



## Vanadium-based highly active and selective catalysts for oxidative dehydrogenation of ethyl lactate to ethyl pyruvate

Dhananjay S. Doke<sup>a,b</sup>, Sonali B. Khomane<sup>a</sup>, Swati L. Pandhare<sup>a</sup>, Mohan K. Dongare<sup>a,c</sup>, Franck Dumeignil<sup>d</sup>, Shubhangi B. Umbarkar<sup>a,b,\*</sup>

<sup>a</sup> Catalysis Division, CSIR-National Chemical Laboratory, Pune, 411008, India

<sup>b</sup> Academy of Scientific and Innovative Research, CSIR, Ghaziabad, 201002, India

<sup>c</sup> Malati Fine Chemicals Pvt. Ltd, 4/A Durvankurdarshan Society, Pune, 411008, India

<sup>d</sup> Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000, Lille, France

### ARTICLE INFO

#### Keywords:

Ethyl lactate  
Ethyl pyruvate  
Vanadium  
TBHP  
Oxidative dehydrogenation

### ABSTRACT

Pyruvates are important intermediates for various bioactive and pharmaceutical molecules. Synthesis of pyruvates is challenging due to low selectivity, as the pyruvates are prone to polymerisation. In the present work, oxidative dehydrogenation of ethyl lactate to ethyl pyruvate was carried out under very mild conditions using vanadium-based homogeneous and heterogeneous catalysts in the presence of aqueous *t*-butyl hydroperoxide as an oxidant. Homogenous vanadium-based catalyst, VO(acac)<sub>2</sub> in acetonitrile solvent, gave excellent conversion (upto 83%) with 100% selectivity to ethyl pyruvate at room temperature. However, the heterogeneous catalyst, V<sub>2</sub>O<sub>5</sub> exhibited very high activity for oxidative dehydrogenation of ethyl lactate only at higher temperature (80 °C). At higher temperature, significant TBHP decomposition was observed if all TBHP was added in one lot. In case of ethyl lactate dehydrogenation using V<sub>2</sub>O<sub>5</sub> catalyst at 80 °C with two equivalents TBHP, 60% ethyl lactate conversion with 100% TBHP conversions were observed after 5 h when all TBHP was added initially in the reaction mixture. However, the ethyl lactate conversion at 80 °C, after 5 h increased to 72% when the same amount of TBHP was added batch wise over a period of 4 h, indicating improved conversion of TBHP to ethyl pyruvate. The heterogeneous catalyst, V<sub>2</sub>O<sub>5</sub> exhibited up to 98% conversion with 100% ethyl pyruvate selectivity at 80 °C after 10 h with 3 equivalent TBHP added batch wise. The homogeneous catalyst could not be reused while V<sub>2</sub>O<sub>5</sub> could be successfully recycled five times without catalytic performances loss. Oxidation proceeds by radical mechanism, as proved by experiment with radical scavenger.

### 1. Introduction

Decreasing availability of fossil fuel is forcing researchers to develop alternate routes for production of fuels and chemicals using renewable resources. Biomass is one of the renewable resources, abundantly available and rich in hydrocarbons. Biomass can be converted to some valuable products. Fermentation processes give access to various platform molecules, which can be further converted to value added products using bio/chemical routes 1–4. Lactic acid, one of the very important fermentation products of sugar, has been identified as a platform chemical in biorefineries. The bifunctional nature of lactic acid due to the presence of alcoholic OH and carboxylic group, makes it a very important raw material for conversion to a large number of commodity chemicals including pyruvic acid, acrylic acid and its esters for a wide range of applications. They find uses as intermediates in

various industrial products such as perfume, food additives, pharmaceuticals and electronic materials. They are also attractive as raw materials for various bioactive substances such as antiviral and anticancer drugs [5]. Pyruvates are also used in dietary supplements, in food industry. However, the production of pyruvic acid is still based on the conventional reaction scheme through dehydrative decarboxylation of tartaric acid. Although this reaction provides pyruvic acid in good yield, it has a major disadvantage due to the use of excess KHSO<sub>4</sub> as the decarboxylation agent leading to an expensive process with environmental hazards along with high energy consumption [6]. Pyruvic acid/pyruvates are also produced by microbial process using stains of yeast and *E. coli*. However, typical limitations of bioprocesses like very high dilutions and critical control of process parameters during fermentation make those less attractive [7]. Therefore, designing a new process with high atom efficiency for the production of pyruvic acid is essential [8].

\* Corresponding author at: Catalysis Division, CSIR-National Chemical Laboratory, Pune, 411008, India.

E-mail address: [sb.umbarkar@ncl.res.in](mailto:sb.umbarkar@ncl.res.in) (S.B. Umbarkar).

<https://doi.org/10.1016/j.apcata.2019.117246>

Received 28 June 2019; Received in revised form 30 August 2019; Accepted 10 September 2019

Available online 11 September 2019

0926-860X/ © 2019 Elsevier B.V. All rights reserved.

