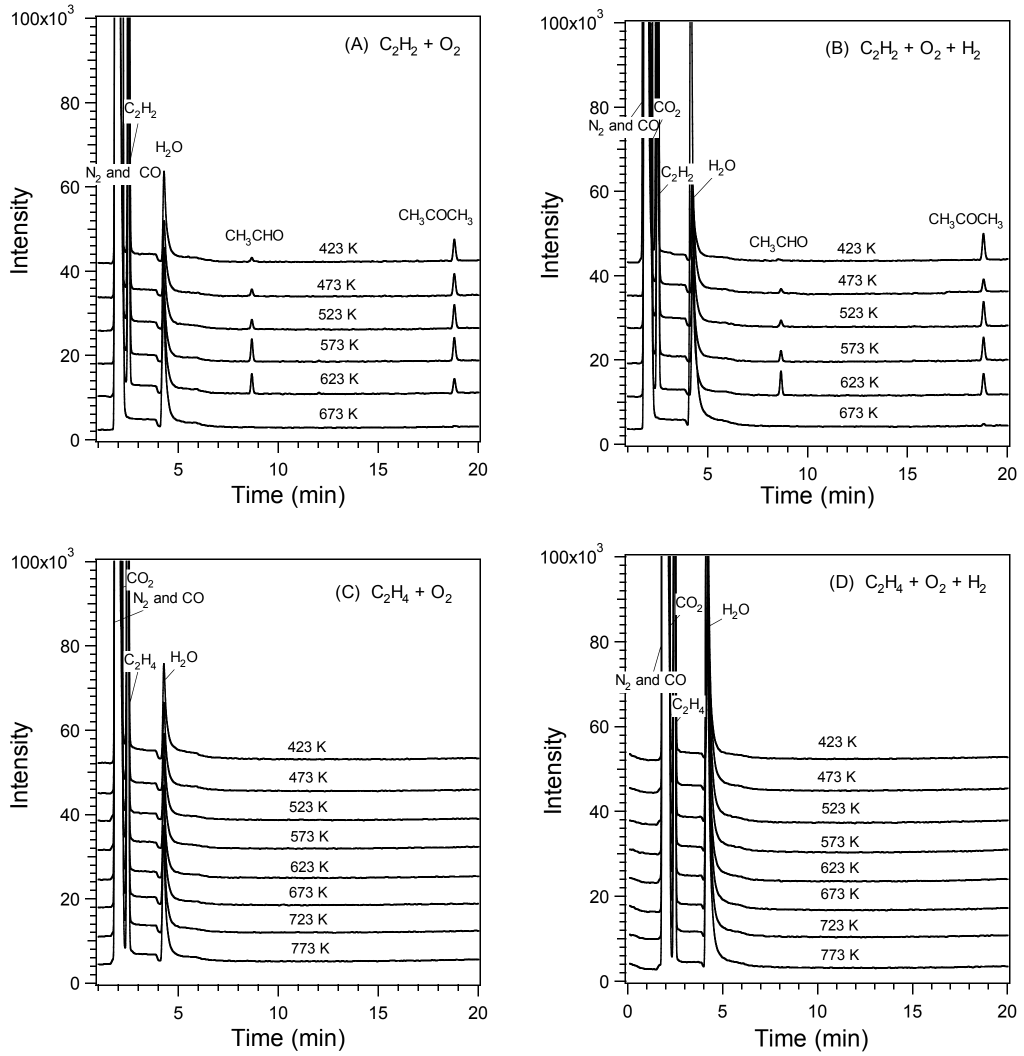
Electronic Supplementary Information

A common feature of H_2-assisted HC–SCR over Ag/Al_2O_3

