Studies on the reaction pathways for the selective oxidation of propane to acrolein over MoPO/SiO₂ catalyst by IR spectroscopy

X.D. Yi *, X.B. Zhang, W.Z. Weng, H.L. Wan *

State Key Laboratory for Physical Chemistry of the Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China

Abstract

To understand possible reaction pathway for propane selective oxidation to acrolein over the MoPO/SiO₂ catalyst, the surface species formed by adsorption of the reactant (propane), possible intermediates or their probe molecules (propene, isopropanol, 1-propanol, 2-Br-propane, allyl alcohol) as well as the reaction products (acrolein, acetone and propanal) on the catalyst and the transformation of these species at elevated temperature under vacuum or under O₂/He atmosphere were studied by IR spectroscopy. When a gas mixture of propane/oxygen was introduced to the catalyst at 473 K for 4 h, the band of adsorbed acetone with a shoulder assigned to adsorbed acrolein was observed. Using 2-Br-propane or isopropanol as the probe molecule, characteristic IR bands associated with isopropoxy species were detected over MoPO/SiO₂ catalyst at 323 K. Upon heating to 423 K, the band of adsorbed acetone and adsorbed acrolein was also observed. The overall spectrum actually seems closely similar to that described above, arising from the adsorption of propane at the same temperature. On the other hand, if 1-Br-propane or *n*-propanol was used as the probe molecule, the formation of propanal was detected via *n*-propoxy. It was found that when propene was adsorbed on the catalyst at 373 K, besides the σ-allyl species, isopropoxy was also detected by the IR spectra. Upon heating to 423 K, two new bands ascribable to the acrolein and adsorbed acetone were observed. Based on these results and density functional calculations, the reaction network for selective oxidation of propane to acrolein over this catalyst was proposed. The propane activation is initiated by the H abstraction from the methylene group, leading to the formation of isopropyl species, which rebounds to the surface to form the isopropoxy species. The isopropoxy species can either undergo α-H elimination to form byproduct acetone or undergo β-H elimination to form the propylene. Propylene can undergo α-H abstraction to form a π-allyl, which is then followed by O insertion to form a σ-allyl, and is eventually dehydrogenated to acrolein.
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1. Introduction

The partial oxidation of light alkanes has attracted much attention because it represents a route to obtain more valuable organic compounds such as alcohols, aldehydes, ketones and acids from low cost saturated hydrocarbons [1,2]. The main challenge for partial oxidation is that light alkanes are usually less reactive than the desired products, and further oxidized to total oxidation products, CO$_x$, is thermodynamically favored. The selective oxidation of propane to acrolein was studied over various catalyst systems, but only a few showed good catalytic performances [3–5].

Current research on propane selective oxidation to acrolein concerns mainly fundamental aspects. In particular, a debate still exists on the reaction mechanism. The partial oxidation products such as propene, acrolein, acetone, propanal, acrylic acid, propionic acid and acetic acid as well as carbon oxides and water were observed when propane oxidation is carried out over different catalysts using flow reactors. Based on these results, significantly different reaction networks have been proposed in the literatures over Ag-Bi-Mo-V-O [6], Bi-Ba-Te-O [7], Te-P/NiMoO [8] and Mo-V-Te-Nb-O catalyst [9,10]. Broadly speaking, three major reaction routes are possible starting from propane. In the first route, propane is oxidized to isopropanol, which can dehydrate to propene or further oxidize to acetone. In the second route, propane forms propene by oxidative dehydrogenation that is oxidized to allyl alcohol and acrolein. In the third route, propane is oxidized to 1-propanol, which dehydrates to

* Corresponding authors.
E-mail addresses: xdyi@xmu.edu.cn (X.D. Yi), hlwan@xmu.edu.cn
(H.L. Wan).

propene or is oxidized to propanal. This reaction network may be further complicated by transformations between intermediates of different routes.

In situ spectroscopy investigations of surface species can provide important insights into the reaction intermediates for the reaction pathways. However, it is unlikely that surface intermediates can be identified by FTIR studies using only propane. The general approach has been to perform FTIR studies for the adsorption of compounds expected to be related to surface species, such as propene, isopropanol and 1-propanol, etc. Several groups have performed in situ IR studies to investigate propane oxidation [11–16]. Busca and co-workers [11–13] investigated the mechanism of propane total oxidation on spinel-type catalysts Mn_3O_4, Co_3O_4 and $MgCr_2O_4$ by IR spectroscopy. A surface reaction network in propane total oxidation was proposed in which isopropoxy species was the major intermediate. Centi et al. [14] studied the adsorption and transformation of propane and possible intermediates on VSbO catalyst in relation to the mechanism of acrylonitrile synthesis from propane. The acrylate species was observed in the spectra of propane adsorption. Their results suggested that the main route of propane conversion is through the formation of propene as intermediate, although a side reaction of acrylate formation via propionate intermediate is also possible. Zaki and co-workers [15] also studied the propane, isopropanol, acetone and acetic acid over ZrO_2, TiO_2 and CeO_2 catalysts by IR spectroscopy. Their analysis indicated that the initial catalytic interaction is the oxidative dehydrogenation of propane into propene, rather than the oxidative addition into isopropanol.

