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# Electronic Supplementary Information

# Catalytic oxidation of 1, 2-dichloroethane over $Al_2O_3$-$CeO_2$ catalysts: Combined effects of acid and redox properties

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## 1. Catalysts characterization

### 1.1. X-ray diffraction

The powder X-ray diffraction patterns (XRD) of samples were recorded on a Rigaku D/Max-rC powder diffractometer using Cu Kα radiation (40 kV and 100 mA). The diffractograms were recorded in the 2θ range of 10-80 ° with a 2θ step size of 0.01° and a step time of 10 s.

### 1.2. Nitrogen adsorption/desorption

The nitrogen adsorption and desorption isotherms were measured at 77 K on an ASAP 2400 system in static measurement mode. Samples were outgassed at 160 °C for 4 h before the measurement. The specific surface area was calculated using the BET model.

### 1.3. Transmission electron microscopy

The TEM images of the powder samples were recorded on a JEM-1400 instrument operated at 120 kV. High-resolution transmission electron microscopic (HRTEM) images were taken on a JEM-2100 field emission transmission electron microscope that operated at 200 kV.

### 1.4. $O_2$ Temperature programmed Oxidation

$O_2$-temperature programmed oxidation ($O_2$-TPO) of samples (150 mg) placed at the bottom of the U-shaped quartz tube was investigated by heating samples in $O_2$ flow (30 mL min$^{-1}$) at a heating rate of 10 °C min$^{-1}$ from 100 to 600 °C. The $CO_2$ (m/z=44) and CO (m/z=28) were monitored on the basis of the analysis with a mass spectrometer (Hiden HPR20).

### 1.5. Temperature programmed reduction

$H_2$-temperature programmed reduction ($H_2$-TPR) of samples (100 mg) placed at the bottom of the U-shaped quartz tube was investigated by heating samples in $H_2$ (5 vol. %)/Ar flow (30 mL min$^{-1}$) at a heating rate of 10 °C min$^{-1}$ from 50 to 750 °C. The hydrogen consumption was estimated on the basis of the analysis with a thermo-conductivity detector (TCD), the extent of reduction was quantitatively calculated according to the TPR peak areas and the result was calibrated on the basis of the hydrogen consumption from the reduction of CuO to Cu.

### 1.6 X-ray photoelectron spectroscopy

The XPS measurements were made on a VG ESCALAB MK II spectrometer by using Mg Kα (1253.6 eV) radiation as the excitation source. Charging of samples was corrected by setting the binding energy of adventitious carbon (C1 s) at 284.6 eV. The powder samples were pressed into self-supporting disks, loaded into a sub-chamber, and evacuated for 4 h, prior to the measurements at 298 K.

### 2.1 The temperature-programmed surface reaction (TPSR)

The temperature-programmed surface reaction (TPSR) measurement was carried out under the conditions as the same as that in the catalytic activity tests in order to detect the reactants and products in effluence. First, the feeding Ar/O2 (80/20) stream containing a certain concentration of DCE (such as 1,000 ppm) flowed through the catalyst bed at 50 °C. After the adsorption-desorption of DCE reached an equilibrium, the catalyst bed was heated from 50 to 400 °C at 10 °C min-1. And then temperature maintained at 400 °C for 0.5h. The reactant and products, such as DCE (m/z=98), CO2 (44), CO (28), Cl2 (70), HCl (36), VC (62), TCE (133), 29 (-CHO, the fragment of ClCH2CHO or CH3CHO), 43 (-CH2CHO, the fragment of ClCH2CHO) and 50 (-CH2Cl, the fragment of DCE or ClCH2CHO) in effluence were analyzed on-line by mass spectrometer apparatus (Hiden HPR-20).