Pyruvic acid or esters can be synthesized via catalytic oxidative dehydrogenation of lactic acid/esters, e.g., ethyl lactate to ethyl pyruvate. In this case, the whole process would be based on biomass-derived feedstock, and the reaction could in theory proceed directly from lactic acid to pyruvic acid. As a possible candidate for the synthesis of pyruvic acid, oxidative dehydrogenation of lactates to the corresponding pyruvates in both gas and liquid phases on solid catalysts has received significant attention. Oxidative dehydrogenation of ethyl lactate to ethyl pyruvate either in liquid or gas phase using various binary oxides containing molybdenum such as  $\text{Fe}_2\text{O}_3\text{-MoO}_3$ ,  $\text{TeO}_2\text{-MoO}_3$  and  $\text{MoVNbO}_x$ , vanadium oxide species, and iron phosphate have been investigated by various research groups [1,9,10]. These processes achieve high yields of pyruvate from lactate. In the case of vapor phase dehydrogenation of lactates, besides the requirement for vaporizing lactate at high temperature, a reaction temperature above 473 K is also needed, which increases the running cost of the process. High reaction temperatures may lead to product decomposition and then to low productivity along with high energy demand. There are several reports on liquid phase oxidative dehydrogenation (ODH) of lactates to pyruvates. Kazuhiro et al. have reported  $\text{VOCl}_3$  catalyst in the presence of various oxidants with almost 50% conversion and < 50% selectivity to pyruvate. Water is the by-product of this reaction and the catalyst was not stable in the presence of water.  $\text{VOCl}_3$  is known to be highly sensitive to hydrolysis in presence of water/moisture leading to the formation of  $\text{V}_2\text{O}_5$ . Hence it is essential to remove water formed in the reaction to maintain the activity of the catalyst [11]. Zhou and others have used TS-1 as a catalyst and peroxide as an oxidant with excellent conversion (~100%) and maximum 98.6% selectivity to pyruvate [12]. Shiju and co-workers have reported titanium-based catalysts for ODH using oxygen as an oxidant, but this reaction requires high pressure (1 MPa) and temperature (130 °C). However, selectivity to pyruvate was an issue: Only at lower conversions (~20%) high selectivity (~70%) to pyruvate was reported; with an increase in conversion to 60%, pyruvate selectivity dropped drastically (~25%) due to polymerisation of pyruvate [13]. In a recent work reported by Shiju et al. on the use of mesoporous vanadia-titania catalysts for atmospheric pressure ODH at 130 °C using diethyl succinate as a solvent, a pyruvate selectivity of > 90% at ~20% lactate conversion was observed. However, in this case also the selectivity dropped to 60% at 70% conversion [14]. The same group has again reported vapor phase ODH of ethyl lactate using vanadia supported on different oxides as catalysts in a fixed bed reactor at 180 °C with a maximum 48% yield of ethyl lactate [15]. The liquid phase ODH of lactic acid using solid catalysts such as Pd/C modified by Te and Pb has been reported by Hayashi et al. [16] with maximum 80% conversion and 50% pyruvic acid yield at 90 °C. However, high cost of precious metal is a matter of concern due to high Pd loading (5 wt.%) essential for the reaction. Wang et al. have reported ethyl lactate ODH using carbon nanotubes as catalysts and TBHP as an oxidant with maximum yield of 40% at 90 °C [17]. Hence, development of a catalytic system for efficient oxidative dehydrogenation of lactate to pyruvate under mild reaction conditions using simple and inexpensive catalysts is still highly desired.

Vanadium-based catalysts have been extensively studied for selective oxidation of various organics including ethyl lactate. Various vanadium-based homogeneous catalysts including  $\text{VOCl}_3$  have been studied for the oxidation of ethyl lactate to ethyl pyruvate using gas-liquid micro flow system [11,14]. A maximum yield of 31% has been reported at room temperature using oxygen as an oxidant. Molecular sieves were essential to remove water generated during the reaction as a by-product to avoid hydrolysis of the sensitive catalyst,  $\text{VOCl}_3$ .

Considering the importance of pyruvate and recognizing the previous efforts in this area, we have attempted oxidative dehydrogenation of ethyl lactate to ethyl pyruvate using vanadium-based catalysts in the liquid phase using *t*-butyl hydroperoxide as an oxidant. Interestingly, very high conversion with nearly 100% selectivity to ethyl pyruvate was observed, and the results are presented herein.

## 2. Experimental section

### 2.1. Materials and instrumentation

Ethyl lactate, vanadyl acetylacetonate  $\text{VO}(\text{acac})_2$ , ethyl pyruvate (Aldrich Chemicals),  $\text{FeCl}_3$ , copper acetate (Avra Chemicals India),  $\text{V}_2\text{O}_5$ , *tert*-butyl hydroperoxide (TBHP, 70% aqueous) (Avra Chemicals India) and 5.5 M in decane (Aldrich Chemicals), acetonitrile (Finar Chemicals India) were used as received without further purification.  $\text{MoO}_2\text{Cl}_2(\text{DMSO})_2$  and  $\text{MoO}_2\text{Cl}_2(\text{DMF})_2$  were prepared using literature method [18].

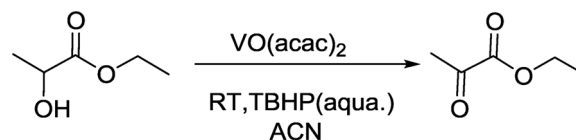
### 2.2. Typical reaction procedure

In a typical ODH reaction, a two-necked round bottom flask (50 ml) was charged with ethyl lactate (0.23 g, 2 mmol), 70% aqueous or organic (5.5 M in decane) TBHP (4 mmol), catalyst (0.04 mmol, 2 mol%), and 6 g  $\text{CH}_3\text{CN}$  as a solvent. The reaction mixture was stirred at desired temperature for specified time. The reaction was monitored by GC. The samples were taken periodically and analyzed using a GC-Hewlett Packard 6890 equipped with an HP-5 column (50 m length, 0.25 mm internal diameter and 1  $\mu\text{m}$  film thickness) and a flame ionization detector (FID). Conversion of ethyl lactate was calculated based on GC-FID results, where substrate conversion (%) = [moles of substrate reacted]/[Initial moles of substrate used]  $\times$  100, and selectivity (%) to products was calculated by [total moles of the product formed]/[total moles of substrate converted]  $\times$  100. The produced ethyl pyruvate was quantified using external calibration curve plotted using commercial ethyl pyruvate. Individual yields were calculated and normalized with respect to the GC response factors. The product identification was carried out by injecting commercial samples in the GC.

## 3. Results and discussion

Oxidative dehydrogenation of ethyl lactate (Scheme 1) was carried out using various commercial metal salts like vanadyl acetylacetonate, copper acetate, iron chloride as well as simple complexes like  $\text{MoO}_2\text{Cl}_2(\text{DMSO})_2$ ,  $\text{MoO}_2\text{Cl}_2(\text{DMF})_2$  as catalysts in the presence of organic TBHP (5.5 M in decane) as an oxidant in acetonitrile as a solvent at 80 °C. The results are reported in Table 1S. The acetonitrile solvent was chosen based on our previous experience in oxidation reactions using Mo-based complexes as homogeneous catalyst and  $\text{H}_2\text{O}_2$  or TBHP as oxidant, where better activity was obtained in acetonitrile compared to other solvents.