However, few details are known about the involved adspecies and their conversion dynamics on the catalyst surface for the selective oxidation of propane to acrolein or acrylic acid. Recently, we have showed that MoPO/SiO$_2$ catalyst was active and selective in the propane selective oxidation to acrolein with the 30.2% selectivity of acrolein at the propane conversion of 19.8% [17,18]. The major products of the propane oxidation over this catalyst are propene, acrolein and carbon oxides, but small amounts of acetone, propanal, acetaldehyde, methanol and cracking hydrocarbon products are also produced. To understand possible reaction pathways for propane selective oxidation to acrolein over the MoPO/SiO$_2$ catalyst, the surface species formed by adsorption of the reactant (propane), possible intermediates or their probe molecules (propene, isopropanol, 1-propanol, 2-Br-propane, allyl alcohol) as well as the reaction products (acrolein, acetone and propanal) on the catalyst and the transformation of these species at elevated temperature under vacuum or under O_2/He atmosphere were studied by IR spectroscopy, respectively.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by impregnation of silica (294 m^2/g) with a solution containing the desired quantities of ammonium heptamolybdate and $NH_4H_2PO_4$. Impregnated samples were dried overnight at 393 K and calcined in air at 653 K

for 4 h followed by at 823 K for a further 6 h. The sample is denoted as MoPO/SiO$_2$ (Mo:P:Si = 3.5:5:100, molar ratio). The surface area of the catalyst as measured by BET methods was 207 m^2/g.

2.2. Catalytic tests

The experiments of propane and isopropanol oxidations were carried out at atmospheric pressure in a continuous flow system with a fixed-bed quartz tubular reactor operated over a wide range of temperatures. The temperature was measured with a coaxial thermocouple. To minimize possible homogeneous reactions, the space of the reactor up and down the catalyst bed was filled with quartz wool. The exit gases were heated to 393 K to prevent product condensation. The reactant and products were analyzed by two on-line gas chromatographs operating three columns: a TDX-601 column and Al_2O_3 column impregnated with squalane for the separation of C_3H_8, C_3H_6, C_2H_4, CH_4, CO and CO_2; a GDX-103 column for the separation of acetaldehyde, acrolein, acetone and propanal.

2.3. Catalyst characterization

The IR spectra were recorded in transmission mode with a Perkin-Elmer Spectrum 2000 FTIR spectrometer using an in situ IR cells (BaF$_2$ windows) connected to an evacuation-gas manipulation apparatus. The catalyst power was pressed into self-supporting discs that were calcined in O$_2$ at 773 K for 1 h, followed by evacuation at the same temperature for 10 min and cooled under vacuum to certain temperature to record the background spectra of the cell and the catalyst wafer. The selective molecule (10–5 Torr, depending on the vapor pressure of the liquid reactants at RT) was then introduced into the cell at 323 K and the gas/solid interface was maintained for 10 min to 4 h. The IR spectra of adsorbed species and gaseous species were recorded under vacuum or under 5% O$_2$/He atmosphere at elevated temperature, respectively, after the gas phase components in the IR cell were removed by evacuation. The spectrum of the adsorbed species was referenced to the background spectrum of the pretreated catalyst recorded under vacuum at the same temperature before the admission of adsorbates.

In the case of propane, due to its inertness, a slightly different protocol was used. A gas mixture of propane/oxygen was contacted with the catalyst at 323, 373, 423, 473 and 523 K, respectively, then recording the spectrum for each temperature.

3. Results and discussion

3.1. Propane oxidation

The results of propane oxidation over catalyst are showed in Table 1. The major products of the propane oxidation over MoPO/SiO$_2$ catalyst are propene, acrolein and carbon oxides (CO and CO$_2$), but small amounts of acetone, propanal, acetaldehyde, methanol and cracking hydrocarbon products (methane and ethylene) were also produced at higher temperature. As the temperature was increased, the selectivity to propene decreases,

Table 1
Propane selective oxidation over MoPO/SiO$_2$ catalyst

Temperature (K)	C$_3$H$_8$ conversion (%)	Selectivity (%)					
		C$_3$H$_6$	ACR	PAL	ACE	Others	CO$_x$
673	5.8	77.2	10.3	–	6.1	–	6.4
723	11.7	50.4	14.7	0.5	4.1	4.4	25.9
773	30.2	30.3	19.8	0.8	6.2	10.8	32.1
823	36.8	22.6	8.5	–	–	14.5	54.4

Reaction conditions: C$_3$H$_8$/O$_2$/N$_2$ = 2/1/4, 6000 ml g-cat.$^{-1}$ h^{-1}; cat., 0.2 g; ACR, acrolein; PAL, propanal; ACE, acetone; CO$_x$, CO + CO$_2$; others, C$_2$H$_4$ + CH$_4$ + acetaldehyde + methanol + formaldehyde.

while the selectivity to acrolein shows a maximum at 773 K. This implies that propene undergoes consecutive oxidation, mainly to acrolein. At 773 K, the conversion of propane was 30.2%, while the selectivities to propene and acrolein are 30.3 and 19.8%, respectively.