Yunbo Yu, Hong He*, Xiuli Zhang and Hua Deng

1. GC–MS analysis



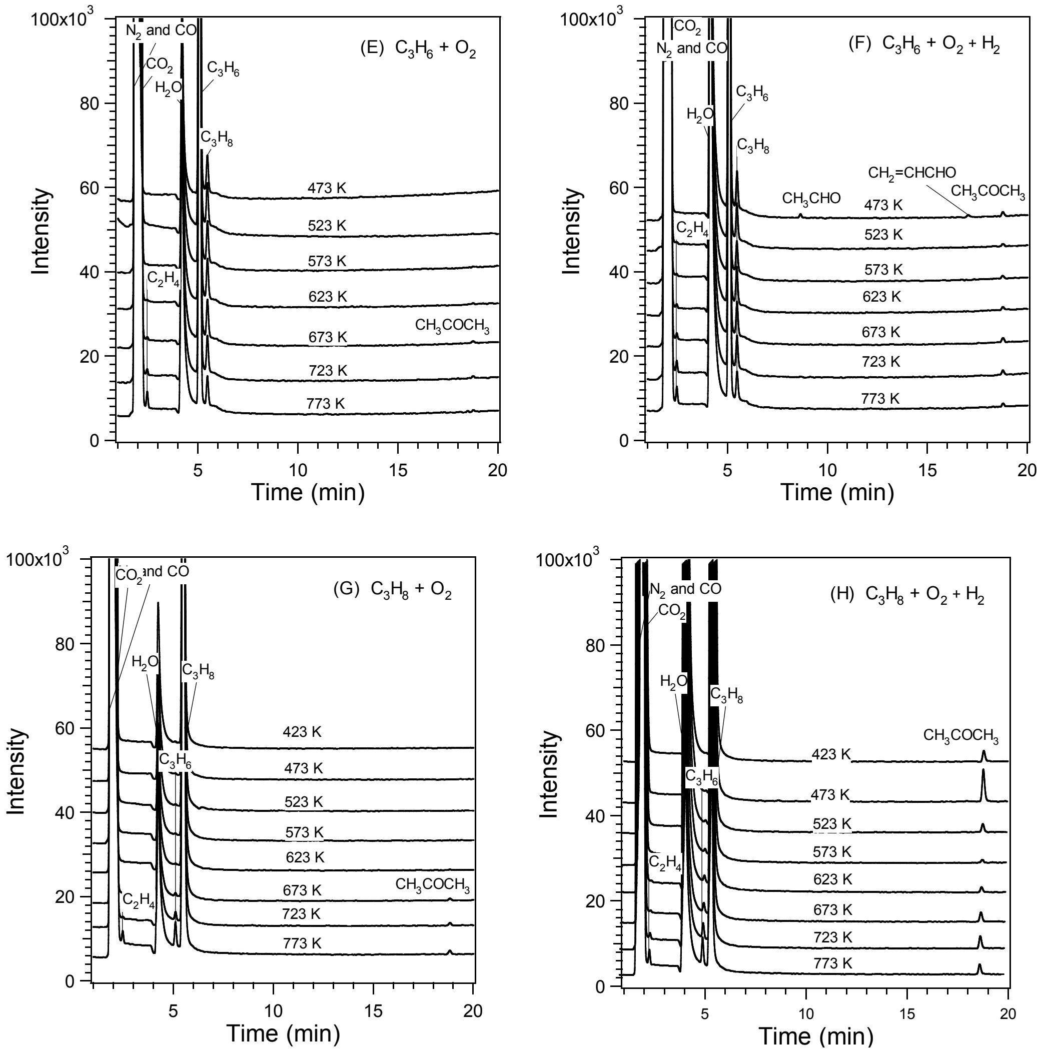
