Ketonisation of acetic acid on metal oxides: catalyst activity, stability and mechanistic insights

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**Abstract**

Ketonisation of acetic acid to acetone was studied in the gas phase using γ-Al2O3, TiO2, ZrO2 and CeO2 as the catalysts in the temperature range of 180-350 oC and ambient pressure. Catalyst activity was found to increase in the order Al2O3 << TiO2 < ZrO2 < CeO2. CO2-TPD showed that relatively weak base sites on oxide surfaces are essential for the ketonisation activity, whereas no relation between oxide acidity and catalytic activity was observed. Catalyst resistance to deactivation increased in the order CeO2 << ZrO2 < TiO2 in parallel with the amount of coke formed. TiO2 (Degussa P25) and ZrO2 were found to exhibit the best performance as represented by their activity and stability to deactivation. CeO2 and ZrO2 could be regenerated by air calcination to regain their activity. DRIFTS studies of acetic acid adsorption on oxide surfaces found facile exchange between adsorbed bidentate bridging acetate species and gas-phase acetic acid at 130 oC, well below temperature threshold of acid ketonisation, indicating fast equilibration of different forms of surface acetate species in the ketonisation system. At higher temperatures typical for acid ketonisation, in the absence of gas-phase acetic acid, the adsorbed bidentate bridging acetate-*d*3 species were found to undergo H/D exchange with proton sites on oxide surfaces. This provides experimental evidence supporting the intermediacy of enolate species in acid ketonisation.

**Keywords**: Acetic acid; Ketonisation; Metal oxides; Catalyst deactivation; Reaction mechanism

1. **Introduction**

Carboxylic acids are readily available from renewable natural resources and can be used for the production of value-added chemicals and carbon-neutral bio-fuels [1,2]. For fuel applications, carboxylic acids require an increase in their caloric value which can be achieved by reduction in their oxygen content. Much current research is focussed on the deoxygenation of carboxylic acids, primarily using heterogeneous catalysis [3-7].

Ketonisation (Eq. (1)) is a chemical reaction which converts two molecules of a carboxylic acid into a ketone, carbon dioxide and water [8,9], thus making a new C-C bond and removing three oxygen atoms. Ketonisation reaction occurs with carboxylic acids possessing α-hydrogen atoms at least in one of the reacting acid molecules. In contrast to catalytic hydrodeoxygenation, no hydrogen is required for the ketonisation of carboxylic acids.

2 CH3COOH → (CH3)2CO+ CO2 + H2O (1)

Ketonisation has long been employed as a clean method for the synthesis of ketones ([8,9] and references therein). Currently, this reaction attracts significant interest for the upgrading of biomass-derived oxygenates, for example, bio-oil produced by fast pyrolysis of biomass. Bio-oil, among other oxygenated compounds, contains lower C1-C4 carboxylic acids, which make the oil unstable and corrosive. Ketonisation can eliminate the adverse effects of carboxylic acids by converting them to non-corrosive ketone products with higher caloric value. The ketones thus produced can be further subjected to aldol condensation to increase the carbon chain length to the gasoline/diesel range [1,2,9].

Ketonisation of carboxylic acids has been extensively studied both in gas phase and liquid phase ([8,9] and references therein). In the gas phase, the reaction is catalysed by many metal oxides in the temperature range of 200-500 oC [8-19]. The best catalytic activity have amphoteric oxides such as CeO2, MnO2, ZrO2, TiO2, etc., with CeO2 showing particularly high activity [8,9, 17]. It is suggested that the high activity of the amphoteric metal oxides results from bifunctional catalysis by surface acid-base pairs M-O involving a Lewis acid site (low-coordinate metal cation) and the neighbouring oxygen anion as the base side [16, 17]. However, despite numerous research efforts, reaction mechanism and the nature of catalytically active sites and intermediates is still under debate [8,9,16-19]. Besides, catalyst deactivation remains a serious problem in the commercialisation of catalytic ketonisation of carboxylic acids. Therefore, the understanding of reaction mechanism and the causes of catalyst deactivation as well as the improvement of catalyst stability remain a challenge [9].

In this work, we study the performance of four typical metal oxide catalysts, namely γ-Al2O3, TiO2, ZrO2 and CeO2, in the ketonisation of acetic acid to acetone (Eq. (1)), primarily focussing on their activity and stability to deactivation. We also aim to provide new insights into ketonisation mechanism and site requirements on oxide surfaces through kinetic studies, characterisation of catalyst acid and base sites and, in particular, IR spectroscopic investigation of reaction intermediates.

