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In situ IR – TPD study of the synthesis of C_3-oxygenates from propylene partial oxidation over a Rh/Al_2O_3 catalyst

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Abstract

Propylene partial oxidation over Rh/Al_2O_3 produced CO_2 as well as C_3 oxygenates (i.e., acetone, isopropanol, and propanal) at 250°C. In situ infrared spectroscopic study revealed that the formation of CO_2 led those of C_3 oxygenates, suggesting that CO_2 and C_3 oxygenates were formed via independent pathways. In the partial oxidation pathway, acetone was produced and further hydrogenated to isopropanol by hydrogen on the Rh surface. Propanal was formed from a separate pathway and strongly adsorbed on the catalyst surface. The C_3 oxygenates can be further oxidized to a stable carboxylate intermediate. The slow rate of change in the IR intensity remer factor of the carboxylate under transient conditions suggests that the carboxylate is a spectator intermediate in propylene partial oxidation. The infrared spectroscopy observation of linear CO on Rh^0 site suggests that the reduced Rh site plays an important role in propylene partial oxidation.

Key words: Acetone; adsorbed species; infrared spectroscopy; isopropanol; Partial oxidation; propanal; rhodium, transient condition, temperature programmed desorption.

Estudio *in situ* por espectroscopía infrarroja de la síntesis de oxigenados de C_3 a partir de la oxidación parcial de propileno sobre un catalizador Rh/Al_2O_3

Resumen

La oxidación parcial de propileno sobre Rh/Al_2O_3 produjo CO_2 así como también compuestos oxigenados C_3 (i.e., acetona, isopropanol y propanal) a 250°C. El estudio in situ por espectroscopia infrarroja reveló que la formación de CO_2 permite la formación de los oxigenados de C_3, lo cuàl sugiere que el CO_2 y los oxigenados C_3 se forman por rutas independientes. En la ruta de oxidación parcial, la acetona se produce y es hidrogenada posteriormente a isopropanol por el hidrógeno que está sobre la superficie del Rh. El propanal se forma por una rutà separada y se adsorbe fuertemente sobre la superficie del catalizador. Los compuestos oxigenados C_3 pueden ser luego oxidados a un intermediario carboxilato más estable. La baja velocidad de cambio en la intensidad de los carboxilatos bajo condiciones "transientes" sugiere que el carboxilato es

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un intermediario espectador en la oxidación parcial de propileno. La observación de espectroscopia infrarroja de CO lineal sobre los sitios de Rh^0 sugiere que los sitios reducidos de Rh juegan un papel importante en la oxidación parcial de propileno.

Palabras clave: Acetona; condición "transiente"; desorción a temperatura programada; especies adsorbidas; espectroscopía infrarrojo; isopropanol; oxidación parcial; propanal; rodio.

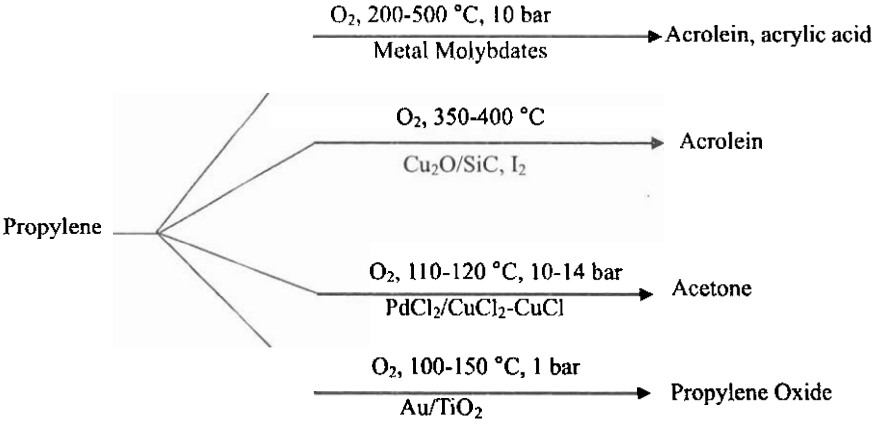
Introduction

Propylene partial oxidation produces a wide range of C_3 oxygenates including acetone, isopropanol, propanal, acrolein, and propylene oxide (1). The selectivity of the reaction can be controlled by the catalyst compositions and reaction conditions (Scheme 1).

Oxide-supported metal catalysts provide the advantage of high surface area, easy catalyst recovery, and feasibility of fine-tuning catalyst activity/selectivity through the use of promoters. Au/TiO_2 catalyst shows exceptionally high selectivity toward propylene oxide (2). However, the catalytic properties of Au/TiO_2 resemble those of majority of partial oxidation catalysts which show that high selectivity toward the desired partial oxidation product can only be achieved at low conversions. Increasing conversion causes a decrease in the selectivity.

Search for a highly active and selective catalyst which can give high yields of a desired oxygenated product remains a subject of extensive interest (3). Recent high throughput studies show that Al_2O_3-supported metal catalysts exhibit a wide range of activities for catalyzing the formation of acetone, propylene oxide, and acrolein at 1 bar over a temperature range of 200-300°C (4). Rh, Pb, and Ir favored acetone formation, while Cu, Mn and W were effective for acrolein. Binary catalysts with at least one metal as Rh exhibited the highest selectivity for propylene oxide. Although high throughput study will facilitate the discovery and optimization of highly active and selective catalysts, an insight into the kinetics and mechanism of the partial oxidation reaction is essential for establishing a scientific basis to guide the development of highly active and selective catalysts.

The mechanism of a catalytic reaction is built on the knowledge of adsorbed intermediates, the nature of active sites, and reaction pathways. Infrared (IR) spectroscopy has been demonstrated to be an effective tool for determining the state of metal sites



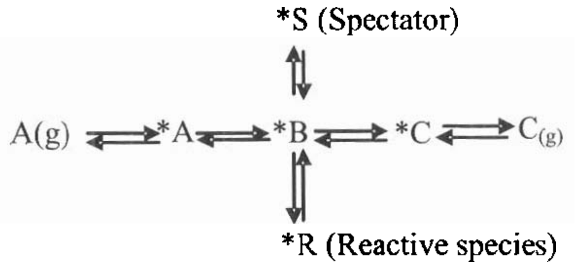
Scheme 1. Catalyst compositions and reaction conditions for producing C_3 oxygenates from propylene.

on supported metal catalysts by probe molecule's IR spectra. For example, at 25 – 30°C, CO can adsorb as linear CO on the Rh^0 sites in 2010-2070 cm^{-1}, bridged CO on the large Rh^0 crystallites at 1800-1880 cm^{-1}; linear CO on Rh^+ sites at 2090-2100 cm^{-1} and gem-dicarbonyl on Rh^+ sites at 2010-2040 and 2090-2100 cm^{-1}; and linear CO on Rh^{2+} sites at 2020 cm^{-1} (5, 6). The wavenumber of adsorbed CO can be used to elucidate the nature of the metal site on the catalyst surface. This approach is usually carried out at room temperature in a controlled environment before and after reaction studies.