Oxidative dehydrogenation of ethyl lactate without catalyst at 80 °C using organic TBHP as an oxidant in acetonitrile solvent did not show any conversion even after 11 h. Under the same conditions, various Mo-, Cu-, and Fe-based catalysts yielded moderate to excellent conversion of ethyl lactate (31–92%) with 100% selectivity to ethyl pyruvate. It is interesting to note that in all cases ethyl pyruvate was formed as a sole product and no other by-products were observed. Mo-based complexes showed 92% ethyl lactate conversion with organic TBHP; however, under identical conditions no reaction was observed with aqueous TBHP, due to catalyst deactivation in the presence of water. All the Mo complexes in presence of water formed blue complexes which were found to be inactive for ODH reaction. It is well documented in the literature that molybdenum blue are the complexes with dimeric structure with very facile electron transfer between both



Scheme 1. Oxidative dehydrogenation of ethyl lactate to ethyl pyruvate.

**Table 1**Effect of temperature on ethyl lactate dehydrogenation using VO(acac)<sub>2</sub> as a catalyst.

Entry	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)	TON
1	80	16	82	100	41
2	40	16	79	100	40
3	RT	16	72	100	36

Reaction conditions: Ethyl lactate 2 mmol; aqueous TBHP 4 mmol; catalyst VO(acac)<sub>2</sub> 0.04 mmol, CH<sub>3</sub>CN 10 g.

molybdenum centers [19]. Note that, attempts to use hydrogen peroxide as an oxidant were not successful with all the tested catalysts.

VO(acac)<sub>2</sub> did not deactivate when using aqueous TBHP as an oxidant. Almost similar ethyl lactate conversion was obtained (82%) in the presence of aqueous TBHP at 80 °C after 16 h (Table 1 entry 1) compared to organic TBHP (80%) under similar reaction conditions, in both cases at 100% selectivity to ethyl pyruvate. Hence, the use of VO(acac)<sub>2</sub> was subsequently explored for optimizing different reaction parameters in order to maximize the ethyl pyruvate yield. Initially, reaction was carried out at different temperatures, and, to our surprise, very high ethyl lactate conversion was obtained even at lower temperatures (40 °C), and even at room temperature though it needed longer reaction times for achieving maximum conversion. After 16 h, the ethyl lactate conversion was 79% and 72% at 40 °C and room temperature, respectively (Table 1 entry 2 & 3) which underlines very high efficiency of VO(acac)<sub>2</sub> for ethyl lactate dehydrogenation even at room temperature.

Ethyl pyruvate is prone to polymerization. Hence, there is a need to use solvent in order to avoid this undesired side reaction [13]. When a solvent is used for the reaction, it reduces the concentration of pyruvate in the reaction medium and in turn reduces the interaction between pyruvate molecules reducing the extent of polymerisation leading to very high selectivity to pyruvate. We thus studied the effect of the amount of solvent on the kinetics of the reaction by varying the amount of acetonitrile with respect to ethyl lactate (Table 2). When ethyl lactate dehydration was carried out without solvent (Table 2 entry 1), 91% conversion was obtained after 16 h, however the selectivity for ethyl pyruvate was only 80% leading to partial polymerization. When one weight equivalent (0.236 g) solvent was used (Table 2 entry 2) the conversion increased to 97% after 16 h with 80% selectivity for ethyl pyruvate. Even with 2 wt equivalent of solvent (Table 2 entry 3) the conversion (98%) and selectivity (80%) remained almost same with partial polymerization. However, when 10 wt equivalents of solvent (Table 2 entry 4) was used; very high conversion (83%) was obtained with 100% selectivity to ethyl pyruvate. With further increase in the solvent amount to 20, 30 and 50 wt equivalents (Table 2 entry 5–7), the conversion gradually decreased to 72% still with 100% selectivity to ethyl pyruvate. These results clearly indicate the need for the use of a solvent to avoid polymerization and to obtain 100% selectivity to ethyl pyruvate. With a substantial excess of solvent, the conversion decreased as expected without decrease in the selectivity. The decrease in the

**Table 2**Effect of amount of solvents on ethyl lactate dehydrogenation using VO(acac)<sub>2</sub> as a catalyst.

Entry	Amount of CH <sub>3</sub> CN, g	Time (h)	Conversion (%)	Selectivity (%)	TON
1	without solvent	16	92	80	46
2	0.236	16	97	80	49
3	0.472	16	98	80	50
4	2	16	83	100	42
5	4	16	81	100	41
6	6	16	72	100	36
7	10	16	72	100	36

Reaction conditions: Ethyl lactate 2 mmol; aqueous TBHP 4 mmol; catalyst 0.04 mmol (2 mol%); room temperature.

**Table 3**Effect of catalyst loading on ethyl lactate dehydrogenation using VO(acac)<sub>2</sub> as a catalyst.

Entry	Catalyst loading	Time (h)	Conversion (%)	Selectivity (%)	TON
1	0.5 mol.%	16	32	100	134
		28	67	100	
2	1 mol.%	16	39	100	76
		28	76	100	
3	2 mol.%	16	83	100	50
		24	100	100	

Reaction conditions: Ethyl lactate 2 mmol; aqueous TBHP 4 mmol; solvent CH<sub>3</sub>CN 2 g, room temperature.

conversion in very dilute reaction mixture is due to low probability of contact of catalyst, substrate and oxidant. Hence 10 wt equivalent of solvent was used for further optimizations.

