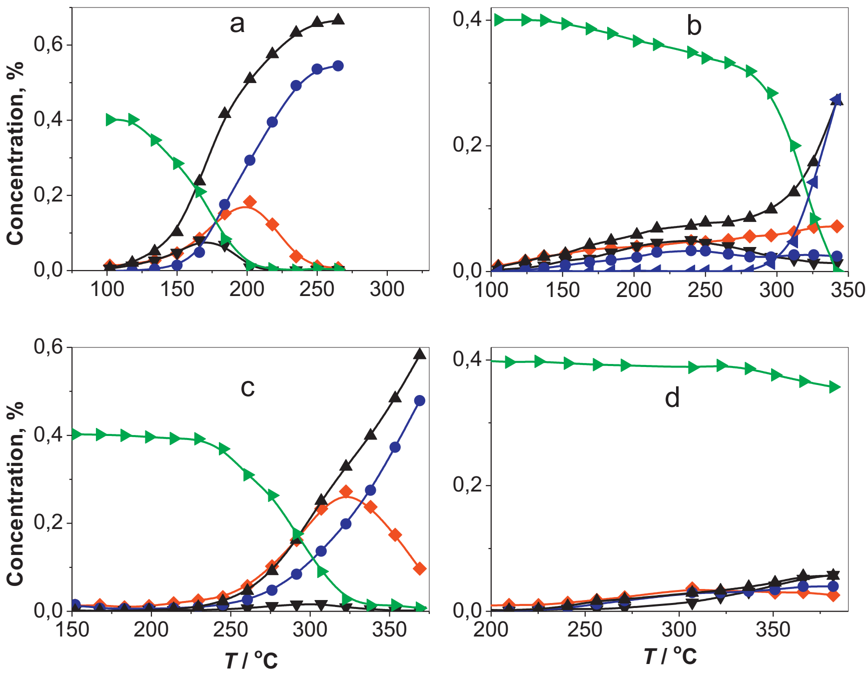


Fig. 6. Propionic acid degradation over V_2O_5/TiO_2 (a and b) and MoVTeNb (c and d) as a function of temperature: concentration of propionic acid (▶), acetic acid (♦), acetaldehyde (▼), CO (●), CO_2 (▲) and diethyl ketone (◀). Feed compositions: 0.4 vol% C_2H_5COOH, 20 vol% O_2 and He balance (a and c); 0.4 vol% C_2H_5COOH and He balance (b and d); GHSV = 3600 h^{-1}.

3.4. Proposed mechanism for the carboxylic acids oxidation

It seems very likely that oxidation of a linear carboxylic acid over V_2O_5/TiO_2 and MoVTeNb follows a general mechanism including one-carbon degradation steps as long as formic acid (or CO) is produced. Worth to note, that there are not too many reactions susceptible to yield C_{n-1} aldehydes upon degradation of C_n carboxylic acids. Literature precedents exist for conversions of 2-hydroxy and 2-hydroperoxy carboxylic acids to aldehydes accompanied by CO [28] and CO_2 [29–31] elimination, respectively. Since CO_2 is the de facto initial co-product of oxidative degradation for both propionic and acetic acids, the intermediacy of 2-hydroperoxy carboxylic acids may be surmised.

A hypothetical reaction mechanism for the catalytic oxidation of acetic and propionic acids is depicted in Scheme 4. The adsorbed carboxylic acid, RCH_2COOH (or corresponding carboxylate, formed on vanadium oxide as a result of dissociative adsorption), undergoes initially hydrogen atom transfer (HAT) [32–34] upon action of vanadium oxides to give radicals **1**. The same radicals were suggested earlier as key intermediates in oxidative reactions of acetic and propionic acids in the presence of Mn(III) acetate [35]. Reaction of **1** with O_2 will give peroxy radicals **2**, which can undergo immediate thermal decomposition to yield corresponding aldehyde RCHO and CO_2 [31] or give rise to 2-hydroperoxy acid **3** (Scheme 4, Pathway 1). The latter can easily transform to RCHO and CO_2 as a result of acid-catalyzed scission [29]. Note that the transient formation of acetaldehyde, proved experimentally for the propionic acid oxidation (Fig. 6a and c), strongly supports the suggested mechanism. In case of the acetic acid oxidation, the intermediate production of formaldehyde is anticipated. However, formaldehyde is readily oxidized to formic acid and therefore not observed [2]. Alternatively, radicals **1** may undergo electron transfer