3.2. IR spectra arising from acetone, isopropanol and 2-Br-propane adsorptions

Since all the intermediates or their probe molecules for propane selective oxidation to acrolein will convert to oxygenated compounds at last over the catalysts, for reading purposes, the experiments concerning the adsorption of oxygenated compounds will be discussed first. For FTIR studies using MoPO/SiO$_2$ catalyst, only bands above 1300 cm^{-1} are observable due to strong adsorption by the catalyst in the region below 1300 cm^{-1}.

3.2.1. Acetone adsorption

The spectra of acetone adsorbed at 323 K show evidence that acetone adsorbs at 323 K without reaction (Fig. 1b). The sharp and very intense band at 1703 cm^{-1} can be assigned to $\nu_{C=O}$ of acetone coordinated to Lewis-acid sites of catalyst surface. Other bands are observed at 1422 and 1373 cm^{-1} (CH$_3$ bendings) [19]. These bands decrease in intensity with increasing temperature up to 473 K.

3.2.2. Isopropanol and 2-Br-propane adsorption

The adsorption of isopropanol on MoPO/SiO$_2$ catalyst at 323 K is characterized by IR bands at 2983, 2943 and 2885 cm^{-1} (ν_{CH}), 1469 and 1461 cm^{-1} (δ_{as,CH_3}), 1389 and 1378 cm^{-1} (δ_{s,CH_3}) and 1343 cm^{-1} (δ_{CH}) (Fig. 2a). These bands can be assigned to the isopropoxy species [11,20]. It is interesting to see that the IR bands shown in Fig. 2a are very similar to those arising from the adsorption of 2-Br-propane over the same catalyst at same temperature. Since the strength of C–Br bond in 2-Br-propane is weak than that of C–H bond in the methylene group of propane, the isopropyl species should be more easily formed from 2-Br-propane than from propane. Therefore, we can use 2-Br-propane as a probe molecule to investigate the conversion of isopropyl species on the catalyst. This observation suggested that isopropoxy species is readily formed by adsorption of 2-Br-propane on the catalyst at 323 K. A rational explanation to the observation is that the carbon–oxygen interaction is stronger than the carbon–metal interaction. Therefore, the isopropyl species interacts most probably with a lattice oxygen atom than with a surface metal cation [21,22]. As the samples were heated to 423 K under vacuum, the band of adsorbed acetone (1688 cm^{-1}, $\nu_{C=O}$) with a shoulder of adsorbed acrolein (1668 cm^{-1}, $\nu_{C=O}$) was observed. This assignment is based on the comparison of the spectra c in Fig. 2 with the IR spectra arising from acetone and acrolein adsorption over the catalyst under the comparable conditions (Figs. 1 and 4).
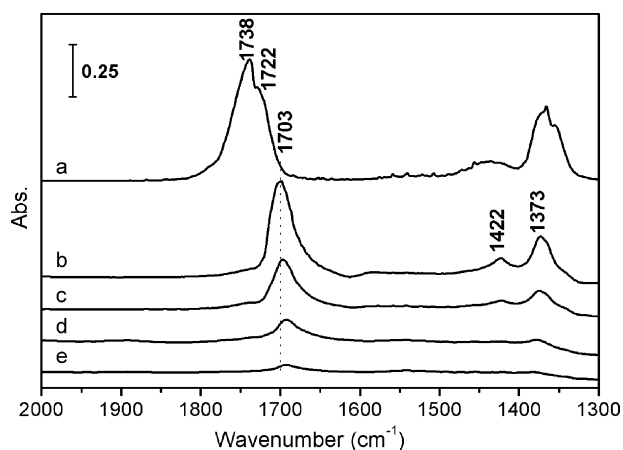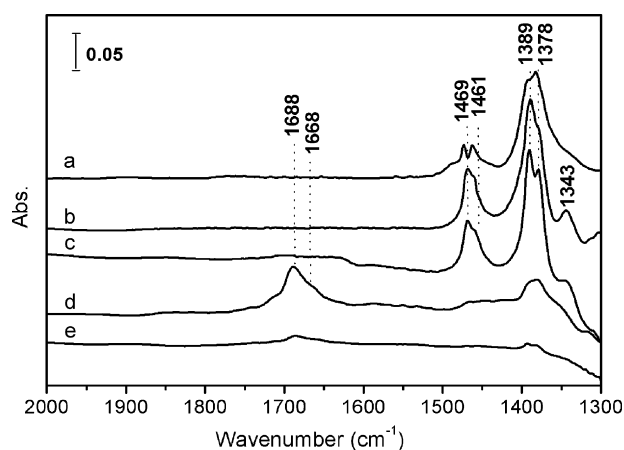

Fig. 1. IR spectra of adsorbed species arising from interaction of MoPO/SiO$_2$ catalyst with (a) gaseous acetone at 323 K for 10 min, followed by evacuation and heating under vacuum to (b) 323 K, (c) 373 K, (d) 423 K and (e) 473 K.