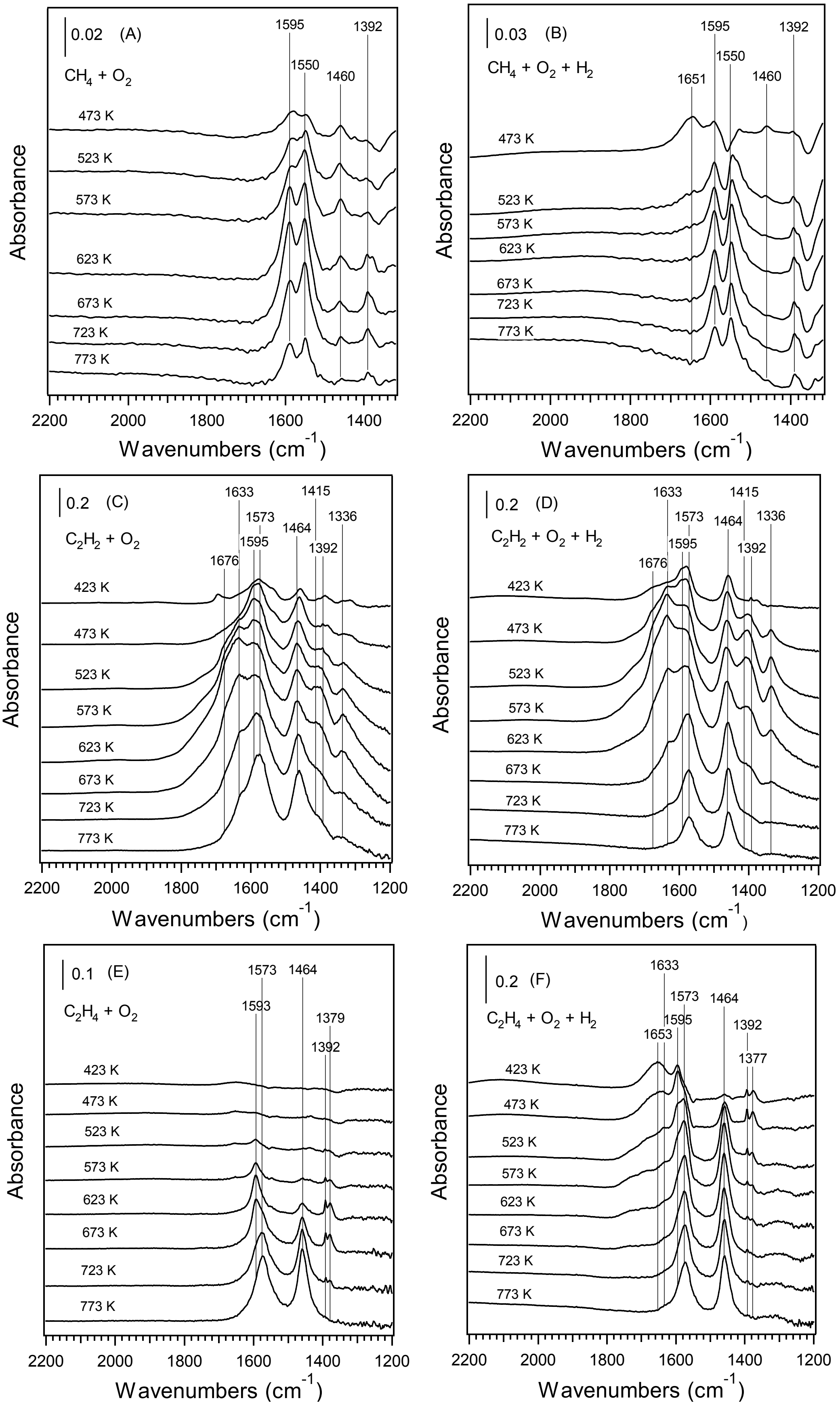
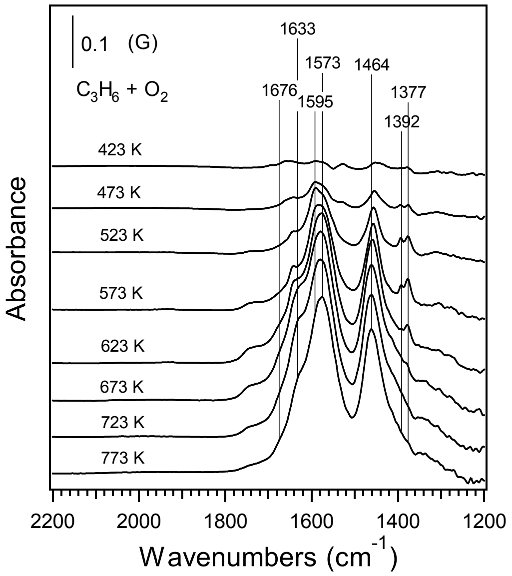
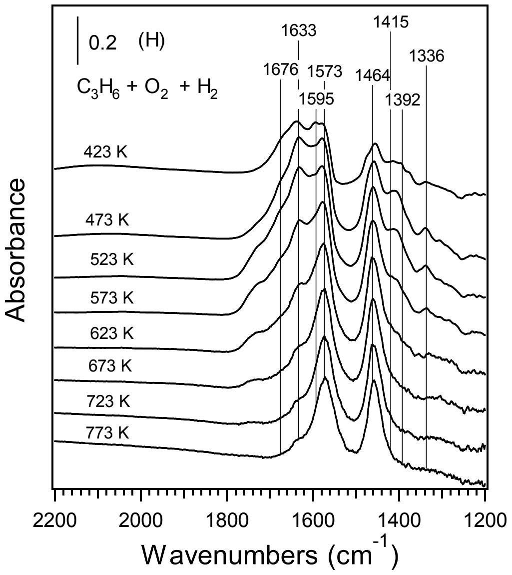