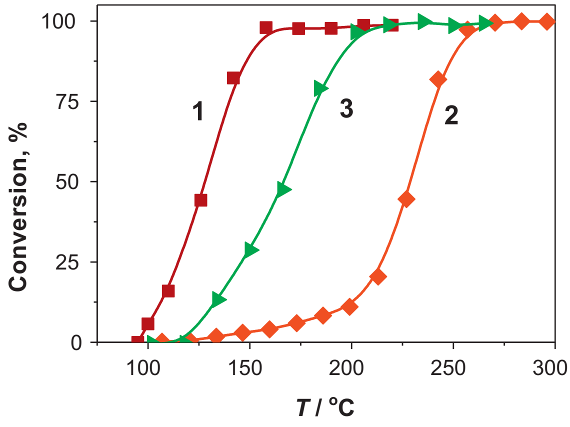
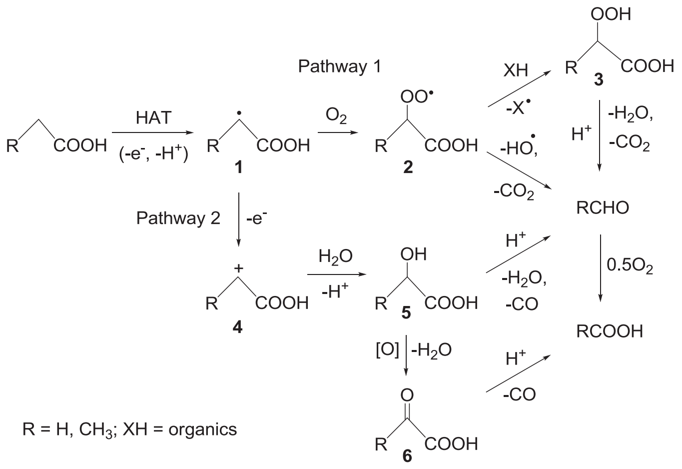


Fig. 7. Catalytic performance of V_2O_5/TiO_2 as a function of temperature: conversions of formic acid (1), acetic acid (2) and propionic acid (3). Feed compositions: 2.5 vol% HCOOH (or 1 vol% CH_3COOH, or 0.4 vol% C_2H_5COOH), 20 vol% O_2 and He balance, GHSV = 3600 h^{-1}.



Scheme 4. Proposed mechanism of one-carbon oxidative degradation of carboxylic acids over V_2O_5/TiO_2 and MoVTeNb mixed oxides.

to give carbocations **4** (Scheme 4, Pathway **2**). The electron transfer seems energetically unfavorable, especially when R = H [36], as the carboxy-carbocations are highly destabilized species. However, formation of **4** (R = CH_3) is more probable. Reaction of this ion with water will lead to producing of lactic acid (**5**, R = CH_3). The latter can undergo acid-catalyzed decomposition into acetaldehyde and CO [28]. Also, lactic acid may be oxidized to pyruvic acid (**6**, R = CH_3) followed by acid-catalyzed decomposition to give equimolar mixture of acetic acid and CO [37,38]. As a result, the increased overall production of CO could happen. Indeed, in case of propionic acid oxidative degradation, the actual ratio of CO to CO_2 exceeds the expected 1:2 ratio assumed by combination of Scheme 2 and Pathway **1** of Scheme 4.

The proposed mechanism of reaction is in agreement with the relatively facile oxidation of propionic acid, which is due to easier formation of **1**, when R = CH_3, because of significant stabilization of such radicals by methyl group [39]. It should be noted also that radicals **1** can be produced additionally as a result of $HO^\bullet$ attack on carboxylic acid [40]. The hydroxyl radicals could be derived from **2** according to Scheme 4, and the process might be partially autocatalytic.