### 2.2. In situ FTIR studies

FTIR spectra were collected with a Nicolet 6700 spectrometer and an in situ flow cell. The spectrometer was equipped with a MCT/A detector cooled by liquid nitrogen. The cell was “capped” by IR-transparent ZnSe crystal windows. Approximately 25~60 mg of the catalyst located at the centre of the cell. Diffuse reflectance spectra were collected in a single beam mode as an average of 64 runs with a resolution of 4 cm-1. Prior to each experiment the catalyst was oxidized at 400 °C for 2 h with Ar/O2 (80/20). After the treatment the cell was flushed with Ar/O2 for at least 30 min and cooled down to 50 °C, spectra of the clean catalyst surface were collected after this process and utilized as background. Subsequently, a mixture of Ar/O2 and DCE were introduced into the cell for 30 min at 50 °C, at a concentration of approximately 2, 000 ppm. The sample was then evacuated for 30 min at the same temperature and cooled to 50°C, before recording the spectrum. The species on the catalysts surface were successively monitored stepwise, by evacuating the sample for 30 min at 100, 150, 200, 250, 300, 350 and 400 °C and cooling to 50 °C between each step, to record the spectrum.

Fig S1 (a) Light-off curves initial activity of 1, 2-dichloroethane over $Al_2O_3$, $CeO_2$ and AlCe50/50-NC catalysts. DCE concentration: 1,000 ppm; GHSV: 15, 000 $h^{-1}$. (b) The selectivity of VC over $Al_2O_3$, $CeO_2$ and AlCe50/50-NC catalysts.