The effect of the catalyst loading on the ethyl lactate conversion was studied by varying the catalyst loading from 0.5 to 2 mol% with respect to ethyl lactate and the results are given in Table 3. As expected, when the catalyst loading increased, the reaction was faster and higher conversion was obtained in a shorter time. After 16 h, the ethyl lactate conversion increased from 32 to 83% with an increase in the catalyst loading from 0.5 mol% to 2 mol%, respectively, with 100% selectivity to ethyl pyruvate. After 28 h, the conversion increased to 67, 76 and 100% respectively for 0.5, 1 and 2 mol% catalyst loading with corresponding TON values of 134, 76 and 50 respectively.

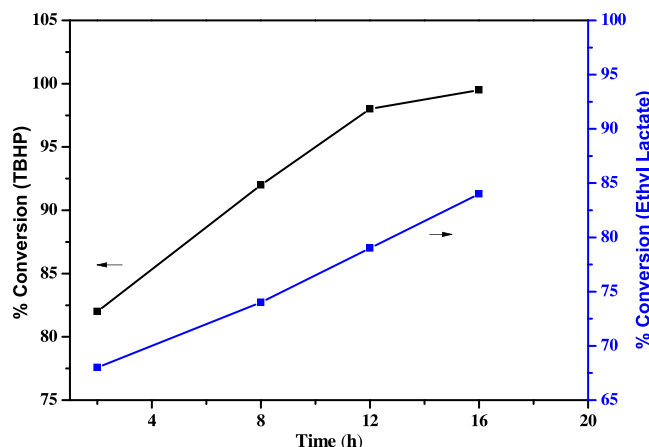
It is well known that peroxides get decomposed in the presence of metal catalysts. The decomposition rate gets accelerated at higher temperature leading to non-availability of sufficient oxidant quantities for the targeted reaction if used in stoichiometric amounts. Hence, excess of oxidants are typically used in catalytic oxidation reactions using metal-based catalysts involving peroxides as oxidants. In the present work, we thus studied as well the effect of the amount of oxidant (TBHP) on ethyl lactate conversion (Table 4). Obviously, for ethyl lactate ODH one molar equivalent of peroxide is needed. However, with 1 equivalent oxidant only 72% conversion was observed indicating partial decomposition of TBHP. With 2 equivalents TBHP very high conversion of 83% was obtained, actually underlining the need for an excess of oxidant to compensate for its parallel undesired decomposition. The conversion of ethyl lactate as well as TBHP were recorded with time (Fig. 1). The results indicated higher conversion of TBHP than ethyl lactate confirming TBHP decomposition. After 16 h TBHP conversion was 100%; however the corresponding ethyl lactate conversion was only 83% indicating 58.5% decomposition of TBHP even at room temperature.

As aforementioned, among the various metal complexes and salts used herein for ethyl lactate ODH, VO(acac)<sub>2</sub> has shown very high efficiency with upto 83% conversion and 100% selectivity to ethyl pyruvate under very mild reaction conditions, and with performances still excellent in the presence of water. However, being homogeneous catalyst, VO(acac)<sub>2</sub> could not be recycled efficiently [20,21]. As vanadium complex has shown efficient oxidation, very simple heterogeneous version of vanadium-based catalyst, V<sub>2</sub>O<sub>5</sub> was used for the same transformation.

**Table 4**Effect of oxidant on ethyl lactate dehydrogenation using VO(acac)<sub>2</sub> as a catalyst.

Entry	Oxidant, (mmol)	Time (h)	Conversion (%)	Selectivity (%)	TON
1	0	16	0	–	–
2	2	16	72	100	36
3	4	16	83	100	42

Reaction conditions: Ethyl lactate 2 mmol; solvent CH<sub>3</sub>CN 2 g, room temperature, catalyst 0.04 mmol (2 mol%), oxidant aq. TBHP.



**Fig. 1.** Ethyl lactate and TBHP conversion with time using VO(acac)<sub>2</sub> catalyst. Reaction conditions: Ethyl lactate 2 mmol; solvent CH<sub>3</sub>CN 2 g, room temperature, catalyst 0.04 mmol (2 mol%), oxidant aq. TBHP 4 mmol.

**Table 5**

Effect of temperature on ethyl lactate oxidative dehydrogenation using V<sub>2</sub>O<sub>5</sub> catalyst.

Entry	Temperature, °C	Time, h	Conversion, %	Selectivity, %
1	RT	5	0	–
		<sup>a</sup> 16	<sup>a</sup> 72	
2	40	5	26	100
		<sup>a</sup> 16	<sup>a</sup> 79	
3	80	5	60	100
		<sup>a</sup> 16	<sup>a</sup> 82	

Reaction conditions: Ethyl lactate 4 mmol; solvent CH<sub>3</sub>CN 4 g, oxidant aq. TBHP 8 mmol, catalyst V<sub>2</sub>O<sub>5</sub> 10 wt.% (w.r.t. substrate);

<sup>a</sup> Catalyst VO(acac)<sub>2</sub> 2 mol.%.

Initially, the effect of temperature was studied to compare the activities of homogeneous and heterogeneous V-based catalysts using 10 wt.% catalyst loading (Table 5). While at room temperature VO(acac)<sub>2</sub> showed very high ethyl lactate conversion, no conversion was observed using heterogeneous V<sub>2</sub>O<sub>5</sub> catalyst, which confirms the lower activity of heterogeneous catalyst compared to homogeneous catalyst. With increasing the temperature to 40 and 80 °C, the heterogeneously catalyzed ethyl lactate conversion after 5 h increased to 26 and 60%, respectively. Thus, 80 °C was used for further performances' optimization.

The effect of the V<sub>2</sub>O<sub>5</sub> catalyst loading on ethyl lactate conversion and ethyl pyruvate selectivity was studied (Table 6). When the catalyst loading was varied from 2 to 10 wt.% with respect to ethyl lactate, conversion after 1 h showed significant difference. The ethyl lactate conversion after 1 h was 12% for the 2 wt.% catalyst loading, which increased to 25 and 35% for 5 and 10 wt.% loading, respectively. Surprisingly, the conversion after 5 h was almost similar (~60%) for all the

**Table 6**

Effect of catalyst loading on ethyl lactate oxidative dehydrogenation using V<sub>2</sub>O<sub>5</sub>.