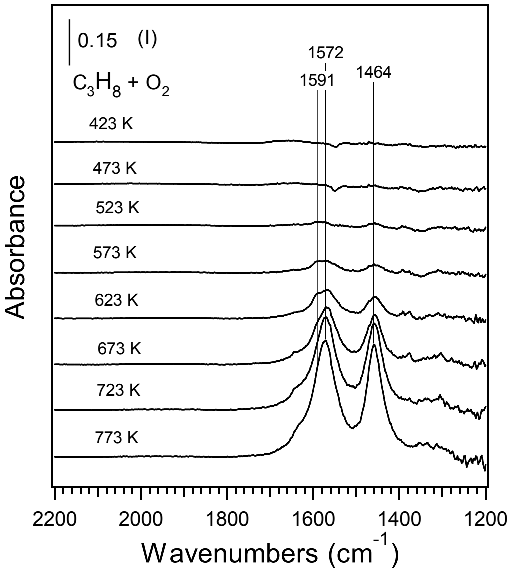
Fig. S1. GC–MS analysis during the oxidation of hydrocarbons without or with H_2 over Ag/Al_2O_3

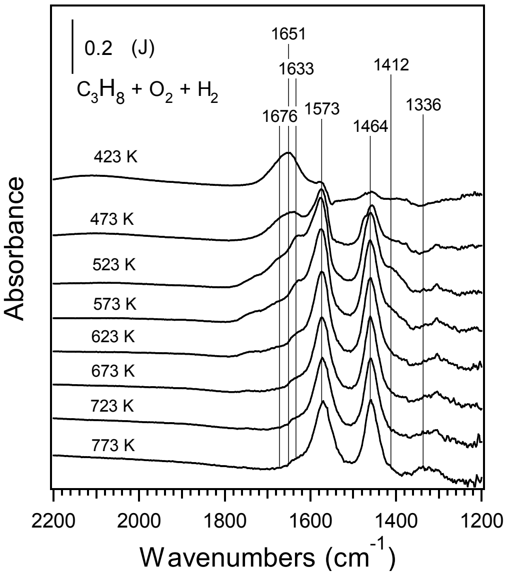
2. In situ DRIFTS studies


0.02 (A)
CH4 + O2
1595
1392
1550
1460
473 K
523 K
573 K
623 K
673 K
723 K
773 K
Absorbance
2200
2000
1800
1600
1400
Wavenumbers (cm-1)
0.03 (B)
CH4 + O2 + H2
1595
1392
1550
1651
1460
473 K
523 K
573 K
623 K
673 K
723 K
773 K
Absorbance
2200
2000
1800
1600
1400
Wavenumbers (cm-1)
0.2 (C)
C2H2 + O2
1633
1415
1573
1336
1464
1595
1392
1676
423 K
473 K
523 K
573 K
623 K
673 K
723 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm-1)
0.2 (D)
C2H2 + O2 + H2
1633
1415
1573
1464
1336
1595
1392
1676
423 K
473 K
523 K
573 K
623 K
673 K
723 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm-1)
0.1 (E)
C2H4 + O2
1573
1464
1593
1379
1392
423 K
473 K
523 K
573 K
623 K
673 K
723 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm-1)
0.2 (F)
C2H4 + O2 + H2
1633
1573
1464
1595
1392
1653
1377
423 K
473 K
523 K
573 K
623 K
673 K
723 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm-1)


0.1 (G)
$C_3H_6 + O_2$
1633
1573
1464
1676
1595
1377
1392
423 K
473 K
523 K
573 K
623 K
673 K
723 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm^{-1})


0.2 (H)
$C_3H_6 + O_2 + H_2$
1633
1415
1336
1676
1573
1464
1595
1392
423 K
473 K
523 K
573 K
623 K
673 K
723 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm^{-1})


0.15 (I)
$C_3H_8 + O_2$
1572
1591
1464
423 K
473 K
523 K
573 K
623 K
673 K
723 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm^{-1})


0.2 (J)
$C_3H_8 + O_2 + H_2$
1651
1633
1412
1676
1573
1464
1336
423 K
473 K
523 K
573 K
623 K
673 K
723 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm^{-1})