Fig. 2. IR spectra of adsorbed species arising from interaction of MoPO/SiO$_2$ catalyst with (a) gaseous isopropanol at 323 K for 10 min, followed by evacuation and heating under vacuum to (b) 323 K, (c) 373 K, (d) 423 K and (e) 473 K.
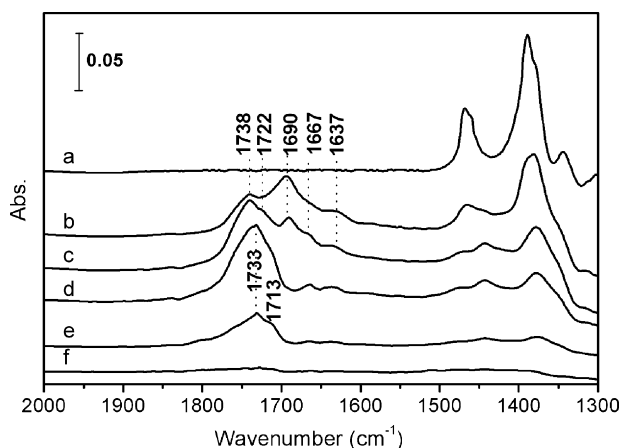
Fig. 3. IR spectra arising from interaction of MoPO/SiO₂ catalyst with isopropanol at 323 K for 10 min, followed by evacuation at (a) 323 K and heating under 5% O₂/He atmosphere to (b) 423 K, (c) 473 K, (d) 573 K, (e) 673 K and (f) 773 K.
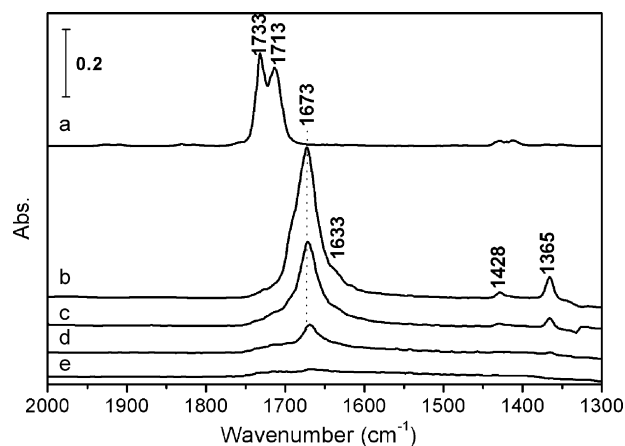

Fig. 4. IR spectra of adsorbed species arising from interaction of MoPO/SiO₂ catalyst with (a) gaseous acrolein at 323 K for 10 min, followed by evacuation and heating under vacuum to (b) 323 K, (c) 373 K, (d) 423 K and (e) 473 K.

In order to obtain the information of gaseous species, the IR spectra of the sample containing the pre-adsorbed isopropoxy species heated under 5% O₂/He atmosphere were also recorded. When the sample containing the pre-adsorbed isopropoxy species was heated under 5% O₂/He atmosphere from 323 to 473 K (Fig. 3c), the IR bands of the adsorbed acetone (1690 cm^{-1}), gaseous acetone (1738 and 1722 cm^{-1}, $\nu_{C=O}$) and propene (1667 and 1637 cm^{-1}, $\nu_{C=C}$) were detected. After heating to 573 K, the broad bands at 1733 and 1713 cm^{-1} ($\nu_{C=O}$), due to gaseous acrolein, are also observed. These observations indicated that acetone, propene and acrolein are the main products of the oxidative conversion of surface isopropoxy species. This is in agreement with the results of the catalytic oxidation of isopropanol using a fixed bed reactor (Table 2).

Conversion of the isopropanol starts to be observable at 423 K and approaches to be total at 523 K. At this temperature, the main products are propene and acetone. As the temperature is increased to 623 K, acrolein is formed and the selectivity to acrolein increases, while the selectivity to propene decreases with increasing temperature. Additionally, small amounts of propanal are also observed at higher temperature and may result from the oxidation of propene.

These results showed that adsorption of isopropanol readily give rise to isopropoxy species, which can either convert to propene by β-hydrogen elimination or to acetone by dehydro-

genation. The former can further convert to acrolein through allylic process.

3.3. IR spectra arising from acrolein, allyl alcohol and propene adsorptions

3.3.1. Acrolein adsorption
The spectra of the adsorbed species of acrolein over MoPO/SiO₂ catalyst and followed by evacuation at higher temperature are shown in Fig. 4. The most intense band assigned to C=O stretching is observed at 1673 cm^{-1}. Other bands are observed at 1633 cm^{-1} (C=C stretching), 1428 cm^{-1} (CH₂ scissoring) and 1365 cm^{-1} (CH deformation) [23]. With increasing temperature, the bands associated with acrolein coordinated to Lewis-acid sites progressively decrease and disappear after evacuation at 523 K.