1. **Experimental** 
   1. *Chemicals and catalysts*

Acetic acid CH3COOH (>99%), CD3COOD (99% D) and CH3COOD (99% D) were purchased from Sigma-Aldrich. γ-Al2O3 catalyst was Aluminiumoxide C from Degussa; it was washed with distilled water, calcined at 400 oC and (5 oC min-1 temperature ramp) for 2 h and ground to a powder of 53-180 μm particle size. Degussa P25 titanium dioxide was used as received without further modification. ZrO2 and CeO2 were prepared in-house by the literature procedures [20,21] and calcined in air, ZrO2 at 400 oC for 5 h and CeO2 at 500 oC for 3 h (5 oC min-1 ramp rate), then ground to a powder of 45-180 μm particle size.

* 1. *Catalyst characterisation techniques*

The texture of catalysts was characterised by nitrogen physisorption using Brunauer-Emmett-Teller (BET) method to determine catalyst surface area, pore diameter and pore volume (Micromeritics ASAP 2010 instrument). Prior to measurement, the catalysts were pre-treated at 240 °C in vacuum for 2 h. Powder X-ray diffraction (XRD) patterns of catalysts were recorded on a PANalytical Xpert diffractometer with a monochromatic CuKα radiation (*λ* = 1.542 Å). Temperature programmed desorption of CO2­ (CO2-TPD) was measured on a Micromeritics TPD/TPR 2900 instrument in He flow (60 mL min-1). The oxide catalysts (0.1-0.4 g) were pre-treated at 450 oC in He flow for 1 h, then pure CO2 was adsorbed at 100 oC followed by sample heating to 450 oC at a rate of 10 oC min-1.

DRIFT (diffuse reflectance infrared Fourier transform) spectra of pyridine adsorbed on oxide catalysts were taken on a Nicolet Nexus FTIR spectrometer. Catalyst samples were pre-treated at 150 oC/1 Pa for 1 h. The samples were then exposed to pyridine vapour at room temperature for 1 h, followed by pumping out at 150 oC/1 Pa for 1 h to remove physisorbed pyridine. The DRIFT spectra of adsorbed pyridine were recorded at room temperature by averaging 254 scans in the 4000-500 cm-1 range with a resolution of 4 cm-1 against pure oxide background. The same instrument was used to record DRIFT spectra of acetic acid adsorbed on oxide catalysts. Unless stated otherwise, the catalysts were pre-treated at 130 oC/1 Pa for 1 h. Acetic acid was then adsorbed at room temperature followed by evacuation at 130 oC/1 Pa for 1 h to remove physisorbed acid. After that the DRIFT spectra were recorded at room temperature against pure oxide background as described above. CH3COOH/CD3COOD exchange on oxide catalysts was monitored by DRIFT spectroscopy as follows. First, CH3COOH was adsorbed on a catalyst sample and the DRIFT spectrum was taken as above. Then this sample was exposed to CD3COOD vapour at ca. 1 kPa partial pressure and a specified temperature (130-270 oC) for 0.5 h followed by evacuation at 130-270 oC/1 Pa for 1 h and the DRIFT spectrum was taken again. FTIR spectra of CH3COOH and CD3COOD in the gas phase were recorded using a gas cell of 10 cm path length at acetic acid partial pressure of ca. 1 kPa in N2.

The heat and the amount of ammonia adsorption on oxide catalysts were measured using a Setaram TG-DSC 111 differential scanning calorimeter by a pulse method in a flow system as described previously [20]. Catalyst samples (10–70 mg) were placed in the calorimeter and pre-treated under nitrogen flow (30 mL min-1) at 300 oC for 1 h. Then the temperature was lowered to 150 oC and, after sample weight stabilisation (about 1 h), the measurement was performed at 150 oC by successive 2 mL pulses of pure ammonia into the N2 flow using a loop fitted in a 6-port valve. Sufficient time was allowed after each pulse for adsorption equilibrium to be reached (about 30 min). Weight gain due to NH3 adsorption and the corresponding heat of adsorption were recorded, from which the enthalpy of NH3 adsorption (∆*H*) and the total amount of NH3 adsorbed were determined as a measure of acid site strength and acid site density of catalysts, respectively. The ammonia pulses applied (2 mL) were large enough to ensure the accurate measurement of the amount of ammonia adsorbed. Such a pulse corresponded to a 30-40% of surface coverage of oxide catalysts. A representative example of TG-DSC analysis for ammonia adsorption on ZrO2 is shown in the Supporting Information (Fig. S1 and S2).

The amount of carbon deposited on post-reactor catalysts was measured by combustion elemental analysis.