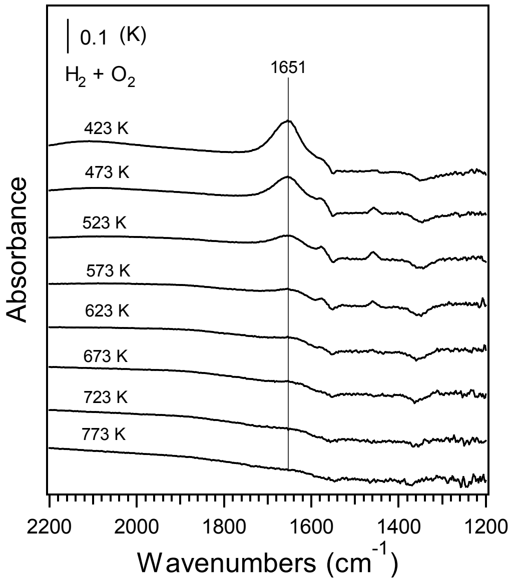

0.1 (K)
$H_2 + O_2$
1651
423 K
473 K
523 K
573 K
623 K
673 K
723 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm^{-1})

Fig. S2. In situ DRIFTS spectra of Ag/Al_2O_3 during the oxidation of hydrocarbons without or with H_2 (A–J), and during the reaction between H_2 and O_2 (K).

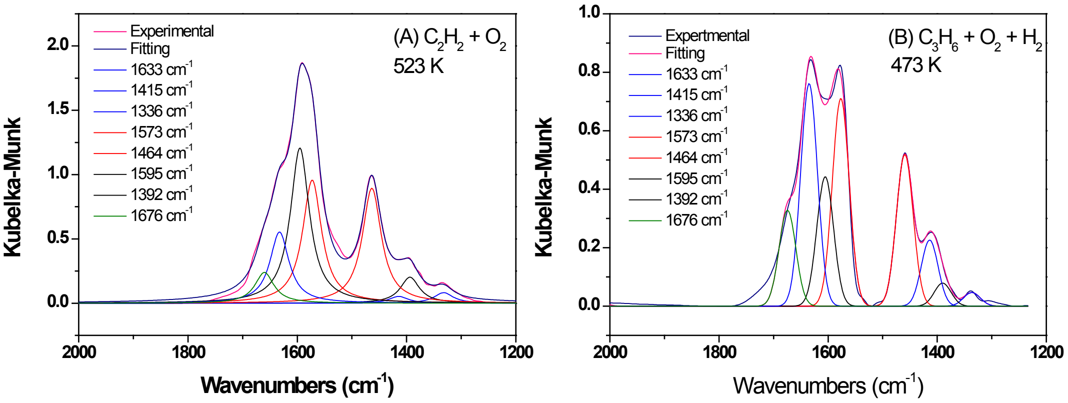
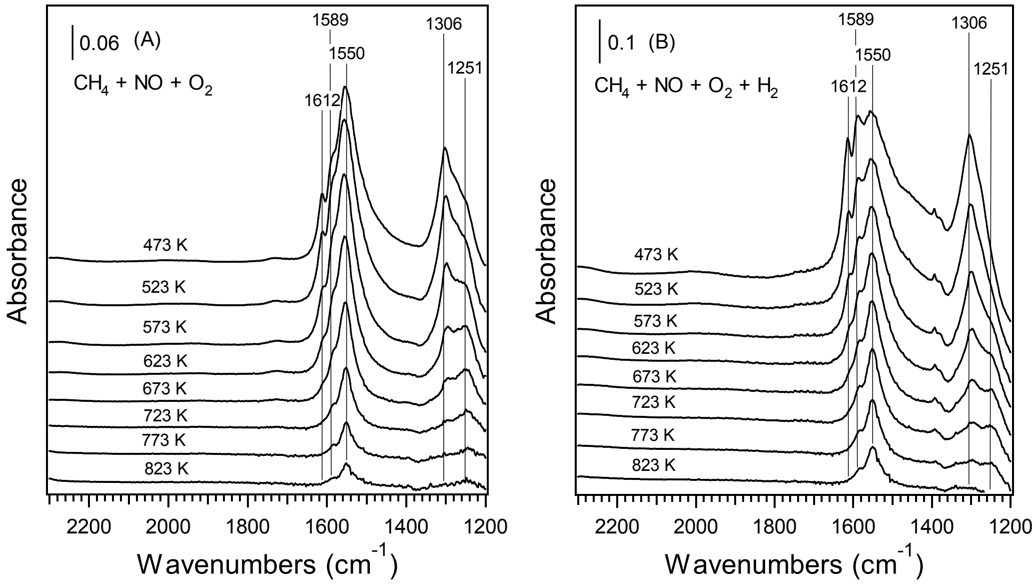
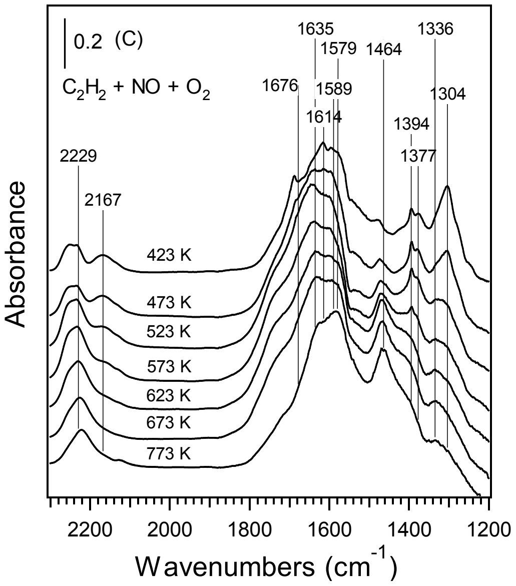
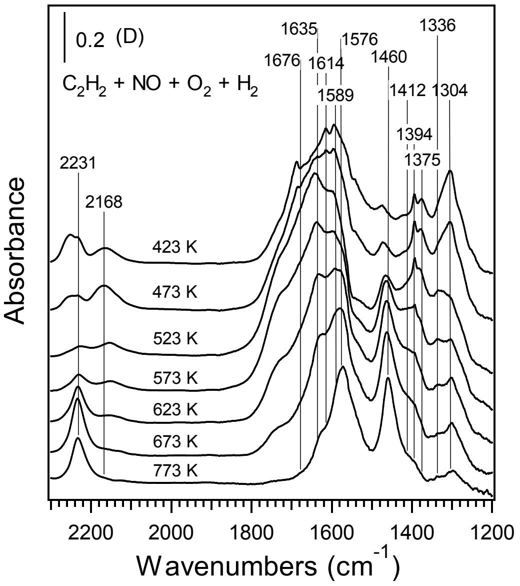
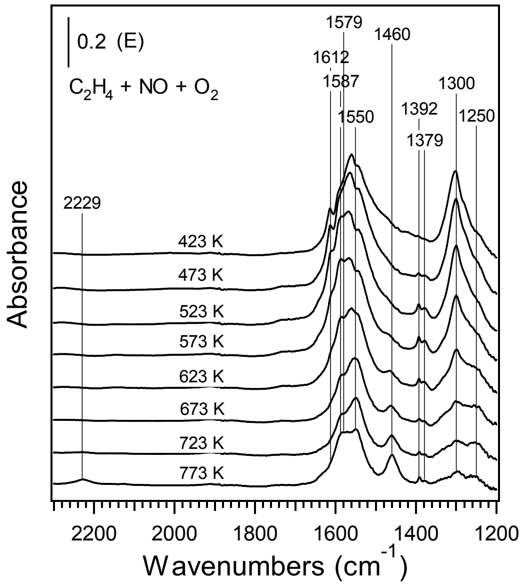