4. Conclusions

In summary, degradation resistance of formic, acetic and propionic acids in the presence of TiO_2, V_2O_5/TiO_2 and MoVTeNb mixed oxides was investigated. Formic acid appeared to be the most unstable of the carboxylic acids due to comparatively facile, acid-catalyzed decarbonylation, which occurred regardless of aerobic or anaerobic conditions. Acetic acid, in its turn, showed notably higher stability than propionic acid.

Unlike V_2O_5/TiO_2, MoVTeNb mixed oxides ensure more resistance both of acetic and propionic acids toward oxidative and non-oxidative reactions. This could be a reason for the extraordinary selective ethanol oxidation to acetic acid catalyzed by MoVTeNb oxides [11]. In addition, this is in line with the suppressed CO_x formation during propane (amm)oxidation to acrylonitrile and acrylic acid in the presence of MoVTeNb oxides, which are regarded as the most efficient catalysts in such reactions [41,42].

The preferred mechanism of the vanadia catalyzed oxidation of acetic and propionic acids includes one-carbon degradation steps until formic acid (or CO) and CO_2 are produced. The key intermediacy of 2-(hydro)peroxy carboxylic acids is proposed on the basis of consideration of primary and secondary reaction products.

Acknowledgments

The authors thank Dr. G.Y. Popova, Dr. E.V. Ischenko and Dr. V.M. Bondareva (Boreskov Institute of Catalysis) for supplying and characterizing samples of the examined catalysts.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.06.018.