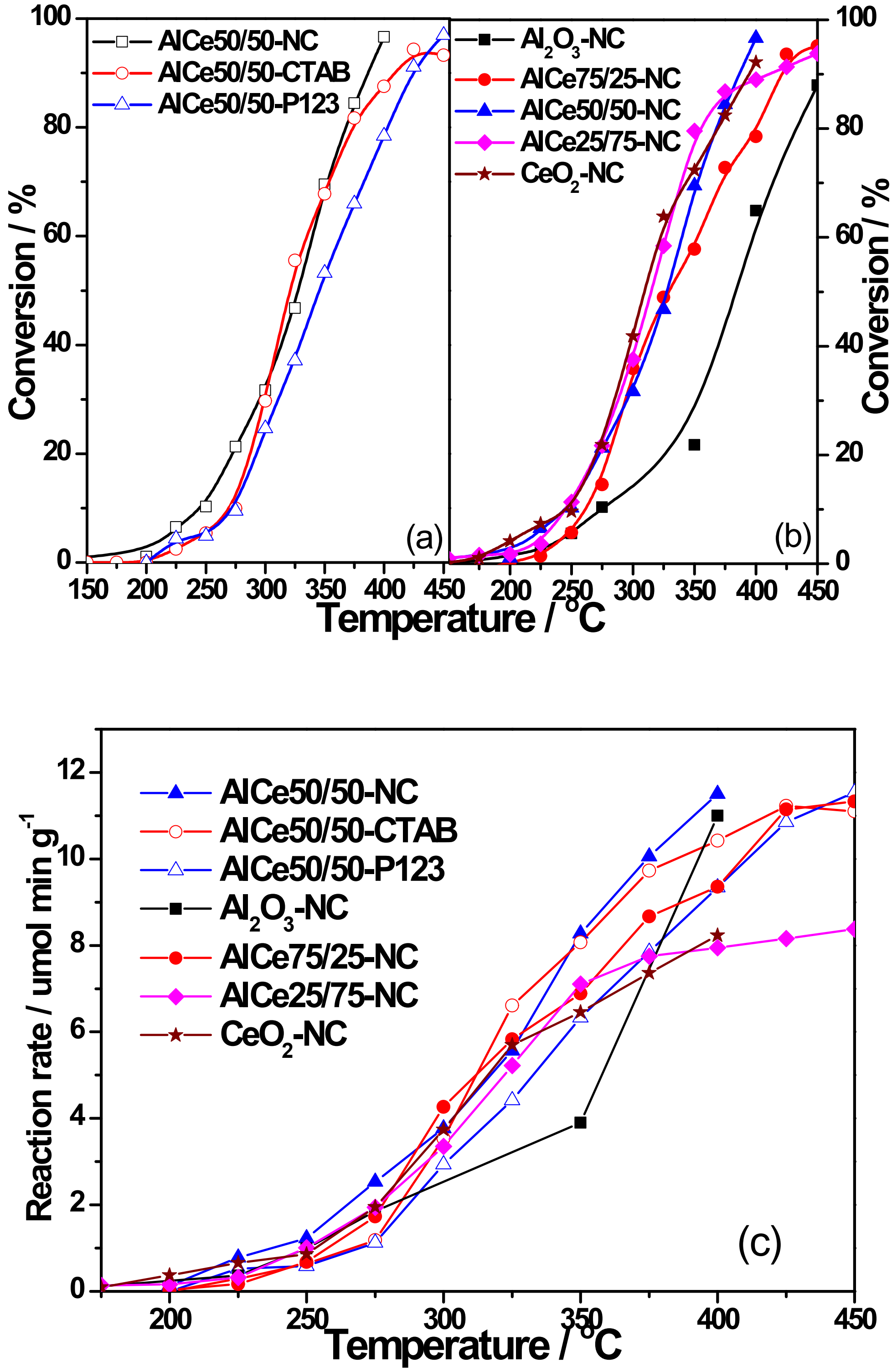

Fig S2 Light-off curves stable activity of 1, 2-dichloroethane over Al-Ce compound oxides catalysts prepared by different methods (a) and at different rates of Al:Ce (b). DCE concentration: 1,000 ppm; GHSV: 15, 000 h$^{-1}$ and (c).reaction rates of different catalysts.

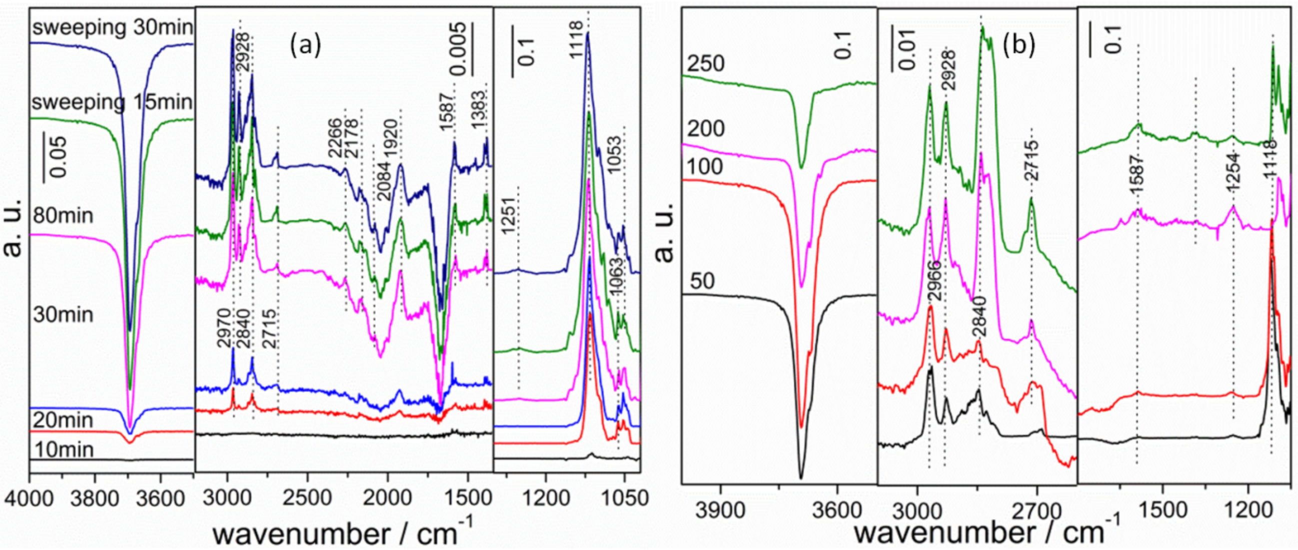

Fig S3 DRIFTS spectra of ethanol adsorbed on pure $CeO_2$ catalysts.