* 1. *Catalyst testing*

The ketonisation of acetic acid was carried out in the gas phase at 180-350 oC and atmospheric pressure in a vertical down-flow fixed-bed Pyrex reactor (9 mm internal diameter) with on-line gas chromatographic (GC) analysis (Varian Star 3400 CX instrument with a 30 m x 0.32 mm x 0.5 μm CP-WAX capillary column and a flame ionisation detector), as described elsewhere [15]. The temperature in the reactor was controlled by a Eurotherm controller using a thermocouple placed at the top of the catalyst bed. Acetic acid was fed by passing N2 carrier gas flow controlled by a Brooks mass flow controller through a stainless steel saturator which held the liquid acid at an appropriate temperature to maintain the chosen reactant concentration in the gas flow. Typically, the reaction was carried out at an acetic acid partial pressure of 3.35 kPa and an N2 flow rate of 20 mL min-1 unless stated otherwise. The downstream gas lines and valves were heated to 150oC to prevent substrate and product condensation. The reactor was loaded with 0.10-0.20 g of catalyst powder (45-180 μm particle size). Prior to reaction, the catalysts were heated at the reaction temperature in N2 flow for 1 h. Once reaction started, the downstream gas flow was analysed by the on-line GC to obtain reactant conversion and product selectivity. The product selectivity was defined as moles of product formed per one mole of acetic acid converted and quoted in mole per cent; thus 100% acetone selectivity would mean 1 mol of acetic acid converted to form 0.5 mol of acetone. CO2 formed in the reaction (Eq. (1)) was not quantified and not included in reaction selectivities. The mean absolute percentage error in conversion and selectivity was ≤ 5%. The molar balance between acetic acid and the reaction products (acetone and isobutene) was maintained within 95%. Reaction rates (*R*) were determined as *R = XF/W* (in mol gcat-1h-1), where *X* is the fractional conversion of acetic acid, *F* is the molar flow rate of acetic acid (in mol h-1), *W* is the catalyst weight (in grams) and *W/F* is the contact time (gcat h mol-1). For rate measurements, the reaction was carried out for 4 h time on stream (TOS) at differential conditions (*X* ≤ 0.1), where *X* is directly proportional to the reaction rate. All oxide catalysts, except TiO2, suffered from deactivation in the initial stage of reaction, reaching a steadier conversion after ca. 1.5 h TOS (Sect. 3.2.). To minimise the effect of catalyst deactivation, the reaction rates were calculated from average acetic acid conversion over a TOS period of 1.5 – 4 h.

1. **Results and discussion**

*3.1. Catalyst characterisation*

Information about the catalysts studied is given in Table 1. This includes catalyst surface area and porosity as well as acid properties. The latter include the total density of acid sites (Brønsted and Lewis), the ratio of numbers of Brønsted and Lewis acid sites (B/L) and the enthalpy of ammonia adsorption as a measure of acid site strength. As can be seen, all oxides possess predominantly Lewis acidity, in agreement with the literature [22-25]. The number of Brønsted acid sites is negligible (B/L ≈ 0), except for ZrO2 having a B/L value of 0.1, in agreement with a previous IR study [25]. This was determined by infrared spectroscopy of adsorbed pyridine (Fig. 1, Fig. S3) assuming equal integral extinction coefficients for infrared bands of Brønsted (1540-1550 cm-1) and Lewis (1450-1460 cm-1) acid sites [22-24]. From the enthalpies of ammonia adsorption, the acid strength of oxides decreases in the order: ZrO2 > Al2O3 > TiO2 ≥ CeO2. The total acid site density of ZrO2 (0.23 mmol g-1) measured at 150 oC is in agreement with the literature value of 0.27 mmol g-1 obtained from microcalorimetry of NH3 adsorption at 80 oC [26]. In contrast, CeO2 had the lowest acid site density and the weakest acid strength among these oxides (Table 1). This is also in agreement with data [26], which shows a much weaker acidity of CeO2 compared to ZrO2 [26].

Comparing these results with the literature, it should be taken into account that the acid strength of oxides depends on their preparation and pre-treatment [23,24]. The heat of ammonia adsorption on solid acid catalysts depends on ammonia surface coverage, decreasing with increasing the NH3 coverage [27]. Therefore, our Δ*H* values obtained at an NH3 coverage of 30% will differ from those extrapolated to zero NH3 coverage. An IR study of pyridine adsorption [25] has reported TiO2 having the strongest Lewis acidity in the same series of oxides based on the shift of νCC(N) vibration band for H-bonded pyridine observed at 1600-1633 cm-1 (not shown in Fig. 1 and Fig. S3). However, it has been demonstrated that this band is sensitive to the nature and coordination number of the metal centre and cannot be used for comparison of acid strength of different metal centres [22-24].

Powder XRD was recorded for γ-Al2O3 Degussa catalyst, TiO2 Degussa P25 catalyst, as well as for ZrO2 and CeO2 samples prepared in-house (Fig. 2). The XRD patterns obtained are in agreement with the literature [21,28,29]. From these data, ZrO2 contained tetragonal and monoclinic zirconia in a weight ratio of 1.9:1. The TiO2 catalyst contained anatase and rutile in a 2.4:1 weight ratio. These weight ratios were calculated as described elsewhere [28,29].