3.3.2. Allyl alcohol adsorption
Allyl alcohol in contact with MoPO/SiO₂ catalyst at 323 K (Fig. 5) gives rise to a spectrum with the frequency of the bands modified with respect to those of gaseous allyl alcohol. The bands at 3091, 3024, 2992, 2946 and 2892 cm^{-1} are assigned to ν(C–H) stretching; the band at 1649 cm^{-1} is assigned to ν(C=C) stretching; a stronger and very sharp band at 1426 cm^{-1} is due to the scissoring of the =CH₂ group, while bands at 1460, 1346 and 1380 cm^{-1} are assigned to the scissoring of the −CH₂−O

Table 2
Isopropanol oxidation over MoPO/SiO₂ catalyst

Temperature (K)	2-Propanol conversion (%)	Selectivity (%)					
		C₃H₆	ACR	ACE	PAL	Others	CO$_x$
523	100	47.5	–	39.5	–	7.9	5.1
623	100	55.2	5.3	18.4	–	5.8	15.3
673	100	49.9	9.4	12.5	1.5	7.9	18.8
723	100	40.1	17.9	9.1	1.2	8.5	23.2
773	100	36.1	18.7	6.8	1.0	7.2	30.2

Reaction conditions: isopropanol/O₂/N₂ = 2/1/4, 6000 ml g-cat.$^{-1}$ h^{-1}; cat., 0.2 g; ACR, acrolein; PAL, propanal; ACE, acetone; CO$_x$, CO + CO₂; others, C₂H₄ + CH₄ + acetaldehyde + methanol + formaldehyde.
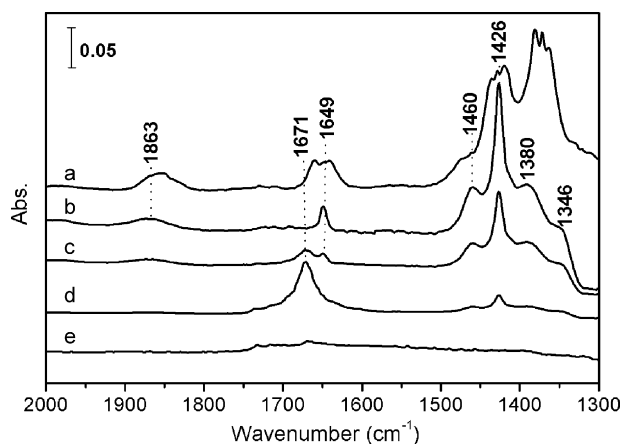
Fig. 5. IR spectra of adsorbed species arising from interaction of MoPO/SiO$_2$ catalyst with (a) gaseous allyl alcohol at 323 K for 10 min, followed by evacuation and heating under vacuum to (b) 323 K, (c) 373 K, (d) 423 K and (e) 473 K.

Fig. 7. IR spectra of adsorbed species arising from interaction of propene with MoPO/SiO$_2$ catalyst at 373 K for 30 min, followed by evacuation at (a) 373 K and heating under vacuum to (b) 423 K and (c) 473 K.

group and CH$_2$ wagging. The absence of the adsorption band related to the OH stretching (3663 cm^{-1}) and the value of the ν(C=C) frequency shifted down with respect to the gaseous allyl alcohol (1654 cm^{-1}, $\nu_{C=C}$) indicate that these bands are due to allyl alcoholate [11]. As the temperature increases under vacuum, a progressive increase in the intensity of the band at 1671 cm^{-1} is observed up to 423 K which indicates that acrolein, not present initially, forms progressively with a parallel decrease in the relative intensity of the bands of allyl alcoholate.

The IR spectra of the sample containing the pre-adsorbed allyl alcoholate species heated under 5% O$_2$/He atmosphere from 323 to 773 K are shown in Fig. 6. With increasing temperature, the bands associated with allyl alcoholate progressively decrease, while the bands of gaseous acrolein (1733 and 1713 cm^{-1}, $\nu_{C=O}$) increase in relative intensity up to 473 K, and then decrease at higher temperatures. However, additional band at 1763 cm^{-1} indicates the formation of gaseous propanal. Since propanal is not observed starting from acrolein adsorption, it is reasonable to consider that propanal may result from allyl alcoholate
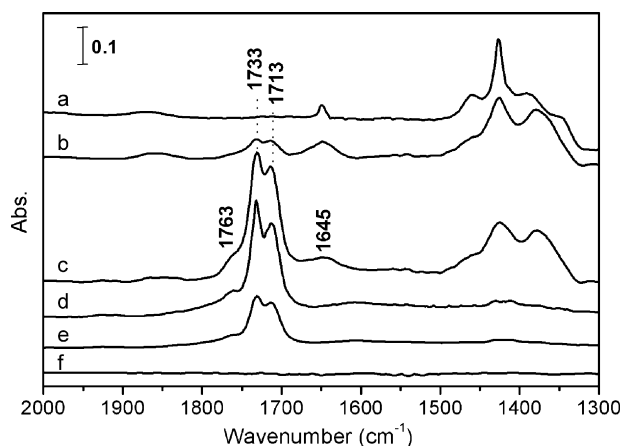