References

[1] B.M. Weckhuysen, D.E. Keller, Catal. Today 78 (2003) 25–46.
[2] G.Ya. Popova, T.V. Andrushkevich, E.V. Semionova, Yu.A. Chesalov, L.S. Dovlitova, V.A. Rogov, V.N. Parmon, J. Mol. Catal. A 283 (2008) 146–152.
[3] M. Gubelmann-Bonneau, US Patent 5840971 (1998).
[4] B. Jørgensen, S.B. Kristensen, A.J. Kunov-Kruse, R. Fehrmann, C.H. Christensen, A. Riisager, Top. Catal. 52 (2009) 253–257.
[5] K.Yu. Koltunov, V.I. Sobolev, Katal. Prom-sti 3 (2012) 20–25 (Catal. Ind. (Engl. Transl.), 4 (2012) 247–252).
[6] T.Yu. Kardash, L.M. Plyasova, V.M. Bondareva, T.V. Andrushkevich, L.S. Dovlitova, A.I. Ischenko, A.I. Nizovskii, A.V. Kalinkin, Appl. Catal. A 375 (2010) 26–36.
[7] M. Roussel, M. Bouchard, K. Karim, S. Al-Sayari, E. Bordes-Richard, Appl. Catal. A 308 (2006) 62–74 (references therein).
[8] T. Ushikubo, K. Oshima, A. Kayou, M. Vaarkamp, M. Hatano, J. Catal. 169 (1997) 394–396.
[9] H. Tsuji, K. Oshima, Y. Koyasu, Chem. Mater. 15 (2003) 2112–2114.
[10] X. Li, E. Iglesia, Chem. Eur. J. 13 (2007) 9324–9330.
[11] V.I. Sobolev, K.Yu. Koltunov, ChemCatChem 3 (2011) 1143–1145.
[12] M. Roussel, M. Bouchard, K. Karim, S. Al-Sayari, E. Bordes-Richard, Appl. Catal. A 308 (2006) 62–74.
[13] T. Machold, W.Y. Suprun, H. Papp, J. Mol. Catal. A 280 (2008) 122–130.
[14] W.Y. Suprun, D.P. Sabde, H.-K. Schadlich, B. Kubias, H. Papp, Appl. Catal. A 289 (2005) 66–73.
[15] W. Suprun, E.M. Sadovskaya, C. Rüdinger, H.-J. Eberle, M. Lutecki, H. Papp, Appl. Catal. A 391 (2011) 125–136.
[16] E.J. Grootendorst, R. Pestman, R.M. Koster, V. Ponec, J. Catal. 148 (1994) 261–269.
[17] K.S. Kim, M.A. Barteau, J. Catal. 125 (1990) 353–375 (references therein).
[18] W.Y. Suprun, D. Kiebling, T. Machold, H. Papp, Chem. Ing. Tech. 79 (2007) 117–122.
[19] G.Y. Popova, T.V. Andrushkevich, Y.A. Chesalov, L.M. Plyasova, L.S. Dovlitova, E.V. Ishenko, G.A. Aleshina, M.I. Khramov, Catal. Today 144 (2009) 312–317.
[20] G.A. Ropp, J. Am. Chem. Soc. 80 (1958) 6691.
[21] P. Mars, J.J.F. Scholten, P. Zwietering, Adv. Catal. 14 (1963) 35–113.
[22] Y. Yasaka, K. Yoshida, C. Wakai, N. Matubayasi, M. Nakahara, J. Phys. Chem. A 110 (2006) 11082–11090.
[23] S.A. Halawy, S.S. Al-Shihry, M.A. Mohamed, Catal. Lett. 48 (1997) 247–251.
[24] G.Ya. Popova, Yu.A. Chesalov, E.M. Sadovskaya, T.V. Andrushkevich, J. Mol. Catal. A 357 (2012) 148–153.
[25] M.D. Jud, B.A. Plunkett, M.I. Pope, J. Therm. Anal. 6 (1974) 555–563.
[26] M.A. Hasan, M.I. Zaki, L. Pasupulety, Appl. Catal. A 243 (2003) 81–92.
[27] M.A. Barteau, Chem. Rev. 96 (1996) 1413–1430.
[28] M. Zielinski, A. Zielinska, H. Papiernik-Zielinska, G. Czarnota, G. Kasprzyk, W. Staedter, L. Gumolka, Isotopenpraxis Environ. Health Stud. 30 (1994) 333–347.
[29] Y. Akakabe, T. Nyuugaku, Biosci. Biotechnol. Biochem. 71 (2007) 1370–1371.
[30] F. Castiglione, A. Baggioli, A. Citterio, A. Mele, G. Raos, J. Phys. Chem. A 116 (2012) 1814–1819.
[31] G. da Silva, J. Phys. Chem. A 114 (2010) 6861–6869.
[32] J.M. Mayer, Acc. Chem. Res. 44 (2011) 36–46.
[33] N. Dietl, M. Schlangen, H. Schwarz, Angew. Chem. Int. Ed. 51 (2012) 5544–5555.
[34] W. Lai, C. Li, H. Chen, S. Shaik, Angew. Chem. Int. Ed. 51 (2012) 5556–5578.
[35] R.E. Van Der Ploeg, R.W. De Korte, E.C. Kooyman, J. Catal. 10 (1968) 52–59.
[36] E.I. Heiba, R.M. Dessau, W.J. Koehl Jr., J. Am. Chem. Soc. 90 (1968) 2706–2707.
[37] G.A. Olah, L.T. Ku, J. Sommer, J. Org. Chem. 36 (1970) 2159–2164.
[38] N. Yonezawa, T. Hino, T. Kinuno, T. Matsuki, T. Ikeda, Synth. Commun. 29 (1999) 1687–1695.
[39] A.S. Menon, D.J. Henry, T. Bally, L. Radom, Org. Biomol. Chem. 9 (2011) 3636–3657.
[40] Y. Ogata, K. Tomizawa, K. Takagi, Can. J. Chem. 59 (1981) 14–18.
[41] N. Watanabe, W. Ueda, Ind. Eng. Chem. Res. 45 (2006) 607–614.
[42] R. Lopez-Medina, I. Sobczak, H. Golinska-Mazwa, M. Ziolek, M.A. Banares, M.O. Guererro-Perez, Catal. Today 187 (2012) 195–200.