*3.2. Ketonisation of acetic acid over oxide catalysts*

*3.2.1. Comparison of catalyst activity and stability to deactivation*

Table 2 compares the catalytic activity of Al2O3, TiO2, ZrO2 and CeO2 in the ketonisation of acetic acid to acetone at 300 oC, a contact time *W/F* = 120 g h mol-1 and 4 h time on stream (TOS). As seen, the activity increases in the order Al2O3 << TiO2 < ZrO2 < CeO2. In all cases, the selectivity to acetone based on the converted acetic acid was ≥ 99 mol%, with traces of isobutene also found. Acetone condensation to form isobutene on metal oxides has been reported previously [30].

Fig. 3 compares a longer-term performance of the more active TiO2, ZrO2 and CeO2 catalysts (24 h TOS) at a comparable conversion of 50-70%, revealing a different stability of these oxides to deactivation. It can be seen that the resistance to deactivation increases in the order CeO2 << ZrO2 < TiO2, with TiO2 exhibiting practically no deactivation and ZrO2 only a small deactivation after reaching steady state. Based on their high activity and strong resistance to deactivation, TiO2 (Degussa P25) and ZrO2 exhibited the best catalytic performance in acid ketonisation among the oxides studied, in agreement with the literature [9].

The spent CeO2 catalyst was notably darker than TiO2 and ZrO2, which indicates catalyst coking. Table 3 gives the carbon content in spent catalysts after the reactions shown in Fig. 3. Regarding the amount of coke formed, CeO2 clearly stands out with its 5.6% carbon content. Usually, coking of solid acid catalysts is the result of acid catalysed oligomerisation of organic molecules present in the reaction system [31]. This appears to be unlikely for CeO2 because its acidity is weaker than that of the other oxides (Table 1). An IR study [25] of acetone condensation on the same oxide series suggests that strong Lewis base sites found on the CeO2 surface have a great capacity toward adsorption of condensation products and thus can be responsible for the profound deactivation of CeO2 in acetone condensation. However, in acid ketonisation reaction, strong base sites could be poisoned by CO2 formed as the reaction by-product. As CeO2 is a relatively strong one-electron oxidant, its intense coking might also result from a radical polymerisation initiated by the Ce(IV)/Ce(III) redox couple, however there is no proof of this as yet. The observed deactivation of oxide catalysts could therefore be primarily attributed to the catalyst coking, i.e., the most coked CeO2 was the fastest to deactivate, whereas the least coked TiO2 and ZrO2 were more resistant to deactivation. Degussa P25 TiO2, produced by flame hydrolysis of TiCl4 with a moderate surface area of 44 m2g-1, was the most stable toward deactivation.

Previously, phase-pure anatase and rutile TiO2 possessing larger surface areas (240 and 160 m2g-1, respectively) have been found to suffer from deactivation [16]. Addition of Cu/SiO2 to the phase-pure TiO2 and ZrO2 by physical mixing and co-feeding H2 have been reported to reduce catalyst deactivation [16]. However, our attempt to decrease the deactivation of ZrO2 by adding Cu/SiO2 and H2 had no effect; in the case of CeO2, this even exacerbated the deactivation, which may be due to reduction of CeO2 [32,33].

We found that CeO2 could be successfully regenerated by calcination of spent catalyst in air at 500 oC for 3 h (5 oC min-1 temperature ramp rate). Fig. 4 shows two successive ketonisation runs on CeO2 with catalyst regeneration after each run. As seen, almost full recovery of catalyst activity and selectivity was achieved. The catalyst, black after reaction, regained its initial light yellow colour after regeneration. Some reduction in the catalyst surface area was observed, though, from 85 m2g-1 for fresh CeO2 catalyst to 73 m2g-1 after regeneration. Similar air calcination procedure (400 oC/5 h) was also successful for regeneration of ZrO2.

*3.2.2. Kinetic results*

Our kinetic studies included the measurement of apparent activation energies, specific reaction rates and CH3COOH/CH3COOD kinetic isotope effects. We also looked at the effect of acetic acid pressure on the reaction rate. Recently, a thorough kinetic investigation of the ketonisation of C2-C4 carboxylic acids over phase-pure TiO2 and ZrO2 oxides complemented by DFT calculations has been published [16]. Kinetics of C2-C4 acid ketonisation over Ru/TiO2 catalyst has also been reported [34].