Fig. 6. IR spectra arising from interaction of MoPO/SiO$_2$ catalyst with allyl alcohol at 323 K for 10 min, followed by evacuation at (a) 323 K and heating under 5% O$_2$/He atmosphere to (b) 373 K, (c) 423 K, (d) 573 K, (e) 673 K and (f) 773 K.
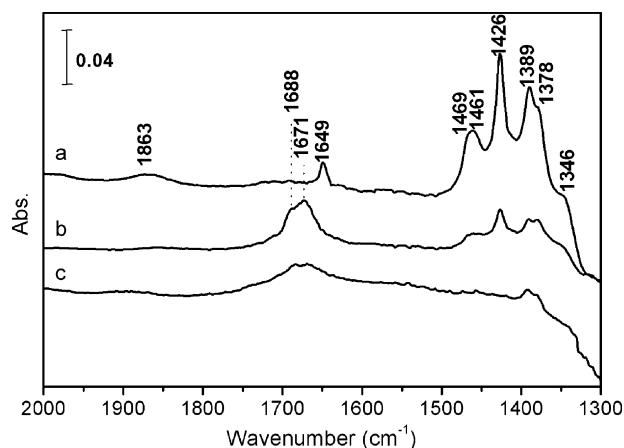
isomerization, the direct isomerization of the allyl alcoholate to propanal by-passing the acrolein formation (allyl alcoholate → enolate → propanal) [24]. These results showed that the adsorption of allyl alcohol readily gives rise to allyl alcoholate species at 323 K, which further converted to acrolein and small amounts of propanal at higher temperatures.

3.3.3. Propene adsorption

The IR spectra recorded after propene was introduced to the catalyst at 373 K and followed by evacuation are showed in Fig. 7a [18]. Compared to the spectra shown in Fig. 2b, the bands at 2983, 2943, 2885, 1461, 1389, 1378 and 1346 cm^{-1} can be assigned to isopropoxy species. However, additional bands at 1863 cm^{-1} (2w_{CH_2}-), 1649 cm^{-1} ($\nu_{C=C}$) and 1426 cm^{-1} ($\delta_{=CH_2}$) can be assigned to allyl alcoholate species, since the similar IR bands are observed after adsorption of allyl alcohol on the catalyst (Fig. 6b). This is further confirmed by the bands observed in the ν_{CH} region above 3000 cm^{-1}. The other bands of allyl alcoholate species are overlap with those of isopropoxy species. As the temperature was increased to 423 K under vacuum, the intensity of the bands of isopropoxy species and allyl alcoholate species decreases considerably, while two new bands ascribable to the acrolein (1671 cm^{-1}, $\nu_{C=O}$) and adsorbed acetone (1688 cm^{-1}, $\nu_{C=O}$) were observed. These results showed that two major routes may be involved in the oxidation of propene: The first one involves breaking of the C–H bond of the methyl group with subsequent oxygen insertion to give allyl alcoholate, which then convert to acrolein; the second route is associated with the electrophilic attack of the Brønsted acid sites on the catalyst at the propene double bond, giving rise to isopropoxy species, which is then oxidized to acetone. A likely intermediate in the first route is the formation of π-allyl species, either anionic or radical, as proposed for the selective oxidation of propene to acrolein. Anionic allyl species have been identified on ZnO and ZrO$_2$, which are not active allylic oxidation catalysts [25]. When propene was adsorbed over MoVTeNbO catalyst, the band at 1493 cm^{-1} due to π-allylic compound was observed [26]. While on uranyl antimonite catalyst, only acrolein
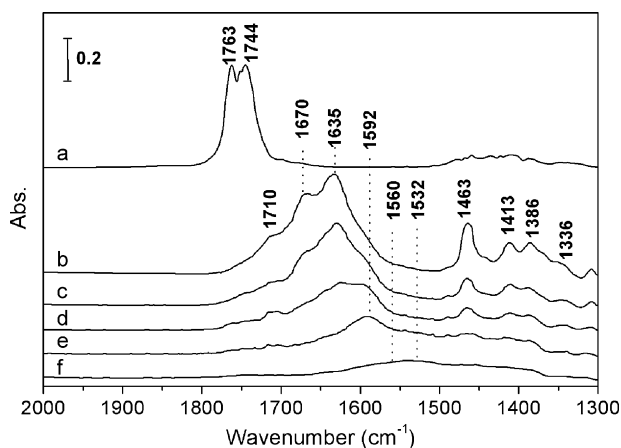
Fig. 8. IR spectra of adsorbed species arising from interaction of MoPO/SiO$_2$ catalyst with (a) gaseous propanal at 323 K for 10 min, followed by evacuation and heating under vacuum to (b) 323 K, (c) 373 K, (d) 423 K, (e) 473 K and (f) 523 K.

was found upon propene adsorption, but neither the π-allyl intermediate nor allyl alcoholate was detected spectroscopically [27]. This is probably because π-allyl species was oxidized so rapidly to allyl alcoholate species that it cannot be observed. This also implies that the rate-determining step of propene oxidation is the first hydrogen abstraction from the methyl group.