Characterization of the catalyst surface state before the reaction by IR spectra of adsorbed probe molecule can be used to determine the reproducibility of the catalyst preparation and serve as a reference for comparing the catalyst states at different stages of catalyst development. However, the state of the catalyst characterized by the IR spectra of adsorbed probe molecules may not be directly relevant to the state of the active sites during catalyst reaction. This is because the reactants could further oxidize/reduce the catalytic sites and/or change the surface structure of the catalytic sites. Thus, it is difficult to extrapolate results of room temperature IR spectroscopy characterization to reaction conditions for elucidation of a catalytic reaction mechanism. For mechanistic study, it would be highly desirable to acquire the infrared spectra of adsorbed species under reaction conditions.

Scheme 2 illustrates the pathway of a generic catalytic reaction which involves adsorption of gaseous reactant A, surface reaction $(*A \leftrightarrow *B \leftrightarrow *C)$, and desorption of $*C$ to gaseous product C as well as side reactions leading to a spectator intermediate or other reactive intermediate.

While IR spectra of adsorbed species under reaction condition can be used to determine the structure of adsorbed species, linking the IR-observable adsorbed intermediates to develop a fundamental understanding of reaction pathways requires knowledge of the dynamic behavior of these adsorbed intermediates. For example, the adsorbed species of which concentration does not vary with those of reactants/products under transient condition can be classified as a spectator intermediate. The presence or absence of a spectator intermediate has little impact on the reaction rate and selectivity.



Scheme 2. Generic pathway of a heterogeneous catalytic reaction.

The objective of this study was to investigate the dynamics of the adsorbed species and their reaction pathways for propylene partial oxidation over Rh/Al_2O_3. Investigation of Rh/Al_2O_3, which exhibits a wide range of partial oxidation activities for producing acetone, propanal, and propylene oxide, will allow determination of the nature of active sites under reaction conditions, reaction network, and factors governing the selectivity to desired C_3 oxygenates.

Experimental

Catalyst preparation

2 wt% Rh/Al_2O_3 was prepared by the incipient wetness impregnation method. An aqueous solution of $RhCl_3$ was impregnated onto γ-Al_2O_3 (Alfa-Aesar) with a surface area of 100 m^2/g. The impregnated $RhCl_3/Al_2O_3$ was calcined in air at 500°C and reduced in flowing hydrogen at 500°C. The catalysts were further reduced prior to the reaction studies. The catalysts were characterized by TEM and XRD (7).

Experimental apparatus

The experimental apparatus for in situ infrared Spectroscopy study shown in Figure 1 IR consists of gas flow meters, a 4- and a 6-port valve, a DRIFTS reactor, a tubular reactor, and an analysis section. For each experiment, a total of 150 mg of catalyst powder was used. Approximately 30 mg of Rh/Al_2O_3 was placed in a DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy, Spectra-Tech model 0030-102) reactor while the remaining 120 mg were charged to the tubular reactor (which was placed either upstream or downstream of the DRIFTS) to increase the conversion of reactants. The DRIFTS reactor resided in a Nicolet Magna 550 Infrared (IR) Spectrometer bench; all spectra were collected at a resolution of 4 cm^{-1} with 32 co-added scans. The effluent of the DRIFTS/tubular reactor was monitored via a Prisma QMS 200 mass spectrometer (MS), allowing the determination of reactant conversions, product selectivity, and rate data. Separate temperature control systems existed on each of the reactors, allowing for ease of maintaining equal temperature between the two reactors at all times.

C_3H_6 (Praxair, 99.99%), O_2 (Praxair, 99.998%) and Ar (Praxair, 99.999%) flows were controlled to the reactor via Brooks 5850 mass flow controllers at a pressure of 0.1 MPa. Prior to each experiment, the catalyst was reduced in H_2 for 2 hours at 500°C. Partial oxidation was carried out by pulsing O_2 (1 cm^3) into flowing C_3H_6/Ar (3/37 cm^3/min) over Rh/Al_2O_3 at 250°C by a 6-port switching valve with a 1 cm^3 loop.

The experimental apparatus employed for TPD studies is similar to Figure 1 except the tubular reactor was not used. A saturator filled with C_3 oxygenate (propanal, acetone, isopropanol) was placed before the DRIFTS reactor. Ar flow was directed into the saturator through a pair of interconnected three-way valves, delivering a gaseous flow of C_3 oxygenate to the DRIFTS reactor. IR-TPD (Infrared-Temperature Programmed Desorption) was carried out by the following steps: (i) reduction of Rh/Al_2O_3 at 500°C, (ii) the adsorption of a specific C_3 oxygenate at room temperature, and (iii) heating the adsorbate/catalyst in the DRIFTS at 10°C/min with 40 cm^3/min of Ar flow. Variation in IR spectra of adsorbed species and the effluent composition during pulse partial oxidation and IR-TPD studies was monitored by infrared spectroscopy and mass spectroscopy, respectively.

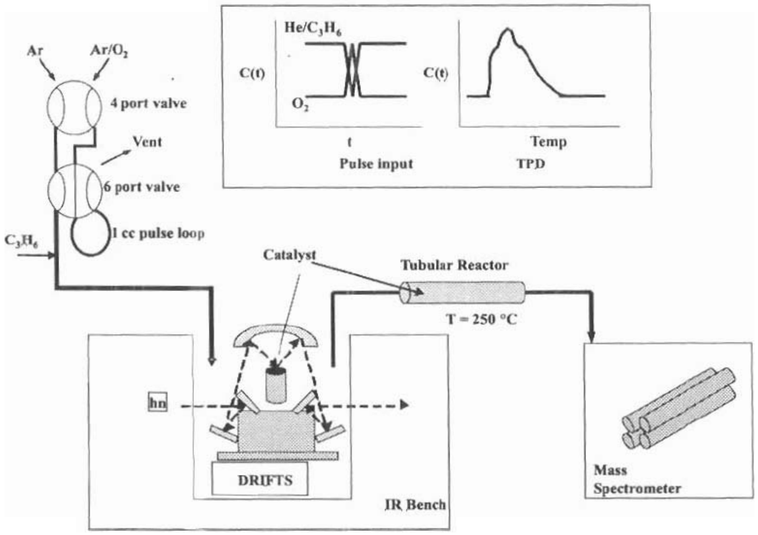


Figure 1. Experimental apparatus.

The m/e signals monitored by the mass spectrometer during partial oxidation and TPD experiments were 2 for H_2, 18 for H_2O, 27 for propylene, 29 for propanal, 31 for propanol, 32 for O_2, 40 for Ar, 43 for acetone, 44 for CO_2, 45 for iso-propanol and 58 for propylene oxide. Table 2 lists the intensity factor for mass fragments of C_3-oxygenates calculated from mass spectrometer signals. The IR bench is a single beam instrument and therefore it is necessary to collect background spectra (reference spectra) of the catalyst prior to each experiment. IR data are presented in absorbance units in this paper. The formula used to calculate absorbance is as follows: $A(v) = -\log\{I(v)/I(\nu 0)\}$, where $I(v)$ and $I(v_0)$ refer to as sample and background intensities.