Fig S4 DRIFTS spectra of ethanol adsorbed on pure $Al_2O_3$ catalysts.

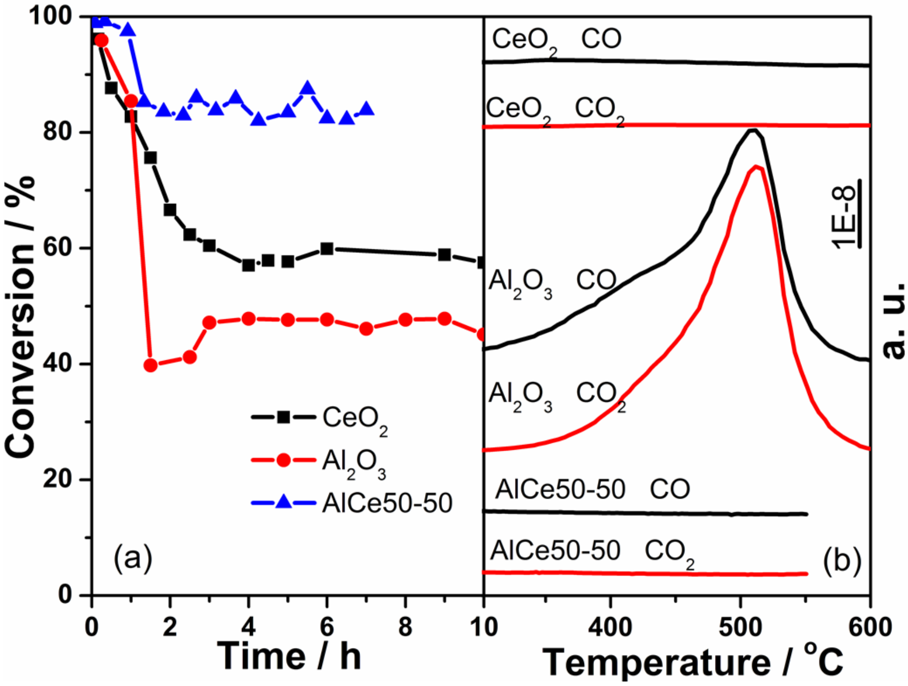

Fig S5 (a) The stability of $Al_2O_3$ and $CeO_2$ catalysts at 300 °C, DCE concentration: 250 ppm; GHSV: 15, 000 $h^{-1}$; (b) The $O_2$-TPO of the $Al_2O_3$ and $CeO_2$ catalysts after the stability test, DCE concentration: 1, 000 ppm; GHSV: 15, 000 $h^{-1}$, 300 °C.