3.4. IR spectra arising from propanal and 1-propanol adsorptions

3.4.1. Propanal adsorption

The adsorption of propanal on the catalyst at 323 K and followed by evacuation at increasing temperature is shown in Fig. 8. The bands at 1710, 1670 and 1635 cm^{-1} are assigned to $\nu_{C=O}$ of propanal coordinated with different Lewis-acid sites of catalyst surface. Other bands are observed at 1463 cm^{-1} (methyl asymmetric deformation), 1413 cm^{-1} (CH$_2$ deformation), 1386 cm^{-1} (CH deformation) and 1336 cm^{-1} (CH$_2$ scissoring) [28]. Increasing the temperature up to 473 K leads to a decrease in the intensity of the bands of propanal coordinated to Lewis-acid sites and an increase in the intensity of the broad band centered at 1592 cm^{-1}. The band at 1592 cm^{-1} cannot be assigned to carboxylate species, because it occurs at much higher frequency than $\nu(CO_2{}^-)$ frequency of carboxylate species on MoPO/SiO$_2$ catalyst. In fact, enolate anions have been found to be responsible for bands in the region 1640–1540 cm^{-1} [29]. Therefore, it is suggested that propanal enolate anion is formed by proton extraction on the cation–anion couple sites, responsible for the band at 1592 cm^{-1} (C=C–O stretching). Further heating at 523 K under vacuum leads to appearance of the broad bands near 1560 and 1532 cm^{-1}. However, the spectrum does not correspond either to that of formate species or that to propionate species only and perhaps due to a mixture of formate species, acetic species and propionate species.

3.4.2. 1-Propanol adsorption

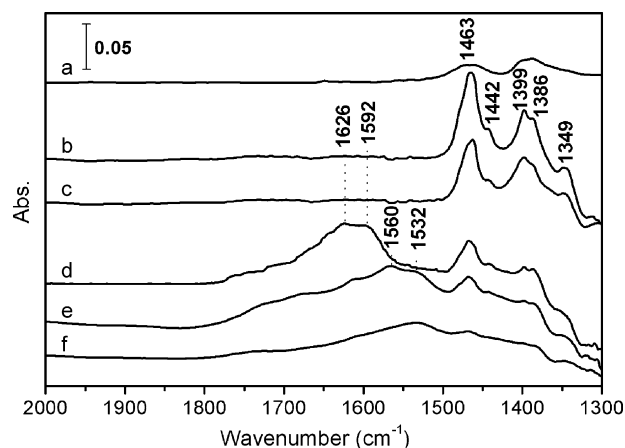The adsorption of 1-propanol on the catalyst at 323 K and followed by evacuation at increasing temperature is shown in

Fig. 9. IR spectra of adsorbed species arising from interaction of MoPO/SiO$_2$ catalyst with (a) gaseous 1-propanol at 323 K for 10 min, followed by evacuation and heating under vacuum to (b) 323 K, (c) 373 K, (d) 423 K, (e) 473 K and (f) 523 K.

Fig. 9. 1-Propanol adsorption at 323 K gives rise to propoxy species characterized by bands at 1463, 1442, 1399, 1386 and 1349 cm^{-1} (CH$_3$ and CH$_2$ deformations) [11]. With heat treatment the spectra are due to adsorbed propanal (1626 cm^{-1}), enolate anion (1592 cm^{-1}), and a mixture of formate species, acetic species and propionate species (1560 and 1532 cm^{-1}) were observed, in agreement with the spectra observed for the adsorption and evacuation of propanal at comparable temperatures.

3.5. IR spectra arising from propane adsorption

No surface species was detected when a gas mixture of propane/oxygen was introduced to the catalyst until the temperature of the sample was raised to 473 K (Fig. 10). After the gas mixture of C$_3$H$_8$/O$_2$ was introduced to the catalyst at 473 K for 4 h, the IR spectra of the adsorbed acetone (1688 cm^{-1}, $\nu_{C=O}$), gas phase acetone (1738 and 1722 cm^{-1}, $\nu_{C=O}$) and propene (1667 and 1637 cm^{-1}, $\nu_{C=C}$) were detected (Fig. 10a). When the gas phase components were removed by evacuation,
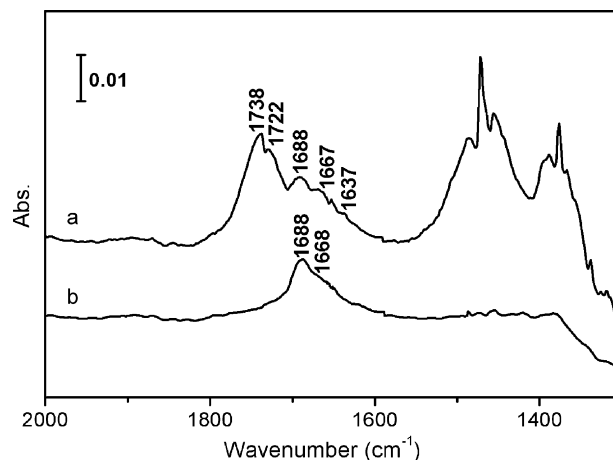

Fig. 10. IR spectra arising from interaction of MoPO/SiO$_2$ catalyst with propane/O$_2$ at (a) 473 K for 4 h, followed by evacuation at (b) 473 K.

the overall spectrum actually seems closely similar to those described above, arising from the adsorption of isopropanol and 2-Br-propane at the same temperature. The band of adsorbed acetone (1688 cm^{-1}, $\nu_{C=O}$) with a shoulder at 1668 ($\nu_{C=O}$) cm^{-1} assigned to adsorbed acrolein was observed (Fig. 10b).