Results and Discussion

Propylene interaction with Rh/Al_2O_3

Figure 2 shows the infrared spectra resulting from flowing propylene over Rh/Al_2O_3 and Al_2O_3 at 250°C; Figure 3 shows the MS profiles of the products in the effluent of the in situ IR cell. Flowing propylene over Rh/Al_2O_3 at 250°C for 0.25 min produced a linear CO band at 2040 cm^{-1} and the IR bands at 2958 and in the 1600 - 1630 cm^{-1} region. The 2958 cm^{-1} band can be assigned to the C-H stretching of the CH_3; the band in the 1600 - 1630 cm^{-1} region can be assigned to the C=C stretching of the propylene π-complex formed on the metal cations (Rh^+ and Al^{3+}) present on the Rh/Al_2O_3 surface (8, 9). The interaction of the propylene π bond with the metal cations resulted in a weak C-H stretching band in the CH_2=CH portion of adsorbed propylene π-complex as shown in the IR spectra at 0.25 min.

The 1600 cm^{-1} band at 0.25 min is indicative of the C=C stretching resulting from the π bond interaction with Rh^+ which gave the 2094 cm^{-1} (Rh^+CO) band. The formation of H_2 and CO as shown in Figure 3a appears to cause the reduction of Rh^+ to Rh^0, producing linear CO on Rh^0 at 2040 cm^{-1} and lead-

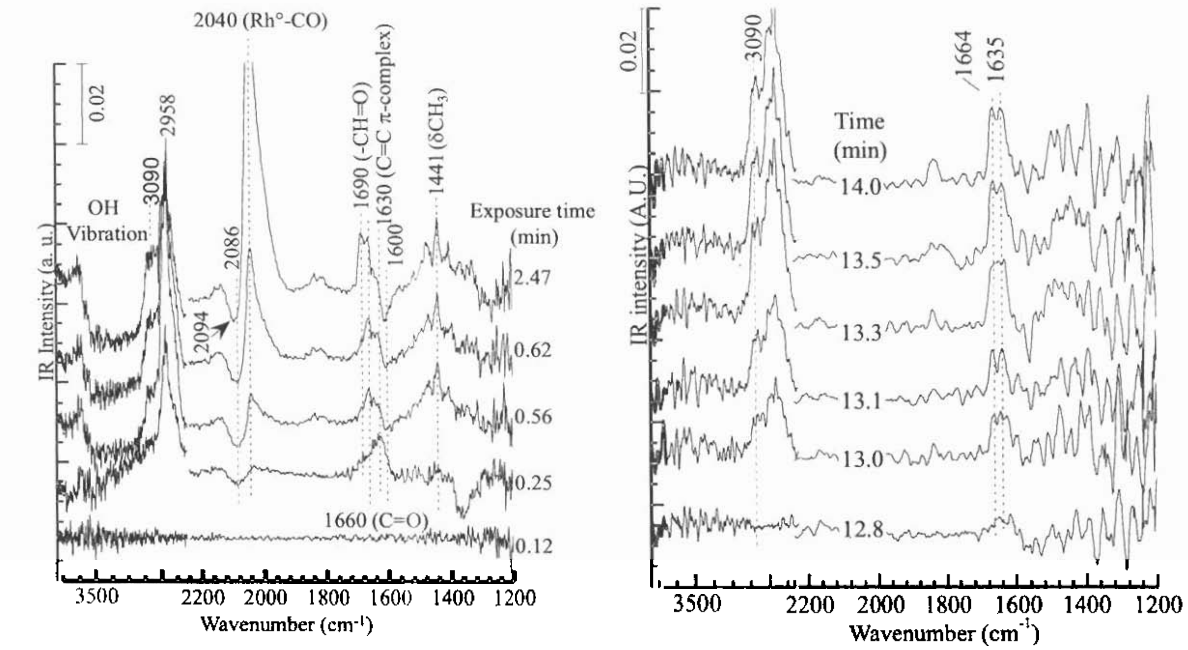


Figure 2. DRIFTS during exposure of (a) Rh/Al_2O_3 and (b) Al_2O_3 to propylene.

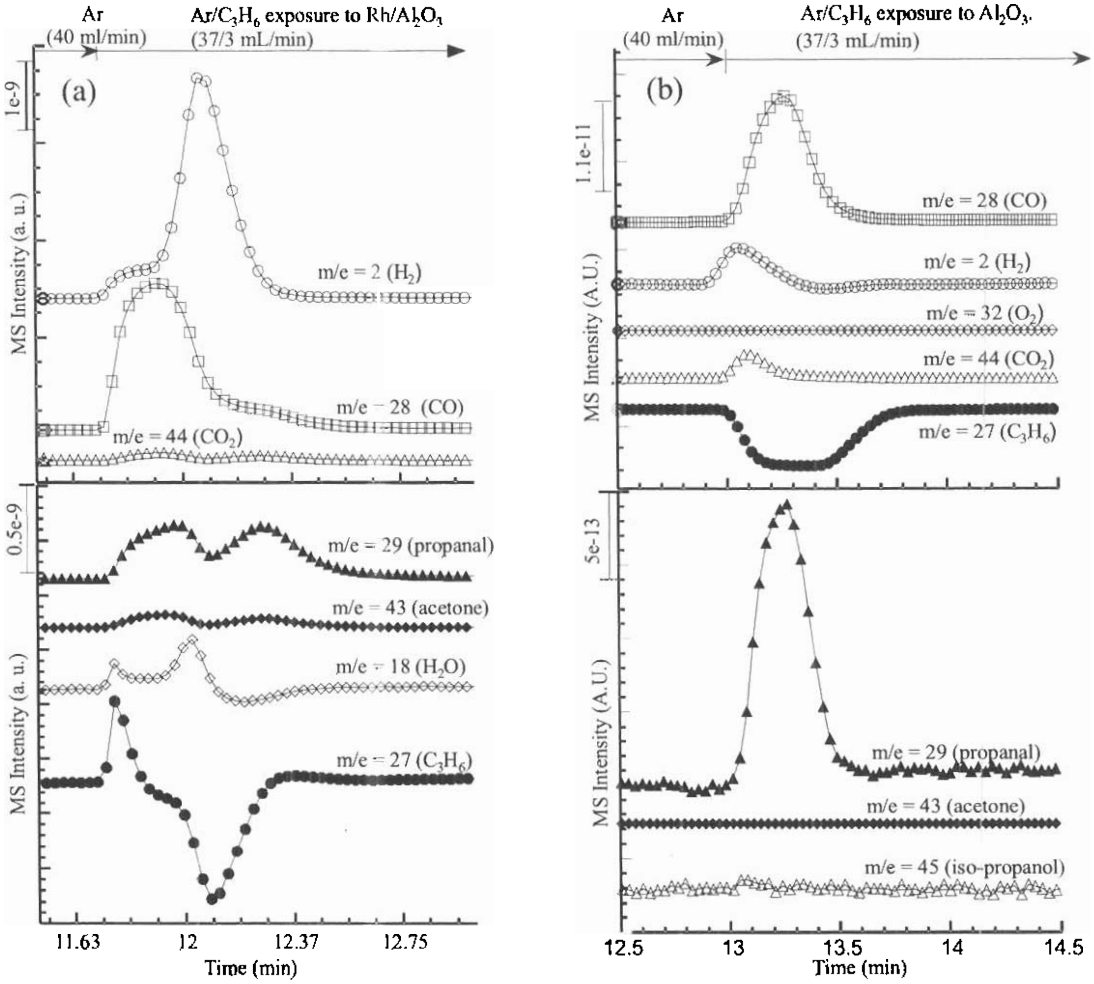


Figure 3. MS profiles during exposure of (a) Rh/Al_2O_3 and (b) Al_2O_3 to propylene.