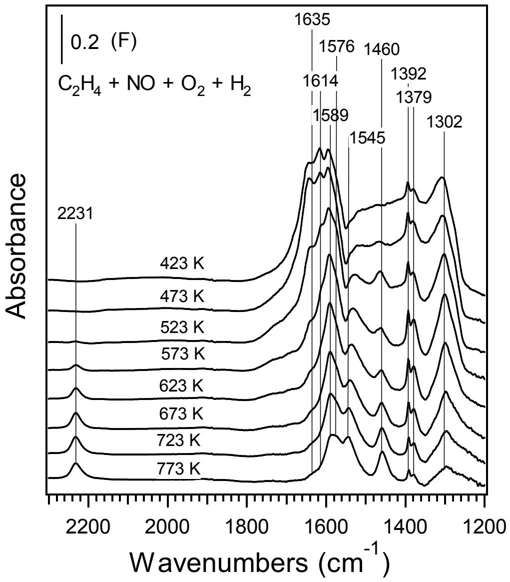
Fig. S3. The deconvolution and curve fitting results for DRIFTS spectra during C_2H_2 oxidation at 523 K (A) and C_3H_6 oxidation in the presence of H_2 at 473 K over Ag/Al_2O_3 (B).

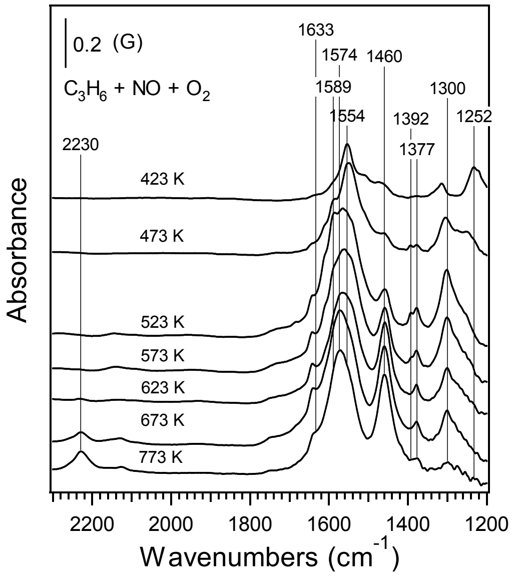


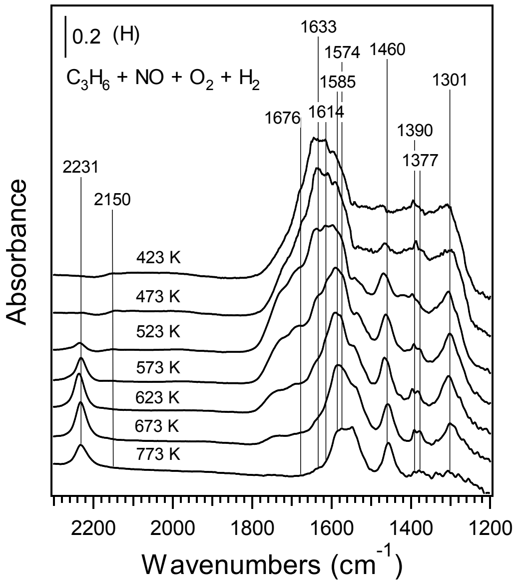

0.2 (C)
C_2H_2 + NO + O_2
2229
2167
1676
1635
1614
1589
1579
1464
1394
1377
1336
1304
423 K
473 K
523 K
573 K
623 K
673 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm^{-1})


0.2 (D)
C_2H_2 + NO + O_2 + H_2
2231
2168
1676
1635
1614
1589
1576
1460
1412
1394
1375
1336
1304
423 K
473 K
523 K
573 K
623 K
673 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm^{-1})


0.2 (E)
C_2H_4 + NO + O_2
2229
1612
1587
1579
1550
1460
1392
1379
1300
1250
423 K
473 K
523 K
573 K
623 K
673 K
723 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm^{-1})


0.2 (F)
C_2H_4 + NO + O_2 + H_2
2231
1635
1614
1589
1576
1545
1460
1392
1379
1302
423 K
473 K
523 K
573 K
623 K
673 K
723 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm^{-1})


0.2 (G)
C_3H_6 + NO + O_2
2230
1633
1589
1574
1554
1460
1392
1377
1300
1252
423 K
473 K
523 K
573 K
623 K
673 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm^{-1})


0.2 (H)
C_3H_6 + NO + O_2 + H_2
2231
2150
1676
1633
1614
1585
1574
1460
1390
1377
1301
423 K
473 K
523 K
573 K
623 K
673 K
773 K
Absorbance
2200
2000
1800
1600
1400
1200
Wavenumbers (cm^{-1})