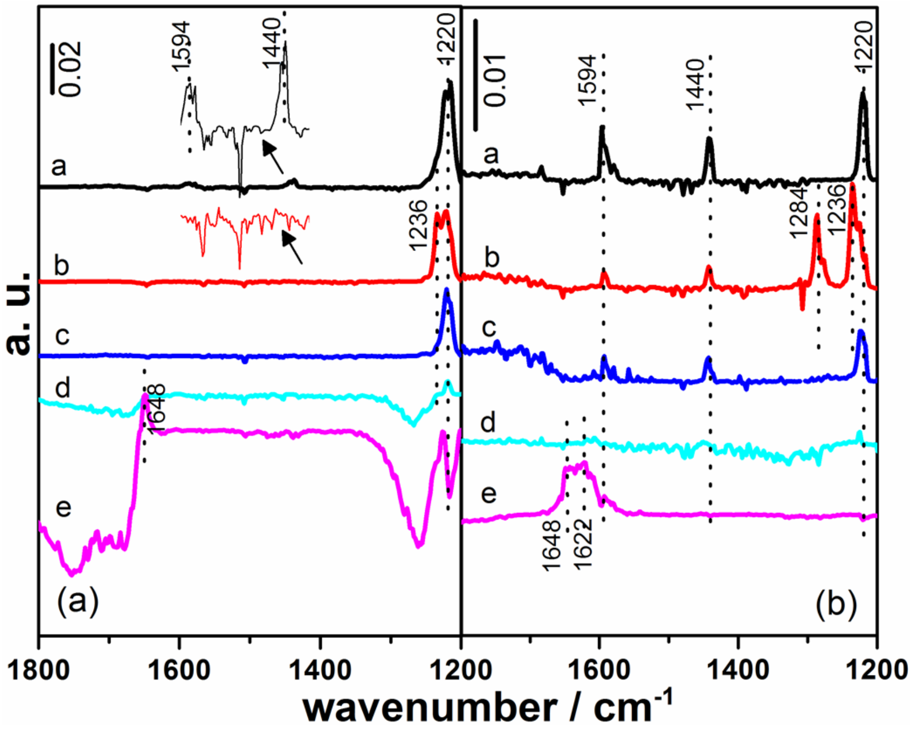

Fig S6 Inhibition of DCE decomposition on $CeO_2$ (a) and AlCe50-50 (b) by using preadsorbed pyridine to block acid sites. a. preadsorded pyridine, b. adsorded DCE at 50 °C, c. sweeping 30min at

50$^{o}$C, d. adsorded DCE at 150 $^{o}$C, e. adsorded DCE at 300 $^{o}$C.