ing to disappearance of the 1600 cm^{-1} band. The emergence of 1630 cm^{-1} band at 0.56 and 0.62 min reflects the interaction of the π bond with a cation of high oxidation state such as Al^{3+}. It has been shown that the C=C stretching frequency shifted to a high wavenumber as the oxidation state of the cations increased (10, 11).

As the exposure time increased, the intensity C=C stretching band at 1630 cm^{-1} decreased while the intensity of the carbonyl band at 1660 - 1690 cm^{-1} band increased. These results suggest the occurrence of the conversion of the propylene p-complex to the adsorbed propanal. Adsorbed propanal further desorbed as gaseous propanal which was observed in the effluent of the reactor by the mass spectrometer (Figure 3). Comparison of the infrared results of flowing propylene over Rh/Al_2O_3 and Al_2O_3 in Figure 2 revealed the reaction between propylene and adsorbed H_2O only occurred on the Rh/Al_2O_3 catalyst. The Rh/Al_2O_3 surface provides adsorbed H_2O for the reaction and the reduced Rh^0 site for the linear CO. Comparison of mass spec results in Figure 3 shows that the amount of propanal produced on Rh/Al_2O_3 is three orders of magnitude higher than that on Al_2O_3; the amount of CO/H_2 produced on Rh/Al_2O_3 is two orders of magnitude higher than that on Al_2O_3.

Pulse of 1 cm^3 of O_2 into Ar/C_3H_6 with DRIFTS upstream of tubular

Figure 4 shows the IR spectra and MS profiles during pulsing O_2 into the steady-state C_3H_6 (7.5% in Ar) flow over the Rh/Al_2O_3 catalyst surface. The DRIFTS reactor was placed in the upstream of the tubular reactor where 20% of the catalyst for the reaction study was located. Pulsing O_2 into C_3H_6 produced H_2 (*m/e* =2), CO_2 (*m/e* = 44), CO (*m/e* =28), and C_3 oxygenates including isopropanol (*m/e* = 45), propanal (*m/e* =29), acetone (*m/e* = 43), propylene oxide (*m/e* = 58), evidenced by their positive *m/e* profile peaks in Figure 4 (b) and (c). The formation of these gaseous products, along with the consumption of C_3H_6 (*m/e*=27) displayed by its negative profile, revealed the occurrence of partial and total oxidation of C_3H_6 over the catalyst surface. The MS profiles in Figure 4 (b) and (c) also revealed the lead-lag relationship of products desorbing from the catalyst surface, giving an insight of the reaction sequence occurring during introduction of oxygen into the propylene flow inside the reactor. The evolution of CO_2 led that of C_3 oxygenates (propanal, acetone, isopropanol, and propylene oxide), suggesting that the majority of CO_2 was produced from the direct oxidation of C_3H_6 independent of the partial oxidation leading to C_3 oxygenates.

The spectra in Figure 4(a) were obtained from subtracting the IR spectrum shown at 2.47 min in Figure 2 from the sub-

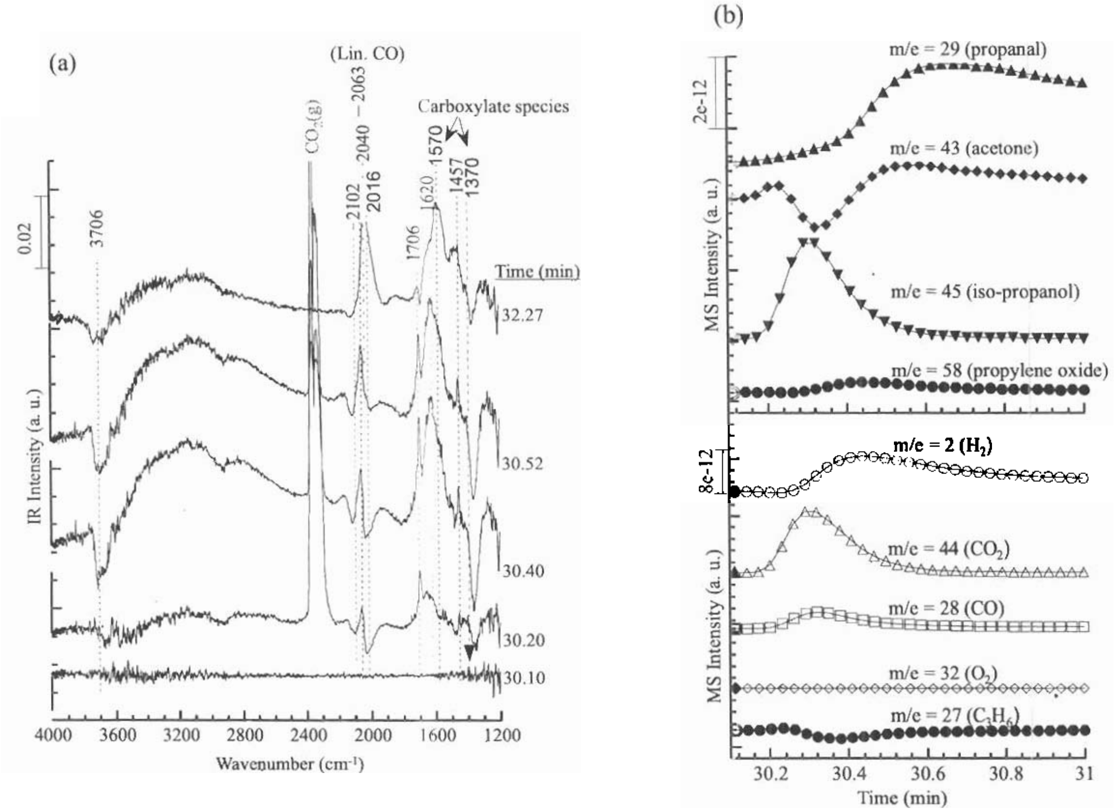


Figure 4. O_2 pulse into steady state Ar/C_3H_6 flow over Rh/Al_2O_3 at 250°C analyzed by (a) DRIFTS, (b) and (c) Mass spectrometry. DRIFTS reactor was placed upstream of tubular reactor.

sequent spectra during the O_2 pulse. Pulsing of O_2 led to the formation of CO_2 at 2350 cm^{-1} and H_2O at 2800-3600 cm^{-1}, linear CO at 2040 cm^{-1}, the carbonyl band at 1706 cm^{-1}, C=C stretching at 1620 cm^{-1}, and C-H rocking (i.e., bending) in the 1400 – 1590 cm^{-1} region. The 1706 cm^{-1} band can be assigned to the carbonyl of an adsorbed propanal. A band in the region was also found on the adsorption of isopropanol on Rh/Al_2O_3 (Figure 8). The C-H rocking is resulted from adsorbed propanal, iso-propanol, and acetone. These IR band assignments are based on the IR-TPD studies of C_3 oxygenate species on Rh/Al_2O_3. The results of the IR-TPD studies will be further discussed.