The formation of acrolein and acetone during the propane adsorption suggests that propane is activated by abstracting a hydrogen atom from methylene group. This is followed by bonding of the lattice oxygen near by over the catalyst with the secondary carbon of isopropyl species leading to the formation of an isopropoxy species. This is agreement with the work by Iglesia and co-workers [30]. The study of kinetic isotopic effects for the oxidative dehydrogenation of propane to propene on MoO$_x$/ZrO$_2$ catalyst showed that the methylene C−H bond activation is the rate-determining step for propane dehydrogenation reaction.

This is also agreement with the work by Busca et al. [12]. They studied the interaction of light hydrocarbons (methane, ethane, propane, propene, *n*-butane, isobutene, 1-butene, benzene ad toluene) over the MgCr$_2$O$_4$ by IR spectroscopy [12]. It has been concluded that every hydrocarbon reacts at its weakest C−H bond giving rise to the corresponding alkoxide species. The earlier intermediates (alkoxides, carbonyl compounds) are detectable only with the most reactive hydrocarbons (propane, *n*-butane, isobutene, propene, 1-butene and toluene) while with the least reactive hydrocarbons (methane and benzene), only the final intermediates are detectable (carbonates, carboxylates). In our case, the results showed that propene reacts at its allylic position giving rise to allyl alcoholate, while propane likely reacts at C(2) giving rise to isopropoxy species on MoPO/SiO$_2$ catalyst. The formation of isopropoxy species cannot be detected under the experimental conditions of propane adsorption over MoPO/SiO$_2$ catalyst (Fig. 10a), since the IR spectra shown in Fig. 2 clearly indicated that the conversion of isopropoxy species to acetone over the catalyst took place at 423 K.

Furthermore, Our group have systematically investigated the C−H bond initial activation of light alkanes (C$_1$ and C$_3$) on the cluster models of high valence transition metal oxides (V$_3$O$_6$Cl$_3$, Cr$_3$O$_9$, Mo$_3$O$_9$ and W$_3$O$_9$) [31–33]. We have explored eight possible activation pathways. H abstraction is a 1 e process, which is referred as a radical mechanism, involving alkyl radical formation. The reactivity of different MO$_x$ was found to be correlated with the H−OMO$_{x-1}$ bond strength. We have considered H abstraction both by terminal oxygen and bridge oxygen. We have also considered H abstraction via anti mode and syn mode. We found that anti H abstraction by terminal oxygen is the most favorable pathway and H abstraction from the methylene group is more feasible than that from the methyl group. All in all, the calculated C−H bond activation barriers are in good agreement with the experimental values. Moreover, our calculations found that the most favorable pathway on Mo$_3$O$_9$ is for methyl to recombine with a nearby oxo. We calculated this rebound step to be a fast process with a small barrier of 8.6 kcal/mol such that H abstraction followed by a fast oxygen atom insertion leads to the formation of stable hydroxyl and alkoxy species [31]. The same is true when propane is concerned, which leads to the formation of isopropoxy species after H abstraction from the methylene
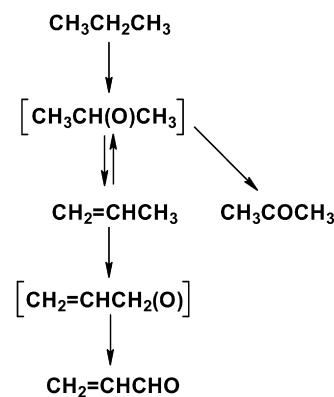
Scheme 1. Reaction network for propane selective oxidation to acrolein over MoPO/SiO$_2$ catalyst.

group. Thus, the density functional theory calculations are also in good agreement with the IR experimental results.

4. Conclusions

In conclusion, the adsorbed species and gaseous species formed by adsorption of the reactant, possible intermediates or their probe molecules as well as the reaction products on the MoPO/SiO$_2$ catalyst and the transformation of these species at elevated temperature under vacuum and under O$_2$/He atmosphere were studied by IR spectroscopy. The results suggest that isopropoxy species is likely the intermediate of propane selective oxidation to acrolein over MoPO/SiO$_2$ catalyst. Isopropoxy specie is converted to propene by β-hydrogen elimination or to acetone by oxidative dehydrogenation. The former can be further oxidized to acrolein through allylic process or to acetone through oxyhydration process. A more detailed reaction network is shown in Scheme 1.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at: doi:10.1016/j.molcata.2007.07.049.

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