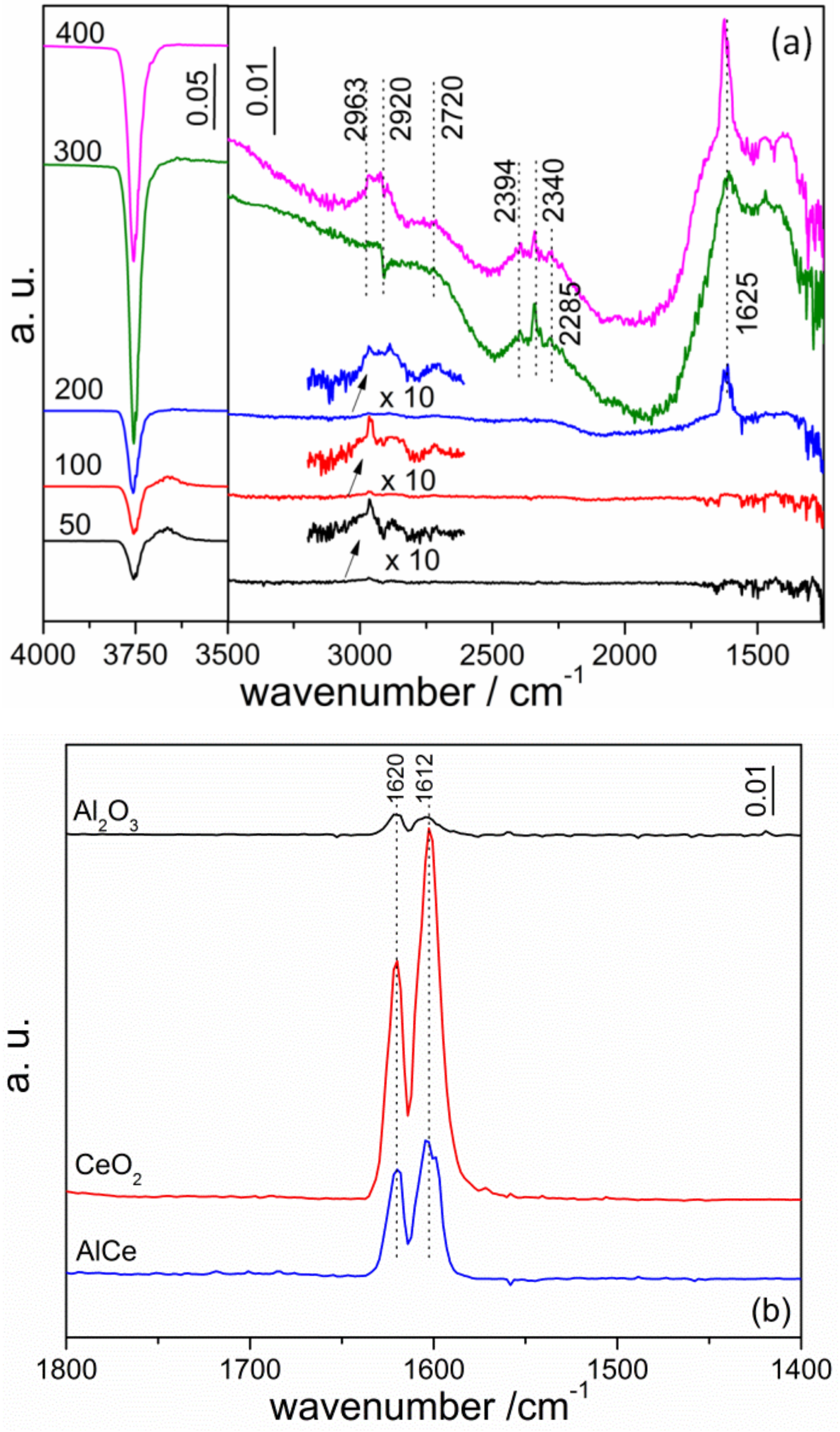

Fig. S7 in situ DRIFTS of DCE oxidation on $Al_2O_3$ at different temperature (a) and adsorption of DCE on $CeO_2$, $Al_2O_3$ and AlCe50/50 catalysts at 50 (b).