Part of the 1706 cm^{-1} band can be attributed to adsorbed propanal which was produced prior to the formation of other species. The gaseous propanal profile lagged behind those of isopropanol and acetone as shown in Figure 4(b). The results indicated that desorption of adsorbed propanal is slower than that of isopropanol and acetone. Part of the 1706 can be attributed to adsorbed isopropal since its rise and decay follow the the MS profile of isopropanol. The decrease in the acetone profile corresponding to the increase in the isopropanol profile suggests that isopropanol is produced from hydrogenation of acetone in the presence of H_2 resulted from partial oxidation of propylene to H_2/CO. Integrating the area of reactants and products and multiplying the area with their respective response factors allowed us to quantify the amounts of C_3 oxygenates produced from the O_2 pulse. The propylene conversion during pulse of 1cm^3 of O_2 into Ar/C_3H_6 (37/3 cm^3/min) is 21% with a CO_2 selectivity at 82%, acetone at 1.8%, propanal at 8.7%, iso-propanol at 4.3% and PO at 1.04% [Table 1]. GC analysis of the steady state partial oxidation revealed that propylene conversion was 10.5% at 250°C; product formation rates were determined to be 1.33 mol/min for acetone, 0.12 mol/min for PO, and 34.3 mol/min for CO_2. The yield calculated on basis of total conversion is 10% for acetone the 1% for PO and 89% for CO_2 (12).

During O_2 pulsing, the linear CO on the reduced Rh (i.e., Rh^0) sites at 2040 cm^{-1} was consumed and linear CO species at 2063 cm^{-1} was observed. The formation of linear CO at 2063 cm^{-1} suggests $Rh^{\delta 0}$ sites were oxidized to $Rh^{\delta +}$ in presence of O_2. The linear CO on completely reduced Rh was formed rapidly after the O_2 pulse traveled through the catalyst bed.

Pulse of 1 cm^3 of O_2 into Ar/C_3H_6 with tubular reactor upstream of DRIFTS

Figure 5 shows the results of pulsing O_2 into the steady state Ar/C_3H_6 (37/3 cm^3/min) flow at 250°C over 2 wt% Rh/Al_2O_3 which was placed in the tubular reactor (120 mg) followed by the DRIFTS reactor (30 mg). The DRIFTS spectra shown in Figure 5(a) were obtained by subtracting the infrared spectrum prior to the O_2 pulse from the subsequent spectra following the O_2 pulse. The negative bands for propylene in the 2800-3200 cm^{-1} and 1400-1600 cm^{-1} region are due to high propylene conversion. The

Table 1

Conversion and selectivity for 1 cm^3 pulse of O_2 into Ar/C_3H_6 (37/3 cm^3/min at 250°C

Catalyst	Conversion (%)		Selectivity (%)					
	C_3H_6	O_2	CO_2	CO	C_2H_5CHO	$(CH_3)_2CO$	$(CH_3)_2CHOH^c$	PO
Rh/Al_2O_3	21.3	100	82.1	-	8.71	1.8	4.38	1.04
Al_2O_3	0.84	100	55.1	17.8	1.81	1.05	2.30	0
Gas-Phase	0.12	78.6	48.3	42.08	0	0	0	0

Table 2

Intensity factor for mass fragments of C_3 oxygenates calculated from the mass spectrometer signals (Intensity factor = abundance of a peak relative to the largest peak; largest peak being 100)

m/e	2	18	27	29	31	43	45	58
Fragments	(H_2)	(H_2O)	$(C_2H_3^+)$	$(C_2H_5^+, CHO^+)$	$(CH_2{=}OH^+)$	$(C_2H_3^+{=}O)$	$(C_2H_4{=}OH^+)$	$C_2H_3{=}OCH_2$
PO	0.12	4.77	58.37	79.84	23.95	22.0	1.28	38.65
$(CH_3)_2CO$	0.66	3.62	11.36	6.67	0.78	100.00	4.71	25.16
CH_3CH_2CHO	0.71	4.24	52.31	100.00	2.87	4.74	3.66	30.78
$(CH_3)_2CHOH$	3.03	18.06	30.95	20.63	8.57	43.01	100.00	9.30