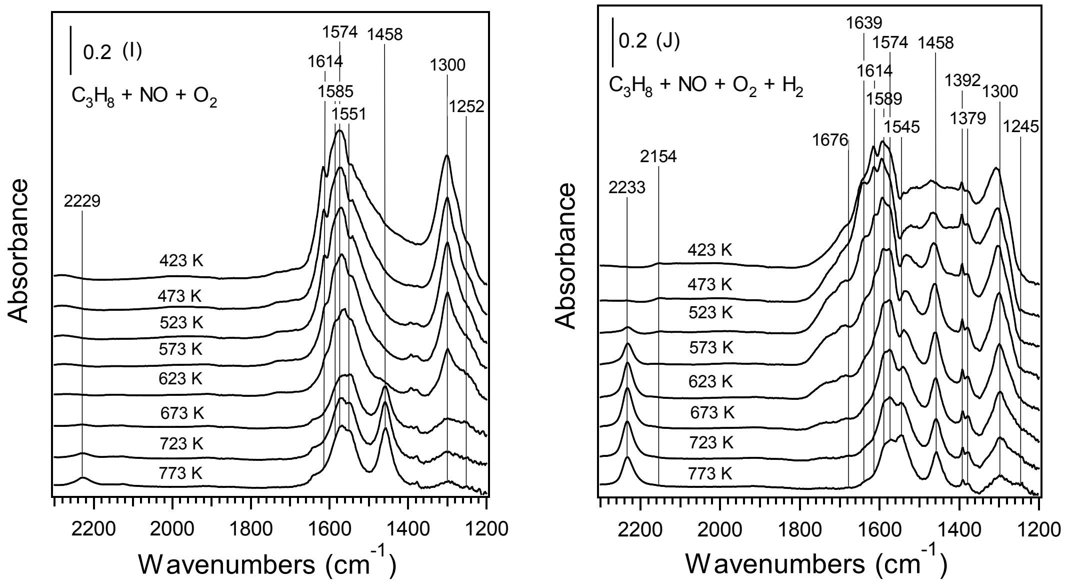


Fig. S4. In situ DRIFTS spectra of Ag/Al_2O_3 during the NOx reduction by different hydrocarbons without or with H_2.

As for CH_4-SCR over Ag/Al_2O_3, monodentate nitrate (1550 and 1251 cm^{-1}), bidentate nitrate (1589 and 1306 cm^{-1}), and bridging nitrate (1612 cm^{-1}) were clearly observed within the temperature range of 473-823 K while the surface species due to the partial oxidation of CH_4 was hardly observed (Fig. S4A). [1,2] Trends such as these were also obvious when H_2 was co-fed into the flow of $CH_4 + O_2 + NO$ (Fig. S4B).

During the NOx reduction by C_2H_2 (Fig. S4C), bidentate nitrate (1589 and 1304 cm^{-1}), and bridging nitrate (1614 cm^{-1}) were also observed. Quite different from CH_4-SCR, large amounts of enolic species (1635 and 1336 cm^{-1}) and acetate (1579 and 1464 cm^{-1}) appeared during the NOx reduction by C_2H_2. As temperature increasing from 423 K to 623 K, decreased intensities of nitrates and enolic species were always accompanied by an increase in the intensity of –NCO species (2229 cm^{-1}) [3], during which a gradually increased intensity of acetate peak was clearly observed at 1464 cm^{-1}. In addition, a peak at 2167 cm^{-1} can be assigned to surface –CN.[3] Similar to the partial oxidation of C_2H_2 (Fig. S2C), the appearance of peak at 1676 cm^{-1} confirmed the formation of surface acetone. All the surface species described above were clearly observed during the H_2-assisted C_2H_2–SCR (Fig. S4D), while a much lower intensity of –NCO peak appeared at above 523 K if compared with Fig. S4C. Keeping the activity measurements (Fig. 1B) in mind, it may suggest that only a fraction of all the –NCO observed by DRIFTS is reactive and potential intermediates for NOx reduction at a given temperature.[4]

As for C_2H_4–SCR (Fig. S4E), C_3H_6–SCR (Fig. S4G), and C_3H_8–SCR (Fig. S4I), three kinds of nitrates described above were clearly observed within the whole temperature range. In contrast, the oxygenated species due to the partial oxidation of C_2H_4, C_3H_6, and C_3H_8, such as acetate and enolic species were hardly observed at low temperatures. These trends were more pronounced during the NOx reduction by C_2H_4 and C_3H_8. In the two cases, no peak due to enolic species can be observed within the whole temperature region, and the peak of 1458–1460 cm^{-1} assignable to acetate did not appear at temperature below 573 K. When H_2 was introduced into the feeding, however, the enolic species (1633–1639 cm^{-1}) with strong intensity appeared even the temperature as low as 423 K (Figs. S4F, S4H, and S4J). Also, the formation of acetate was triggered by H_2 addition at temperature of 423 K on which the peak at around 1458–1460 cm^{-1} can be observed clearly.

References

1. P. Sazama, L. Čapek, H. Drobná, Z. Sobalík, J. Dědeček, K. Arve and B. Wichterlová, *J. Catal.,* 2005, **232**, 302.
2. S. Kameoka, Y. Ukisu and T. Miyadera, *Phys. Chem. Chem. Phys.,* 2000, **2**, 367.
3. S. Tamm, H. H. Ingelsten and A. E. C. Palmqvist, *J. Catal.,* 2008, **255**, 304; F. Thibault-Starzyk, E. Seguin, S. Thomas, M. Daturi, H. Arnolds and D. A. King, *Science,* 2009, **324**, 1048.
4. S. Chansai, R. Burch, C. Hardacre, J. Breen and F. Meunier, *J. Catal.,* 2010, **276**, 49.