Table 4 summarises the apparent activation energies (*Ea*) obtained for acetic acid ketonisation over Al2O3, TiO2, ZrO2 and CeO2 oxides. The corresponding Arrhenius plots are shown in Fig. S4. Due to the large difference in activity of oxides (Table 2), these measurements had to be carried out in different temperature ranges in order to stay within the differential conditions (fractional conversion *X* < 0.1). The *Ea* values thus obtained can be used for extrapolation of reaction rates, but may not be quite comparable across the oxide series studied. As seen, the *Ea* values vary from 106 to 115 kJ mol-1 for Al2O3, TiO2, ZrO2; these high *Ea* values indicate no diffusion limitations in the reaction with these oxides [35]. For the most active catalyst CeO2, a lower activation energy was obtained, *Ea =* 58 kJ/mol. This might be thought to point to internal diffusion limitations [35] for the reaction with CeO2. However, the Weisz-Prater criterion [36] calculated for CeO2, *CWP* = 2·10-3 << 1, indicates no internal diffusion limitations for this catalyst either (see the Supporting Information). The low *Ea* value for CeO2 may be explained by the high reactivity of base sites on CeO2 surface compared to the Al, Ti and Zr oxides, as suggested by the IR study of acetone condensation on these oxides [25]. It should be noted that the apparent activation energies *Ea* include enthalpy contributions from all reaction steps preceding the rate-limiting step. These steps include formation of surface acetate and enolate species, which involves interaction with the surface base sites (Scheme 3), hence the importance of oxide base sites for acid ketonisation (see below).

Table 4 also shows the reaction rates extrapolated to 260 oC using the Arrhenius equation, which allow to compare the catalytic activity of different oxides based on unit catalyst weight and surface area. This shows that the specific catalyst activity (105 mol m-2h-1) decreases in the order: CeO2 (3.4) > ZrO2 (1.7) > TiO2 (1.1) >> Al2O3 (0.047).

The reaction rate (*R*) was found to increase with increasing the partial pressure of acetic acid (*P*HOAc), tending to level off at high partial pressures, as shown in Fig. 5 for the reaction with Al2O3, TiO2 and ZrO2. The reaction with CeO2 also had a close trend (not shown), although the kinetic data was less accurate due to strong catalyst deactivation. Similar kinetics have been reported for C2-C4 acid ketonisation over phase-pure TiO2 and ZrO2 catalysts [16]. These kinetics indicate saturation of catalyst surface with adsorbed acetic acid molecules as *P*HOAc increases [16,34]. Rate equations assuming a mechanism involving fast adsorption of two molecules of acetic acid followed by a rate-limiting step leading to the formation of acetone have been derived elsewhere [16,34].

Kinetic isotope effect (KIE) was measured for the ketonisation of CH3COOH and CH3COOD catalysed by Al2O3, TiO2, ZrO2 and CeO2. The reactions were carried out under differential conditions (fractional conversion *X* < 0.1); the details are shown in Table S1. Both acids CH3COOH and CH3COOD were found to react with the same rate, i.e., no H/D KIE was observed for all oxide catalysts studied: 0.98 ± 0.02 (Al2O3), 1.03 ± 0.02 (TiO2), 1.03 ± 0.02 (ZrO2) and 1.0±0.2 (CeO2). These results are in agreement with the previous report [16], which has found no KIE (acetic acid *d0/d4*) for the phase-pure TiO2 and ZrO2. The lack of acetic acid *d0/d1* and *d0/d4* KIE shows that dissociation of the O-H and C-H bonds of acetic acid is not the rate limiting step of ketonisation reaction [16].

*3.2.3. Effect of catalyst acidity and basicity*

Comparison of reaction rates (Table 4) with acid strengths and densities of Brønsted and Lewis acid sites of the oxide catalysts (Table 1) shows that there is no direct relation between the ketonisation activity and the acid properties of oxide catalysts studied.

In order to gain an insight into the effect of catalyst basicity on ketonisation reaction, we examined base sites in the metal oxides using CO2-TPD. As CO2 is one of the reaction products (Eq. (1)), it will poison strong base sites in oxide catalysts to make them unavailable for ketonisation reaction. Therefore, it was interesting to find out if there were relatively mild base sites in the oxide catalysts that would desorb CO2 within the reaction temperature range to become available for the reaction. On the other hand, stronger base sites that desorb CO2 at higher temperatures could hardly participate in the ketonisation. CO2-TPD has been reported for these oxides [37-39], however, to our knowledge, it has not been used for correlation with ketonisation activity in this series of oxide catalysts.