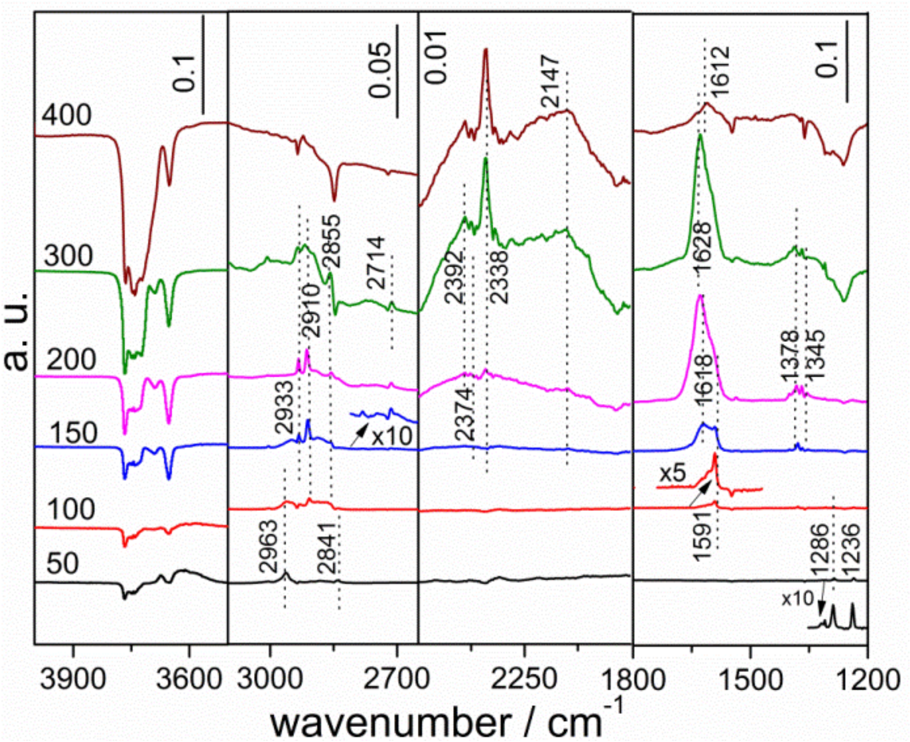

**Fig. S8** *in situ* DRIFTS of DCE oxidation on AlCe50/50 catalysts at different temperature.

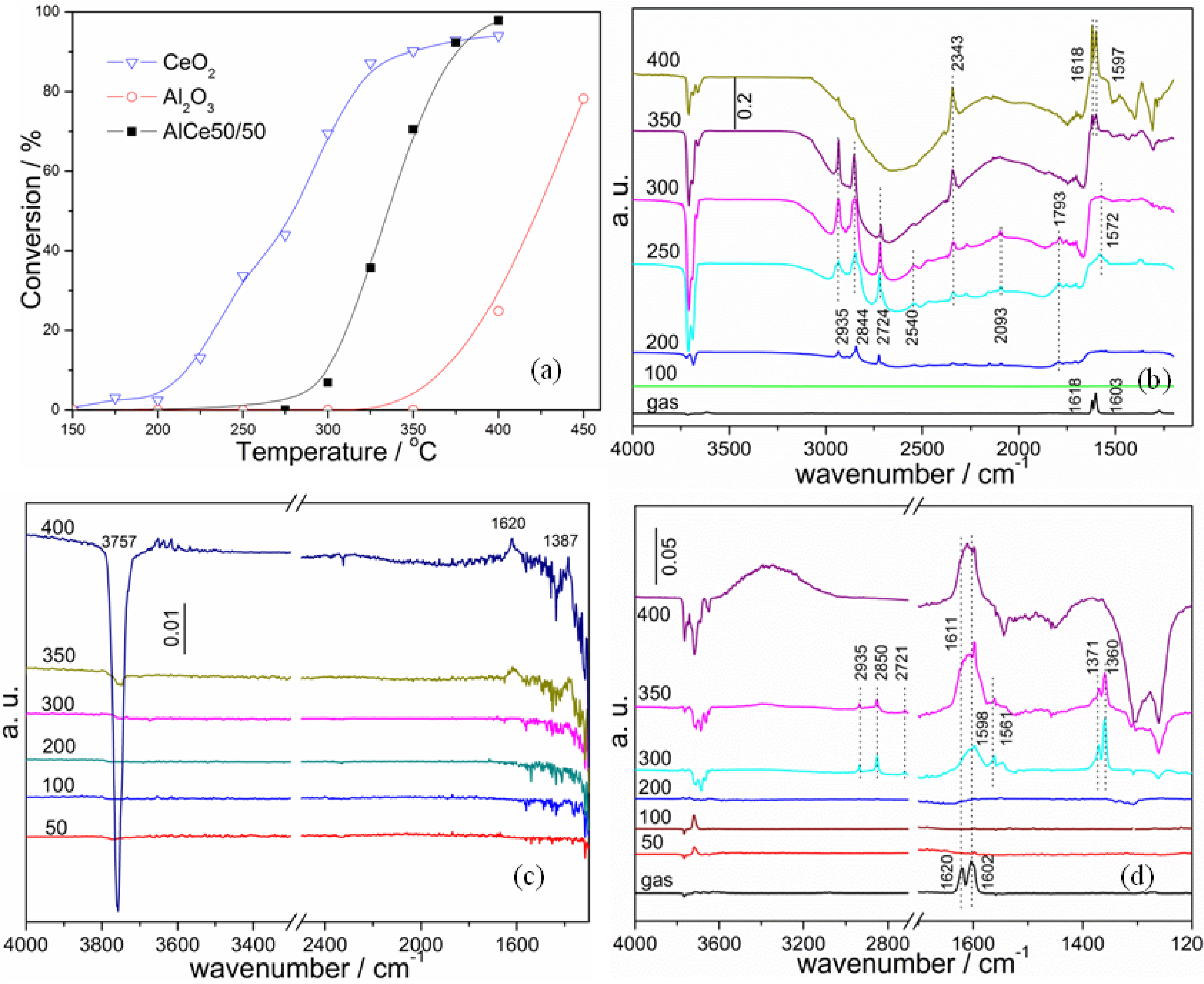

**Fig. S9** Light-off curves and *in situ* DRIFTS of vinyl chloride on on CeO$_2$, Al$_2$O$_3$ and AlCe50/50 catalysts.

### 3.1 *in situ* DRIFTS of vinyl chloride and activity tests

The formation of vinyl chloride as by-product had been identified in the process of activity tests (Fig S1), despite was not reconfirmed via TPSR experiments due to the overlapping of fragments with DCE. *In situ* DRIFTS presented a different result and bands corresponding to vinyl chloride are not observed on CeO$_2$ catalyst. Therefore, the conversion and *in situ* DRIFTS of vinyl chloride were investigated over three catalysts in the range of 50 and 400 °C and shown in Fig S9. Light-off curves (Fig S9 a) showed that all catalysts presented a poor catalytic activity for the vinyl chloride oxidation compared with DCE oxidation, but $CeO_2$ catalyst still exhibited the highest activity among the three catalysts, the 10% and 90% conversion can be achieved at 225 and 350 °C, and only 80% conversion was obtain over $Al_2O_3$ catalyst at 450 °C. Additionally, the catalytic activity of AlCe50/50 catalyst was lower than that of $CeO_2$, but at higher temperature range the increase of activity was more significant when compared to pure $CeO_2$ or $Al_2O_3$, which may be due to the improved resistance to Cl poisoning and coke formation and the same effect had also been observed for DCE oxidation (Fig S1). The *in situ* DRIFTS showed that the adsorption of vinyl chloride was difficult on all the catalysts when the reaction temperature was lower than 200 °C, even the bands corresponding to vinyl chloride and negative bands ascribed the consumption of hydroxyl groups were still not observed on $Al_2O_3$ catalyst at 300 °C, which was probably one of the reasons