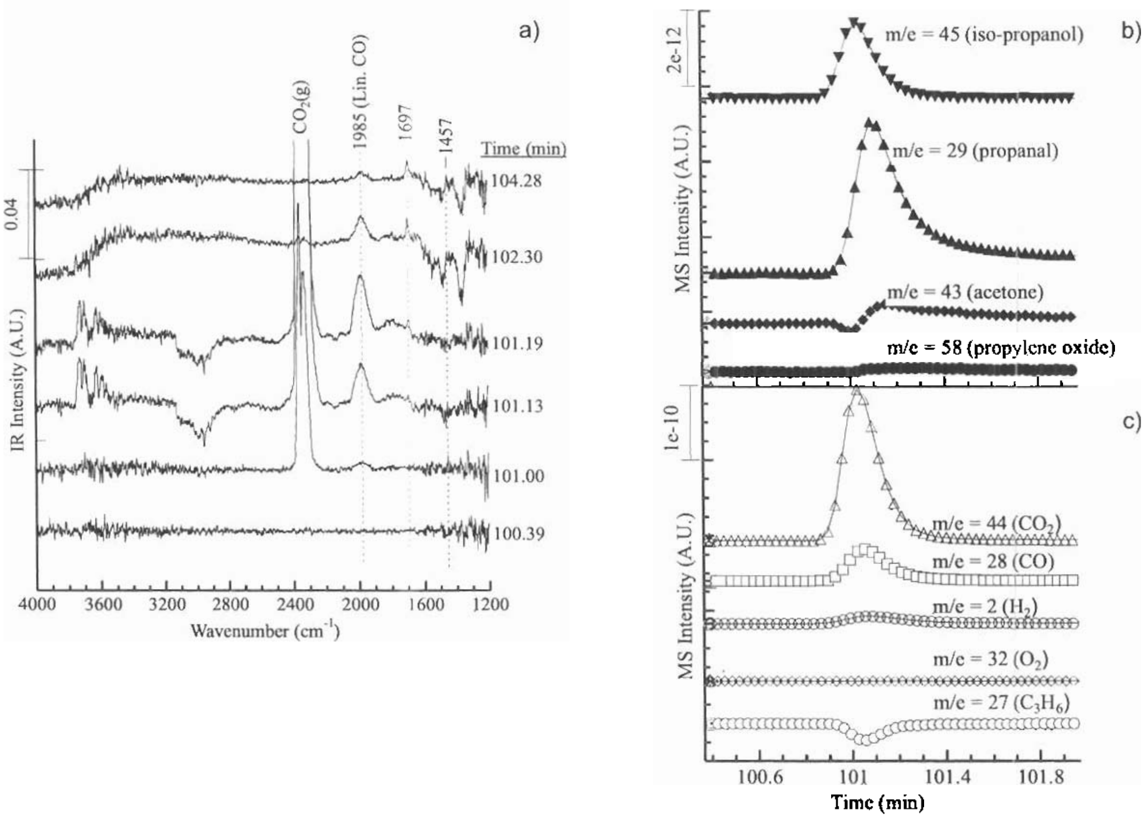


Figure 5. O_2 pulse into steady state Ar/C_3H_6 flow overRh/Al_2O_3 at 250°C analyzed by (a) DRIFTS, (b) and (c) Mass spectrometry. Tubular reactor was placed upstream of DRIFTS.

major adsorbed species observed are linear CO at 1985 cm^{-1}, adsorbed isopropanol at 1697 cm^{-1}, and adsorbed propanal and acetone in the 1400 – 1600 cm^{-1}. Propylene oxide was a minor product of which formation lagged significantly behind that of isopropanol/acetone and propanal. Since no oxygen was observed at the effluent of the reactor, it is very likely that most of oxygen was consumed in the tubular reactor. Therefore, the IR spectra in Figure 5 reflect the spectra of adsorbed species present under reducing environment while Figure 4 provide the spectra of adsorbed species in the presence of the O_2 pulse.

IR-TPD of Propanal over Rh/Al_2O_3

IR-TPD was used to determine the thermal stability and surface reactions of adsorbed species on the catalyst surface as well as to provide the IR spectra of individual adsorbed C_3 oxygenate. The latter will provide the essential background spectra to assist in the assignment of bands observed during partial oxidation of propylene on Rh/Al_2O_3.

Figure 6 shows the IR-TPD study of propanal (C_2H_5CHO) on Rh/Al_2O_3. Flowing C_2H_5CHO in Ar (35 vol% in Ar) over Rh/Al_2O_3 at 25°C produced adsorbed CO and adsorbed propanal species giving C-H stretching vibrations at 2882, 2940 and 2974 cm^{-1}, C=O of a weakly adsorbed propanal at 1733 cm^{-1}, donating on top η^1(C,O) of propanal at 1690 cm^{-1}, carboxylate at 1570 and 1388 cm^{-1}, various forms of C-H bending vibration at 1466 cm^{-1}, C-C vibrations at 1280 cm^{-1}, C-C-C vibrations at 1202 cm^{-1} (13, 14). The formation of linear CO indicates the occurrence of decomposition of propanal to adsorbed CO and C_2 hydrocarbon species. Some of these hydrocarbon species can be attributed to an ethylidyne species because their desorption profile peaks at ethylene at m/e = 27, ethane at m/e = 29, and H_2 at m/e = 2 at 200°C, as shown in the MS profile of Figure 6, are the same as those reported for ethylidyne on Rh or Pt single crystals surface (15-17). The formation of a low wavenumber of linear CO at 2008 cm^{-1} with little variation of linear CO wavenumber with its intensity further suggests that the presence of hydrocarbon fragments prevent the dipole-dipole coupling interaction of adsorbed CO (5).

Comparison of the IR spectra on Rh/Al_2O_3 and Al_2O_3 at 25°C and 250°C shows the distinct difference in the IR bands in the carbonyl region (1600 – 1750 cm^{-1}) re-

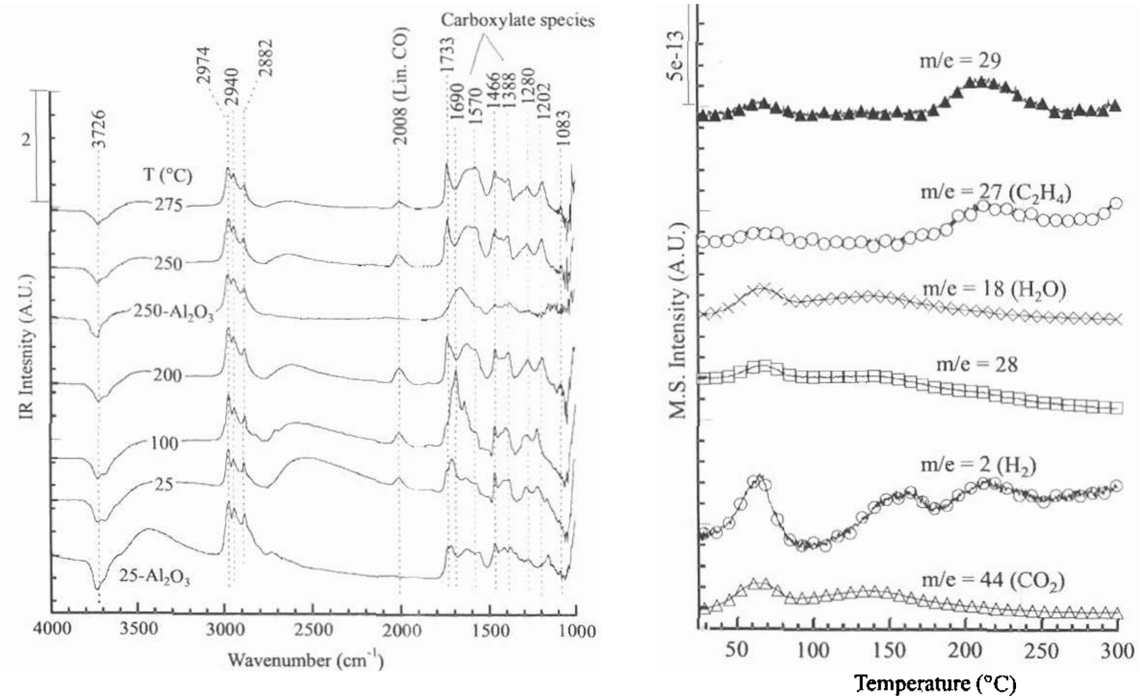


Figure 6. IR and MS analysis during TPD of propanal over Rh/Al_2O_3.

vealed that propanal adsorbs in different form on Rh and Al_2O_3. π-bonded C=O of propanal at 1733 cm^{-1} and carboxylate at 1570 and 1388 become prominent at temperature above 150°C, indicating that the adsorbed propanal strongly adsorbs on the Rh surface and its desorption could be a rate-limiting step for its production. The carboxylate, which has been commonly observed in the adsorption of olefin on the oxide appears to be a stable species, interacts with the Al_2O_3 surface or oxidized Rh surface (19).