Fig. 6 shows CO2 desorption from CeO2, ZrO2, TiO2 and Al2O3 within the temperature range of 100-450 oC, which covers the temperature range of ketonisation reaction on these oxides. The oxides were pre-treated at 450 oC then saturated with pure CO2 at 100 oC and after that the CO2-TPD was measured. It should be noted that such pre-treatment would not release strong base sites with CO2 desorption temperatures above 450 oC. The CO2-TPD results obtained are in agreement with the literature data [37-39]. As seen, the most active oxides, CeO2, ZrO2 and TiO2, show a CO2 desorption peak in the temperature range 160-200 oC (at 168, 176 and 191 oC, respectively), corresponding to relatively weak base sites, with the base strength increasing in that order. In contrast, Al2O3 shows a large peak with an onset at 320 oC centred at ca. 420 oC, which corresponds to stronger base sites. There is also a small peak in CO2-TPD of Al2O3 centred at 150 oC corresponding to very weak base sites, which are probably too weak to be active in the ketonisation reaction. It should be noted that an IR study [25] suggests very strong base sites on CeO2 surface, as compared to ZrO2,TiO2 andγ-Al2O3. This does not contradict our results as we probed only the mild base sites that were released upon pre-treatment of these oxides at 450 oC.Unfortunately, our CO2-TPD data are not accurate enough to quantify the number of base sites for these oxides. Nevertheless these results indicate that the relatively weak catalyst basicity is important for the ketonisation reaction over metal oxides. It can be seen that there is an inverse correlation between the ketonisation activity (Table 4) and the strength of base sites of oxide catalysts. In the presence of CO2 in the reaction system, poisoning catalyst base sites, the stronger the catalyst basicity, the higher the temperature required to release the base sites for the reaction. From the CO2-TPD (Fig. 6), the CO2 desorption temperature increases in the order CeO2 < ZrO2 < TiO2 << γ-Al2O3. This order is in line with the catalytic activity of these oxides in acetic acid ketonisation (Table 4). Ce(IV), Zr(IV) and Ti(IV) oxides, due to the presence of relatively weak base sites on their surfaces, are the more active ketonisation catalysts operating at relatively low temperatures above their CO2 desorption temperatures (Table 4). In contrast, the more basic γ-Al2O3 requires a higher temperature for the reaction to occur due to the stronger CO2 adsorption.

*3.2.4. Infrared spectroscopy of reaction intermediates*

Infrared spectroscopy has been widely used for studying carboxylic acid adsorption on metal oxides such as TiO2, Al2O3, CeO2, SnO2 and MgO [16,17,40-44]. It is well documented that carboxylic acids adsorb dissociatively on the neighbouring surface Lewis acid and base sites M-O-M to form a metal carboxylate in monodentate, bidentate chelate or bidentate bridging bonding mode, with the bidentate bridging acetate more likely to form [40-44] (Eq. (2), charges omitted for simplicity). Different surface acetate species have been suggested as possible intermediates for ketonisation of carboxylic acids, including monodentate [16] and bridging bidentate [17-19,34] acetates.

 (2)

Fig. 7 shows the DRIFT spectra of acetic acid adsorbed on Al2O3, TiO2, ZrO2 and CeO2, which were measured at room temperature in the absence of acetic acid in the gas phase after evacuation at 130 oC against pure oxide background. All these spectra have similar features and are in agreement with those reported previously [17,40-44]. The small peaks in the region of 1700-1716 cm-1 (C=O stretching) indicate the presence of traces of physisorbed acetic acid. The peaks at 1319-1340 cm-1 can be assigned to C-H deformations (CH3 bending). The bands at 1455-1559 cm-1 for TiO2, ZrO2 and CeO2 can be attributed to symmetric and antisymmetric stretching of the OCO group of surface acetate [16,17,40-44], which indicate the bidentate bridging mode for acetate bonding (Eq. (2)) [16,17,40-44]. For the non-transition metal oxide γ-Al2O3, the bands for OCO group exhibit a blue shift to 1475-1595 cm-1, which is in agreement with data [17].

The surface bidentate bridging acetates in the absence of acetic acid in the gas phase are known to be very stable, up to 300 oC [41] and even higher temperatures [17]. Based on DFT calculations and in-situ DRITS studies, it has been suggested that the bidentate bridging acetates are inactive, and it is the monodentate surface acetates that are the likely active intermediates in ketonisation of carboxylic acids over phase-pure TiO2 [16]. Conversely, other DFT studies [18,19,45] consider the bidentate bridging acetates the active intermediates in acid ketonisation on ZrO2. Here, we looked at the behaviour of surface bidentate bridging acetates in the absence and in the presence of acetic acid in the gas phase, the latter conditions portraying the ketonisation reaction. Specifically, we looked at a CH3COOH/CD3COOD exchange at the oxide surface and the behaviour of undeuterated and deuterated surface bidentate bridging acetates *d0* and *d3* using DRIFT spectroscopy.