Entry	Catalyst Loading (wt %)	Time (h)	Conversion (%)	Selectivity (%)
1	2	1	12	100
		5	57	
2	5	1	25	100
		5	60	
3	10	1	35	100
		5	60	

Reaction conditions: Ethyl lactate 4 mmol; solvent CH<sub>3</sub>CN 4 g, 80 °C temperature, oxidant aq. TBHP 8 mmol.

**Table 7**

Change in ethyl lactate conversion using V<sub>2</sub>O<sub>5</sub> catalyst with batch wise addition of TBHP.

Entry.	TBHP addition, mmol	Time, h	Ethyl lactate conversion, %
1	2	1	24
2	2	2	31
3	2	3	49
4	2	4	54
5		4.5	67
6		5	72
7	2	6	75
8	1	7	84
9	1	8	86
10		10	98

Reaction condition: Ethyl lactate - 0.502 g (4 mmol), Catalyst V<sub>2</sub>O<sub>5</sub> 0.05 g, CH<sub>3</sub>CN 4 g, Temp. 80 °C.

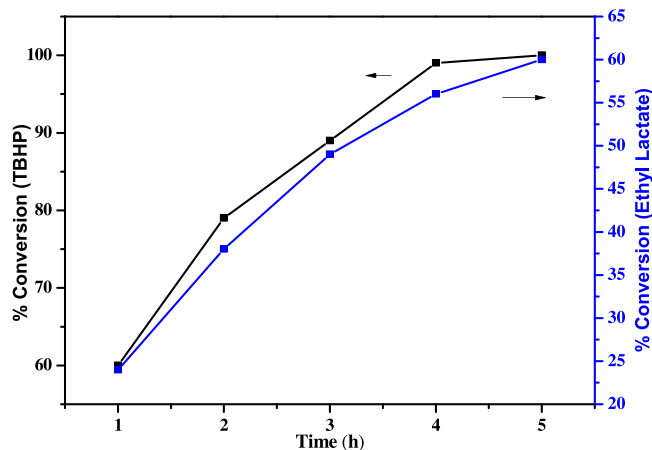
catalyst loadings. This indicated the unavailability of sufficient oxidant during the reaction limiting the maximum conversion to ~60%. This may be due to the relatively high temperature (80 °C) needed for the reaction leading to faster decomposition of TBHP. It is well known that peroxides decompose faster at higher temperatures in presence of metal-based catalysts [22,23]. To confirm this observation, the conversion of TBHP was monitored during the reaction along with ethyl lactate conversion and the results are plotted in Fig. 2.

The results showed almost complete conversion of TBHP in 5 h with only ~60% ethyl lactate conversion indicating TBHP decomposition under reaction conditions due to higher temperature. To control the TBHP decomposition at higher temperature, addition of TBHP was carried out batch wise (Table 7) until quasi-full conversion.

It is very clear from the results (Table 7) that adding TBHP batch-wise enabled better control of the reaction, by limiting its decomposition with an increase in ethyl lactate conversion from 60% (Fig. 2) to 72% after 5 h after addition of 2 equivalents aq. TBHP. Further, addition of 1 equivalent TBHP in small portions led to 98% ethyl lactate conversion with 100% ethyl pyruvate selectivity after 10 h with total 3 equivalents TBHP. The results showed very high efficiency of the V<sub>2</sub>O<sub>5</sub> catalyst for oxidative dehydrogenation of ethyl lactate to ethyl pyruvate.

### 3.1. Catalyst recycling

The main aim of the heterogeneous catalyst (V<sub>2</sub>O<sub>5</sub>) for oxidative dehydrogenation was efficient recycle of the catalyst. Indeed, the catalyst could be recycled five times (Fig. 3) without losing activity in



**Fig. 2.** Ethyl lactate and TBHP conversion with time using V<sub>2</sub>O<sub>5</sub> catalyst. Reaction conditions: Ethyl lactate 4 mmol; solvent CH<sub>3</sub>CN 4 g; oxidant aq. TBHP 8 mmol; catalyst 10 wt.% w.r.t. substrate

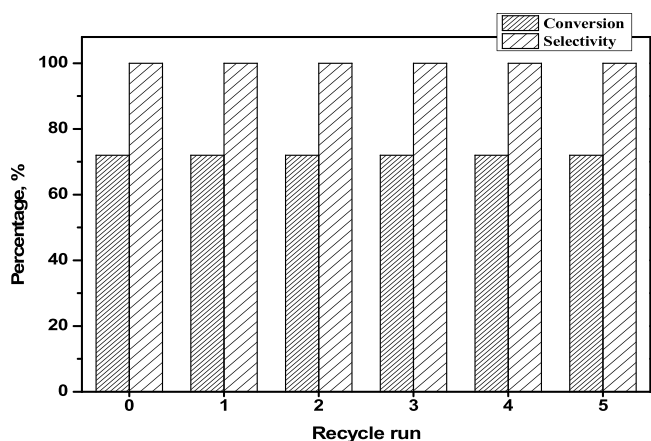


Fig. 3. Catalyst recycle study for ethyl lactate dehydrogenation over  $V_2O_5$ . Reaction conditions: Ethyl lactate 8 mmol; solvent  $CH_3CN$  8 g; oxidant aq. TBHP 16 mmol; catalyst 10 wt.% (w.r.t. substrate); time 5 h.

terms of both ethyl lactate conversion and ethyl pyruvate selectivity. For this study, TBHP (total of 2 equivalents) was added batchwise over a period of 4 h and the reaction was continued further till 5 h, like in the procedure used for Table 7. After reaction, the mixture was decanted leaving behind the catalyst which was dried at  $100^\circ C$  before next run. Thus, the catalyst was recycled efficiently five times with 72% ethyl lactate conversion and 100% ethyl pyruvate selectivity.