Figure 7 shows IR-TPD of acetone on Rh/Al_2O_3. Flowing Ar/CH_3COCH_3 (30 vol% in Ar) over the Rh/Al_2O_3 at 25°C produced C-H stretching vibrations at 2968, 2922 and 2880 cm^{-1}, asymmetric COO^-/(i.e. carboxylate) vibrations at 1580 cm^{-1}, symmetric COO^- vibrations at 1386 cm^{-1}, C-H bending vibrations at 1400-1457 cm^{-1} (8). Increasing temperature led to the formation of linear CO at 1990 - 2013 cm^{-1} and bridged CO at 1831 cm^{-1} which became prominent at 200 – 275°C. During this temperature range, a significant amount of ethane at m/e = 29, ethylene at m/e = 28 and 27, and H_2 at m/e =2 were observed, revealing the occurrence of the decomposition of acetone on the Rh surface. Majority of the IR bands observed in Figure 7 can be attributed to adsorbed species associated with the Rh surface since adsorption of acetone on Al_2O_3 gave week C-H bands at 2700 – 3000 cm^{-1} and a week C=O donating on top η^1(C,O) band 1678 cm^{-1} (19).

Figure 8 shows the IR-TPD study of iso-propanol (5.6 vol% in Ar) on Rh/Al_2O_3. Adsorption of iso-propanol on Rh/Al_2O_3 produced C-H stretching at 2977, 2880,and 2933 cm^{-1}, chelated O-H vibration at 2506 cm^{-1}, C=O at 1697 cm^{-1}, asymmetric COO at 1570 cm^{-1}, symmetric COO^- vibration at 1386 cm^{-1}, CH- bending at 1386 - 1466 cm^{-1} and C-O vibration at 1164 cm^{-1}. The appearance of broad peak at 2506 cm^{-1} could be attributed to a shifted OH vibration arising from simultaneous conjugation and chelation of –OH of isopropanol with C=O of ace-

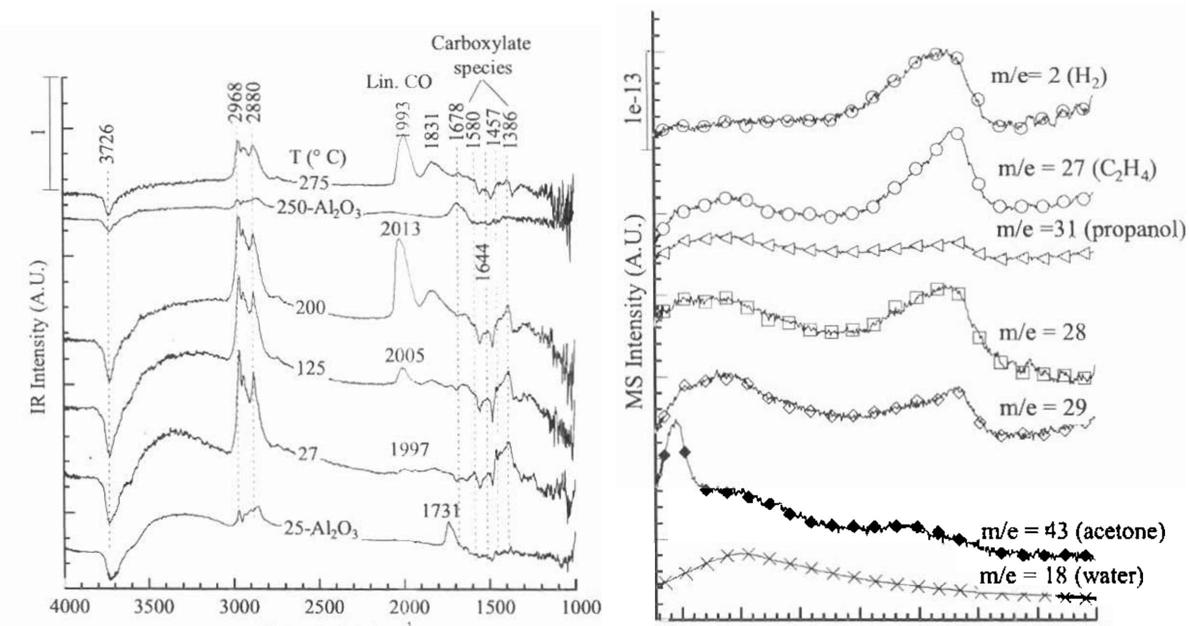


Figure 7. IR and MS analysis during TPD of acetone over Rh/Al_2O_3.

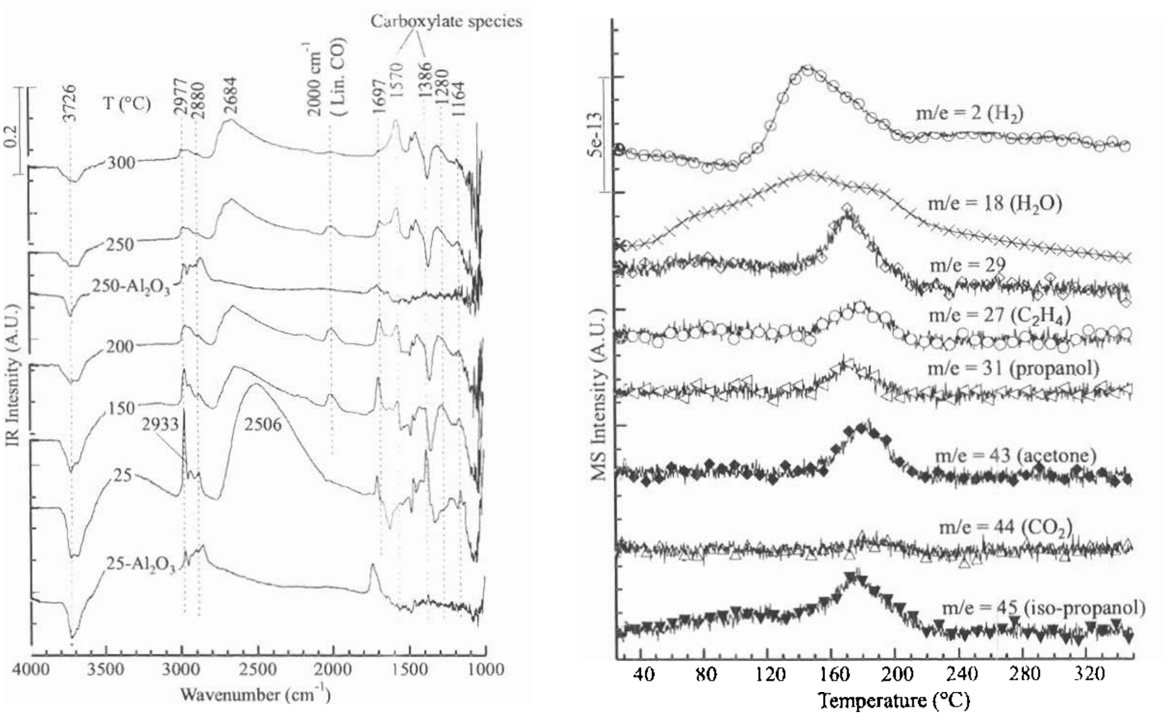
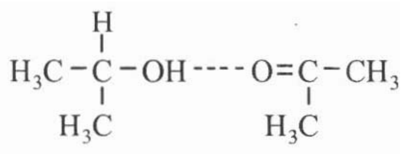