Fig. 8 shows the FTIR spectra of CH3COOH and CD3COOD in the gas phase. It can be seen that the vibration bands for CH3 deformation (1426 cm-1) and C-H and C-D stretching (2959 and 2101 cm-1, respectively) [44] can be used to monitor the CH3COOH/CD3COOD exchange. The results for acid exchange on TiO2 are presented in Fig. 9. It shows the DRIFT spectra of CH3COOH (spectrum 1) and CD3COOD (spectrum 2) adsorbed on TiO2 to form the bidentate bridging acetate *d0* and *d3*, respectively. Each acid (~1 kPa) was adsorbed at room temperature followed by evacuation at 130 oC/1 Pa for 1 h to remove the acids from the gas phase, then the spectra were recorded at room temperature against pure oxide background. Notably, spectrum 1 for the adsorbed CH3COOH shows the CH3 deformation band (1319 cm-1) and the C-H stretch (2936 cm-1), whereas spectrum 2 for the adsorbed CD3COOD lacks these bands, but has the C-D stretch (2115 cm-1) in it. Spectrum (3) represents the CH3COOH sample (1) after exposure to CD3COOD vapour (~1 kPa) at 130 oC for 0.5 h followed by pumping out at 130 oC/1 Pa for 1 h as above. This spectrum looks the same as spectrum 2 for the adsorbed CD3COOD, which clearly points to an H/D exchange in the system. Moreover, the exchange occurred already at 130 oC, i.e., well below temperature threshold for the ketonisation reaction on TiO2 (250-300 oC). This process could be repeated several times, each time showing the H/D exchange. Similar results were also obtained for Al2O3 (Fig. 10), ZrO2 (Fig. S5) and CeO2 (Fig. S6), all exhibited the H/D exchange at 130 oC. It is important that no H/D exchange was observed when CD3COOD was adsorbed on fresh oxides. This would rule out the H/D exchange between the deuterated surface acetate and the proton sites present on the oxide surface, but only if the undeuterated Brønsted acid sites still existed after the exposure of the oxide to gaseous CD3COOD. To prove this, the pre-adsorbed CD3COOD on TiO2 was treated with H2O (~1 kPa) at 130 oC for 0.5 h followed by pumping out at 130 oC/1 Pa for 1 h. This treatment would restore the undeuterated Brønsted acid sites on the TiO2 surface. The resulting DRIFT spectrum is shown in Fig. 9 (spectrum 4). As seen, similar to spectrum (2) for the adsorbed CD3COOD, it does not have the vibration band of CH3 group at 1319 cm-1. This rules out the H/D exchange between the deuterated surface acetate and the proton sites present on the oxide surface at 130 oC. It should be noted that there is a small new unidentified peak at 1265 cm-1 in this spectrum, which might be indicative of some partial H/D exchange between the surface acetate-*d3* and surface proton sites. This will be addressed below in more detail. Notably, spectrum 4 lacks the carbonyl stretch at 1718 cm-1, hence no trace of physisorbed CD3COOD. This can be due to the water treatment of this sample and extended pumping out.

One explanation for these results might be the H/D exchange of the bidentate surface acetate through enolate species (Eq. (3)); the latter has been suggested as an intermediate in acid ketonisation [18,19]. In such a case, the H/D exchange would occur without desorption of bidentate acetate species from the oxide surface and would involve H+ (or D+) surface sites. This would imply that the deuterated bidentate surface acetate-*d3* would undergo H/D exchange with proton sites on the oxide surface without the addition of acetic acid-*d0*. This contradicts the above experimental evidence as no such H/D exchange was observed. Moreover, DFT calculations [18,19] show that the formation of surface enolate requires a high activation energy, which would make it the rate-limiting step in the H/D exchange under the CH3COOH/CD3COOD acid exchange conditions at 130 oC. As a result, the H/D exchange can be expected to depend on the nature of metal oxide. This is not in agreement with experiment either as no such dependence was observed within the time scale of acid exchange. On these bases, the H/D exchange through the surface enolate species can be ruled out at 130 oC.

 (3)

A possible mechanism for the acid exchange on oxide surface at 130 oC is represented in Scheme 1. This mechanism involves desorption of bidentate bridging surface acetates from the oxide surface aided by acetic acid from the gas phase. Here, the bidentate surface acetate **A** formed initially interacts with the co-adsorbed CD3COOD to form intermediate **B**, which would lead to acid exchange to give the deuterated acetate **C** and release CH3COOD into the gas phase (possibly together with CH3COOH due to H/D exchange of CH3COOD with the surface proton sites). Further kinetic studies could reveal the effect of metal oxide nature on the rate of CH3COOH/CD3COOD exchange.