To confirm the integrity of the catalyst during the reaction, FTIR of the fresh and used catalyst was recorded (Fig. 4). The FTIR spectra showed similar patterns with characteristics bands at  $481$ ,  $534$  and  $597\text{ cm}^{-1}$  for symmetric and asymmetric V–O–V stretching vibrations of  $V_2O_5$  as well as at  $832\text{ cm}^{-1}$  for V–O vibrations. The characteristics band at  $1017\text{ cm}^{-1}$  can be attributed to symmetric stretching of V=O bond [24,25]. The similar FTIR patterns before and after reaction suggested no change in structural characteristic of the catalyst after reaction.

The structural integrity was further confirmed by XRD analysis of fresh as well as used catalyst (Fig. 5).

XRD pattern of  $V_2O_5$  showed reflections at  $2\theta$   $20.2$ ,  $26.24$ ,  $30.98$ ,  $15.42$  and  $34.38^\circ$  corresponding to the 001, 110, 301, 200 and 310 planes, respectively, which matched well with JCPDS data file no.77-2418 for orthorhombic  $V_2O_5$  phase. In the used catalyst, additional peaks at  $2\theta$  of  $26$  and  $37.5^\circ$  were observed. However, these additional peaks also corresponded to orthorhombic phase of  $V_2O_5$ . The

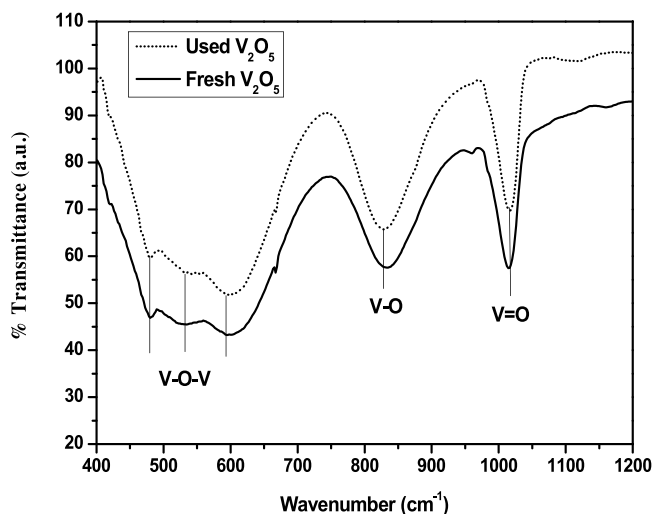


Fig. 4. FTIR spectra of  $V_2O_5$  catalyst before and after ethyl lactate dehydrogenation.

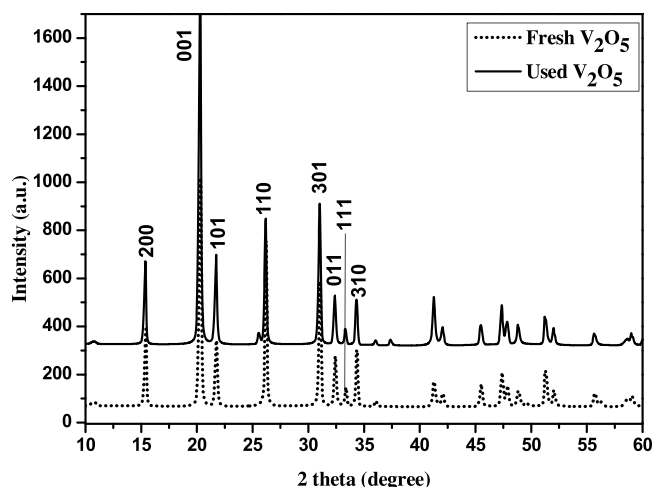


Fig. 5. XRD pattern of fresh and used  $V_2O_5$  catalyst.

XRD pattern of used catalyst showed significant increase in the intensity of the peaks compared to the fresh catalyst indicating increase in the crystallinity. Due to the increased crystallinity of used catalyst, very weak peaks at  $2\theta$  of  $26$ ,  $37.5^\circ$  of orthorhombic  $V_2O_5$ , which were not detected in fresh catalyst, could be observed in used catalyst. Hence, no change in the crystallographic phase of the catalyst after catalytic reaction was observed.

### 3.1.1. Hot filtration experiment

In heterogeneous catalysis, leaching of active component may be a cause of the catalytic activity. Hence, to confirm the heterogeneous nature of the catalyst hot filtration experiment was carried out. Initially, the reaction was carried out for 2 h (Table 8, entry 1) with catalyst after which the catalyst was separated from the reaction mixture by centrifugation followed by decantation. The same reaction was continued further without catalyst for next 3 h. Initially with catalyst after 2 h, 31% conversion was obtained which increased only marginally to 37% after separating the catalyst even after 3 h reaction time indicating no leaching of catalytically active species in the reaction medium. The metal leaching was additionally confirmed by ICP analysis and the results showed the presence of  $< 1\text{ ppm V}$  in the reaction solution confirming no leaching of metal during the reaction.

### 3.2. Plausible reaction mechanism

Typically, oxidation using peroxides proceeds via radical mechanism. To confirm whether this statement applies to our reaction system, one experiment was carried out by adding TEMPO as a radical quencher after 35% conversion. As expected, the reaction did not proceed further after addition of TEMPO, which confirmed the radical mechanism operating as well in the present case. In the literature, various mechanisms have been proposed for oxidative dehydrogenation of ethyl lactate to ethyl pyruvate [12–14,26]. As per the previous reports by Sheldon et al [27], peroxide initially reacts with metal oxo

Table 8  
Hot filtration experiment for metal leaching test.

Entry	Time (h)	Conversion (%)	Selectivity (%)
1	2 <sup>a</sup>	31	100
2	1	37	100
3	2	37	100
4	3	37	100

Reaction Conditions: Ethyl lactate 2 mmol; solvent  $CH_3CN$  6 g; oxidant aq. TBHP 4 mmol; catalyst  $V_2O_5$  10 wt.% w.r.t. substrate.

<sup>a</sup> Before filtration.