Figure 8. IR and MS analysis during TPD of iso-propanol over Rh/Al2O3

tone (20). The chelated structure has been suggested to be



$$H_3C-\underset{H_3C}{\overset{H}{C}}-OH\cdots O=\underset{H_3C}{C}-CH_3$$

Further study is needed to verify the above proposed band assignment for the 2506 cm^{-1} band. The linear CO at 2000 cm^{-1} appeared between 150 – 200°C where desorbed isopropanol (m/e =45) and decomposed products ethylene (m/e = 27), ethane (m/e =29), and acetone (m/e = 43) were observed by mass spectrometer. The observation of the H_2 peak at temperature below 150°C and the acetone peak at temperature above 150°C suggest dehydrogenation of isopropanol produced adsorbed acetone which desorbed after desorption of H_2. Two common species observed during IR-TPD of C_3 oxygenates are linear CO and carboxylate species (COO^-). The latter which exhibits excellent stability at 300°C has been found in the reaction of aldehyde and alcohol with adsorbed oxygen (21).

Figure 9 summarizes the reaction pathways of C_3 oxygenate formation from propylene partial oxidation on Rh/Al_2O_3. Rh plays an important role in all of the catalytic reaction pathways. The activity of Al_2O_3 for the production of H_2 and CO is two orders of magnitude lower than that of Rh/Al_2O_3 during the initial exposure of the catalyst to propylene. Al_2O_3 alone show little activity of propylene partial oxidation and decomposition of C_3 oxygenates.

Although CO_2 can be produced from oxidation of the C_3 oxygenates resulting from propylene partial oxidation, the formation of CO_2 leading that of acetone, isopropanol, and propanal suggests that CO_2 are produced from the direct oxidation of propylene, involving the linear CO at 2102 cm^{-1} on Rh^+ and the linear CO at 2040 cm^{-1}

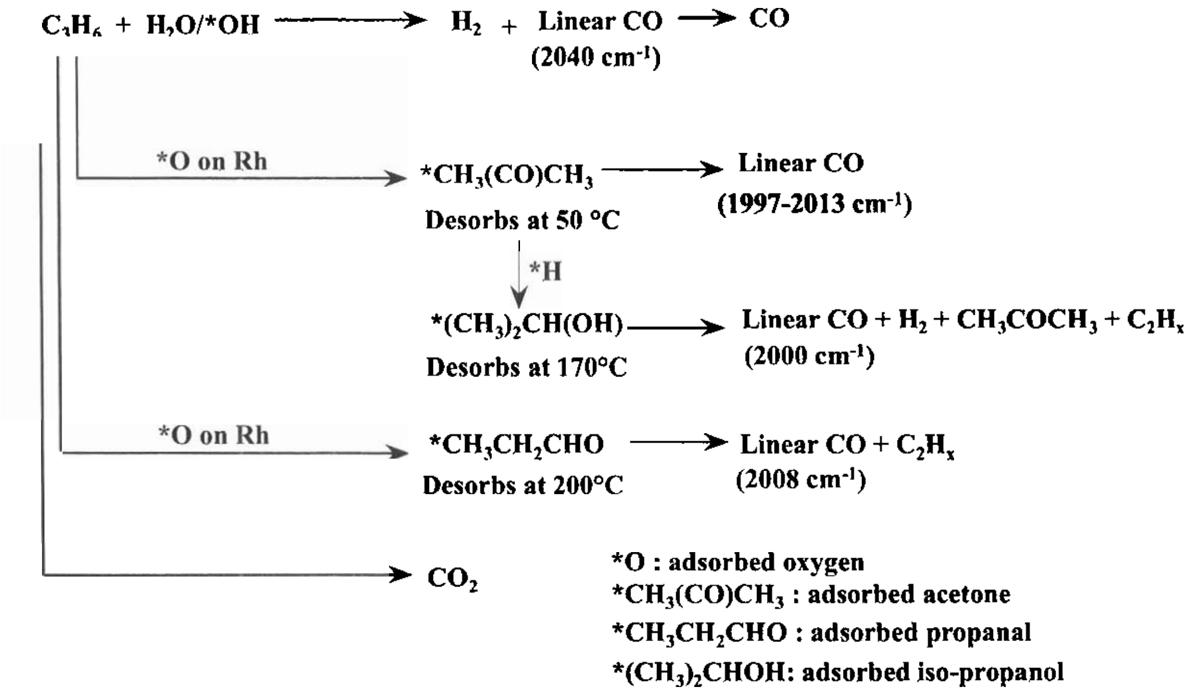


Figure 9. Reaction pathway for propylene partial oxidation over Rh/Al_2O_3.

on Rh^0. Formation of acetone and isopropanol follows a pathway in which acetone is produced and then further hydrogenated to isopropanol with hydrogen produced from the reaction of H_2O with propylene. The hydrogenation of acetone to isopropanol is supported by the observation of the decrease in the acetone profile corresponding to an increase in isopropanol profile as well as the rise of the H_2 profile following that of isopropanol in Figure 4. The delay in the formation of propanal is primarily due to its strong adsorption on the catalyst surface. Although acetone or isopropanol may isomerize to propanal, the possibility of this reaction route is not high considering the number of steps required in bond formation and breaking.

Caboxylate show prominent twin bands at 1570-1580 and 1370-1388 cm^{-1}. The species can be produced from the reaction of C_3 oxygenates with adsorbed oxygen. The absence of carboxylate in Figure 4 where the DRIFTS is in the down stream of tubular reaction and the oxygen is depleted in the DRIFTS further confirms that the formation of carboxylate require the involvement of oxygen. The rate of change in carboxylate intensity is slower than that of propanal at 1706 cm^{-1} and other adsorbed species, suggesting that this species could be a spectator adsorbed on Al_2O_3 surface.

Conclusion

The CO_2 formation pathway in total oxidation was found to be independent of C_3 oxygenate synthesis pathways in propylene partial oxidation. In partial oxidation pathway, acetone was produced and further hydrogenated to isopropanol by hydrogen on the Rh surface; propanal was formed from a separate pathway and strongly adsorbed on the catalyst surface. The C_3 oxygenates can be further oxidized in the presence of the O_2 pulse to a carboxylate intermediate which is stable under reaction condition. The carboxylate species can be considered as a spectator intermediate in propylene partial oxidation. The parallel pathways for CO_2 and C_3 oxygenate formation suggest the selective poisoning could be used to suppress the undesired total oxidation pathway and enhance the reaction selectivity toward the desired product.

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