for the worst activity. For the $Al_2O_3$ catalyst, the available information from the *in situ* DRIFTS was rare and none bands associated with the intermediate species or final product except a weak band of vinyl chloride (1620 $cm^{-1}$) and a negative band of hydroxyl groups (3757 $cm^{-1}$) were recorded above 350 °C. However, a series of bands appeared over $CeO_2$ catalyst above 200 °C. The bands at 2935, 2844, 2724 and 1793 $cm^{-1}$ were assigned to aldehyde species and the band at 2343 $cm^{-1}$ was ascribed to $CO_2$, and the intensities of vinyl chloride reached a max value at 300 °C while $CO_2$ continually enhanced as the temperature increased. Additionally, the band intensity of vinyl chloride also increased with the increasing of reaction temperature, which further suggested that the adsorption of vinyl chloride on catalyst surface only occurred at higher temperature. Thus, the bands of vinyl chloride were not detected during *in situ* DRIFTS experiments of DCE on $CeO_2$ catalyst and this can be ascribed to the difficult adsorption and the dissociation to aldehyde species. Over AlCe50/50 catalyst, besides aldehyde species (2935, 2850 and 2721 $cm^{-1}$) were observed compared with pure $CeO_2$ catalysts, the adsorption/dissociation of vinyl chloride only occurred above 300 °C and besides aldehyde species (2935, 2850 and 2721 $cm^{-1}$) were observed compared to pure $CeO_2$ catalyst, the formation of carboxylate species (1561, 1371 and 1360 $cm^{-1}$) was observed. The carboxylate species were considered to come from the further oxidation of aldehyde species by surface lattice oxygen. By comparison, it can be found that aldehyde species as intermediate species were crucial for the oxidation of DCE and vinyl chloride, even other chloro-alkanes, and the poor catalytic activity for vinyl chloride was due to the difficult adsorption/dissociation on catalysts surface, especially on $Al_2O_3$.