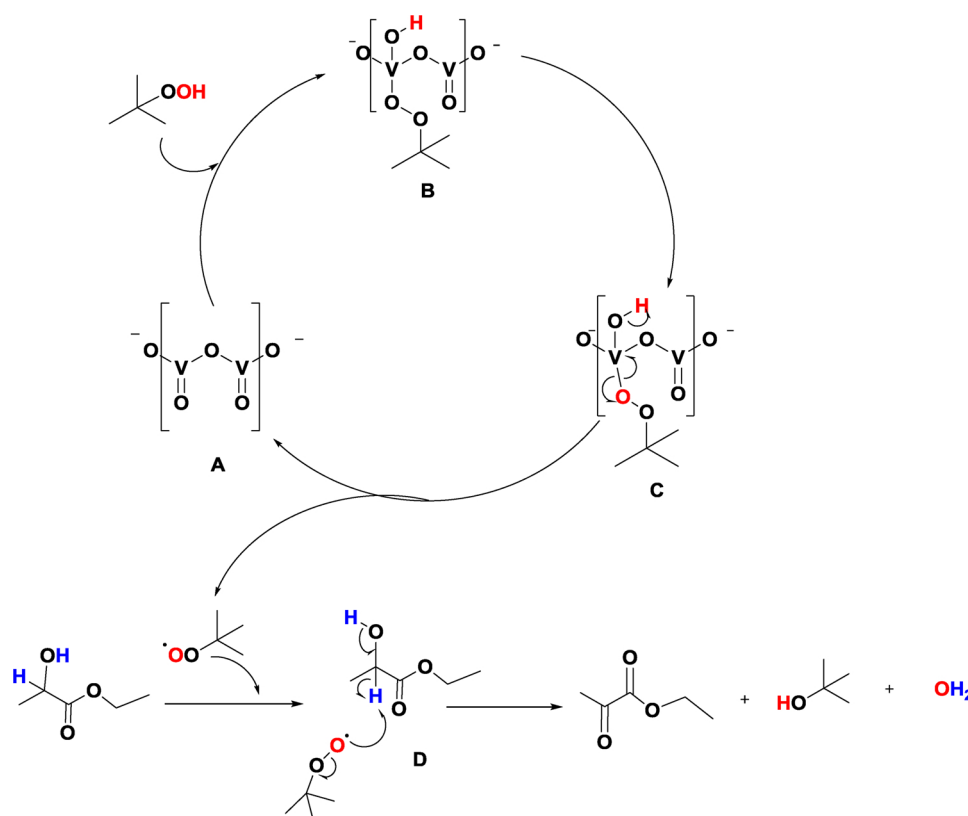


Fig. 6. Plausible reaction mechanism for oxidative dehydrogenation of ethyl lactate to ethyl pyruvate using  $V_2O_5$  catalyst.

Table 9

Comparative results of ethyl lactate conversion with respect to literature.

	Catalyst	Substrate	Reaction conditions	Conversion %	Selectivity %	Ref.
1	MoVNbOx/TiO <sub>2</sub>	Ethyl Lactate	170–190 °C, O <sub>2</sub>	50	80	[10]
2	VOCl <sub>3</sub>	Ethyl Lactate	Room temperature, O <sub>2</sub>	50	31	[11]
3	TS-1	Ethyl Lactate	60 °C, H <sub>2</sub> O <sub>2</sub>	100	97 <sup>a</sup>	[12]
4	TiO <sub>2</sub>	Ethyl lactate	130 °C, 1 MPa O <sub>2</sub>	70	80	[13]
5	NH <sub>4</sub> VO <sub>3</sub> /VO <sub>3</sub> -TiO <sub>2</sub>	Ethyl Lactate	130 °C, 1 MPa O <sub>2</sub>	90	60	[14]
6	V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	Ethyl Lactate	160–180 °C, O <sub>2</sub>	62	78	[15]
7	MoO <sub>3</sub> /TiO <sub>2</sub>	Lactic acid	190 °C, Air	80	80	[28]
8	V <sub>2</sub> O <sub>5</sub>	Ethyl Lactate	TBHP, 80 °C	98	100	Present work
9	VO(acac) <sub>2</sub>	Ethyl Lactate	TBHP, RT,	100	100	Present work

<sup>a</sup> Yield.

center generating metal peroxide as catalytically active species, which further drives the catalytic cycle for formation of the product. Based on the reaction results and literature support, the following mechanism is proposed.

After addition of TBHP to  $V_2O_5$  (A), it forms vanadium peroxy species on the surface (B) (Fig. 6). Then, it forms radical via homolytic cleavage (C) and generates *t*-butyl peroxy radical, which leads to regeneration of catalyst to its original form. Radical of *t*-butyl hydroperoxide initiates the oxidation of ethyl lactate and form ethyl pyruvate with *tert*-butanol and water as a side product.

The obtained results with the present catalytic system for ODH of ethyl lactate to ethyl pyruvate under mild reaction conditions are promising. The comparison of the results with the literature is shown in Table 9.

It is obvious that the results obtained in the present work using homogeneous and heterogeneous vanadium-based catalysts are promising in terms of ethyl lactate conversion as well as ethyl pyruvate selectivity.

#### 4. Conclusion

Very efficient protocol for the oxidative dehydrogenation of ethyl lactate to ethyl pyruvate using aqueous TBHP as an oxidant and  $V_2O_5$  as a very simple and recyclable catalyst was developed. Very high ethyl lactate conversion (upto 98%) was obtained with 100% selectivity to ethyl pyruvate. Homogeneous VO(acac)<sub>2</sub> complex also showed very high efficiency for ethyl lactate dehydrogenation at room temperature with ~83% conversion and 100% selectivity to ethyl pyruvate though the complex could not be recycled. The main highlight of this work is almost complete conversion and 100% selectivity for ethyl pyruvate under mild reaction conditions.

#### Acknowledgements

This work is carried out as a part of collaboration under International Associated Laboratory program between CSIR (NCL) India and CNRS (UCCS) France.

## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcata.2019.117246>.

## References

- [1] T. Ghaffar, M. Irshad, Z. Anwar, T. Aqil, Z. Zulfiqar, A. Tariq, M. Kamaran, N. Ehsan, S. Mehmood, J. Radiat. Res. Appl. Sci. 7 (2014) 222–229, <https://doi.org/10.1016/j.jrras.2014.03.002>.
- [2] H. Oh, Y.J. Wee, J.S. Yun, S.H. Han, S. Jung, H.W. Ryu, Bioresour. Technol. Rep. 96 (2005) 1492–1498, <https://doi.org/10.1016/j.biortech.2004.11.020>.
- [3] S. Jantasee, M. Kienberger, M. Siebenhofer, J. Chem. Technol. Biotechnol. 92 (2017) 2885–2893, <https://doi.org/10.1002/jctb.5237>.
- [4] A. Komesu, J. Oliveira, L.H.S. Martins, M.R. Wolf Maciel, R. Maciel Filho, BioResources 12 (2017) 4364–4383.
- [5] A.J. Muller, J.B. Duhadaway, D. Jaller, P. Curtis, R. Metz, G.C. Prendergast, Cancer Res. 70 (2010), <https://doi.org/10.1158/0008-5472.CAN-09-3613>.
- [6] H. Hayashi, S. Sugiyama, Y. Katayama, K. Sakai, M. Sugino, N. Shigemoto, J. Mol. Catal. 83 (1993) 207–217, [https://doi.org/10.1016/0304-5102\(93\)87020-9](https://doi.org/10.1016/0304-5102(93)87020-9).
- [7] P. Xu, J. Qiu, C. Gao, C. Ma, J. Biosci. Bioeng. Japan 105 (2008) 169–175, <https://doi.org/10.1263/jbb.105.169>.
- [8] S. Lomate, T. Bonnotte, S. Paul, F. Dumeignil, B. Katryniok, J. Mol. Catal. A 377 (2013) 123–128.
- [9] H. Hayashi, S. Sugiyama, N. Masaoka, N. Shigemoto, Ind. Eng. Chem. Res. 34 (1995) 135–139, <https://doi.org/10.1021/ie00040a011>.
- [10] X. Zhao, C. Zhang, C. Xu, H. Li, H. Huang, L. Song, X. Li, Chem. Eng. J. 296 (2016) 217–224, <https://doi.org/10.1016/j.cej.2016.03.088>.
- [11] T. Yasukawa, W. Ninomiya, K. Ooyachi, N. Aoki, K. Mae, Ind. Eng. Chem. Res. 50 (2011) 3858.
- [12] T. Lu, J. Zou, Y. Zhan, X. Yang, Y. Wen, X. Wang, L. Zhou, J. Xu, ACS Catal. 8 (2018) 1287–1296, <https://doi.org/10.1021/acscatal.7b03558>.
- [13] E.V. Ramos-Fernandez, N.J. Geels, N.R. Shiju, G. Rothenberg, Green Chem. 16 (2014) 3358–3363, <https://doi.org/10.1039/c4gc00191e>.
- [14] W. Zhang, G. Innocenti, P. Oulego, V. Gitis, H.-H. Wu, B. Ensing, F. Cavani, G. Rothenberg, N.R. Shiju, ACS Catal. 8 (2018) 2365–2374, <https://doi.org/10.1021/acscatal.7b03843>.
- [15] W. Zhang, G. Innocenti, M. Ferbinteanu, E.V. Ramos-Fernandez, A. Sepulveda-Escribano, H. Wu, F. Cavani, G. Rothenberg, N.R. Shiju, Catal. Sci. Technol. 8 (2018) 3737–3747.
- [16] H. Hayashi, S. Sugiyama, N. Shigemoto, K. Miyaura, S. Tsujino, K. Kawashiro, S. Uemura, Catal. Lett. 19 (1993) 369–373, <https://doi.org/10.1007/BF00767080>.
- [17] D. Wang, W. Liu, Z. Xie, S. Tian, D. Su, Q. Wei, Catal. Today (2018), <https://doi.org/10.1016/j.cattod.2018> in press.
- [18] B. Monteiro, S.S. Balula, S. Gago, C. Grosso, S. Figueiredo, A.D. Lopes, A.A. Valente, M. Pillinger, P. Lourenco, I.S. Gonçalves, J. Mol. Catal. A 297 (2009) 110–117, <https://doi.org/10.1016/j.molcata.2008.09.012>.
- [19] V. Hornebecq, Y. Mastai, M. Antonietti, S. Polarz, Chem. Mater. 15 (2003) 3586–3593.
- [20] L. Stepovik, M. Gulenova, Russ. J. Gen. Chem. 79 (2009) 1663–1670, <https://doi.org/10.1134/S1070363209080143>.
- [21] L.P. Stepovik, M.V. Gulenova, A.N. Tishkina, V.K. Cherkasov, Russ. J. Gen. Chem. 77 (2007) 1254–1262, <https://doi.org/10.1134/S1070363207070183>.
- [22] C.M. Miller, R.L. Valentine, Wat. Res. 33 (1999) 2805–2816.
- [23] C.M. Lousada, A.J. Johansson, T. Brinck, M. Jonsson, J. Phys. Chem. C 116 (2012) 9533–9543, <https://doi.org/10.1021/jp300255h>.
- [24] Y. Zhang, Mater. Sci.-Poland 35 (2017) 188–196.
- [25] G. Fabbri, P. Barbaldi, Infrared Spectra of Stoichiometric Oxides of Vanadium Analytical Chemistry Vol. 44 (1972) No. 7.
- [26] M.V. Kirillova, M.L. Kuznetsov, Y.N. Kozlov, L.S. Shul'Pina, A. Kitaygorodskiy, A.J.L. Pombeiro, G.B. Shul'Pin, ACS Catal. 1 (2011) 1511–1520, <https://doi.org/10.1021/cs200237m>.
- [27] R.A. Sheldon, I.W.C.E. Arends, A. Dijkman, Catal. Today 57 (2000) 157–166.
- [28] K. Liu, X. Huang, E.A. Pidko, E.J.M. Hensen, Green Chem. 19 (2017) 3014–3022.