**Scheme 1.** CH3COOH/CD3COOD exchange on oxide surface at 130 oC.

Now the question is can the H/D exchange between the surface bidentate acetate **A** and the oxide Brønsted acid sites occur at higher temperatures typical of those for acid ketonisation? To prove this, the pre-adsorbed CD3COOD on TiO2 was again treated with H2O (~1 kPa) as above, but this time round at 250 oC to restore the undeuterated surface Brønsted acid sites. The resulting DRIFT spectrum is presented in Fig. 11 (spectrum 2). It clearly shows the band for CH3 vibrations, blue-shifted at these conditions to 1340 cm-1, indicating H/D exchange between the bidentate bridging acetate-*d3* and Brønsted acid sites on TiO2 surface. Increasing the temperature to 270 oC further enhanced the H/D exchange, as can be seen from the increased intensity of this band (spectrum 3). Even without any water treatment, heating the TiO­2-adsorbed CD3COOD at 270 oC caused some H/D exchange, as seen from spectrum 4 in Fig. 11. This means that the relatively weak proton sites on TiO2 surface were not fully deuterated by the adsorbed CD3COOD. Similar results were also obtained for ZrO2 (Fig. 12), which has higher ketonisation activity (Table 4) and higher Brønsted acid site density compared to TiO2 (Table 1). In Fig. 12, spectra 1-3 demonstrate facile CH3COOH/CD3COOD exchange on ZrO2 at 130 oC as in the case of TiO2 (Fig. 9). At 250 oC, without water treatment, the adsorbed CD3COOD did not show any H/D exchange with the surface proton sites possibly due to their deuteration by the CD3COOD, as seen from the absence of CH3 vibration band at ~1330 cm-1 in DRIFT spectrum 4. However, this band clearly showed after the pre-adsorbed CD3COOD was treated with H2O (~1 kPa) at 250 oC to restore the undeuterated Brønsted acid sites on ZrO2 surface, thus supporting the H/D exchange between the bidentate bridging acetate and the surface Brønsted acid sites. The observed H/D exchange can be attributed to the surface enolate species, which have been inferred as the intermediates in acid ketonisation from DFT calculations [18,19]. Therefore, these results provide an important mechanistic insight, giving experimental evidence for the intermediacy of enolate species in ketonisation of carboxylic acids. A plausible reaction pathway for the H/D exchange is represented in Scheme 2.

**Scheme 2.** H/D exchange between bidentate bridging acetate and Brønstedacid sites on oxide surface.

*3.2.5. Ketonisation mechanism*

Several mechanisms have been proposed for acid ketonisation reaction including (i) decomposition of metal carboxylate, (ii) via acid anhydride intermediate, (iii) via ketene intermediate route and (iv) via β-ketoacid intermediate (for a review, see [9,45]). More recent theoretical calculations and experimental data favour the β-ketoacid intermediate route with the rate-limiting step of C-C bond formation [9,16,18,19,34,45,46]. Nevertheless, exact reaction mechanism and the requirements for catalytically active sites are still in controversy [16,45]. From DFT analysis, different surface carboxylate species such as monodentate acetate [16] and bidentate bridging acetate [18,19] have been suggested as active intermediates in this reaction. Also different mechanisms of C-C bond formation have been proposed. These include the C-C coupling (i) between a surface carboxylate and ketene [9,45], (ii) between enolate species and co-adsorbed acid [16], (iii) between enolate species and bidentate bridging carboxylate [45,46], (iv) between enolate species and acylium intermediate [18,19] and (v) via a concerted pathway [18]. The C-C coupling involving the enolate and a surface carboxylate or acylium species is currently considered to be the most plausible reaction mechanism [16,18,19,45].

In this work, we made two mechanistically significant observations. First, we found facile exchange between the bidentate bridging acetate and co-adsorbed acetic acid on the oxide surface under mild conditions well below ketonisation temperatures. This result demonstrates the lability of the surface bidentate bridging acetate species in the ketonisation system. This shows that prior to C-C bond formation various types of surface acetate species are equilibrated in the ketonisation system, which makes them kinetically indistinguishable. Secondly, we observed proton exchange between the bidentate bridging acetates and the Brønsted acid sites on oxide surfaces at typical ketonisation temperatures, which supports the intermediacy of enolate species in ketonisation of carboxylic acids. On this basis, the rate-limiting step of ketonisation reaction involving the C-C coupling to form the β-ketoacid intermediate can be represented by interaction between the enolate and a surface acetate species, for example bidentate bridging acetate, as shown in Scheme 3 [45,46]. The latter species, however, is kinetically indistinguishable from other possible surface acetates, e.g., monodentate acetate [16], existing in equilibrium with the bidentate bridging acetate.



**Scheme 3.** Interaction between enolate and bidentate bridging acetate to formthe β-ketoacid intermediate in ketonisation of acetic acid.

It would be highly desirable to be able to correlate the catalytic activity of oxides to a specific physicochemical property measured on the fresh oxides. There is a concern, however, that such properties of the fresh oxides may not be representative of the properties under reaction conditions, i.e., in the presence of CO2 and water by-products formed in the course of acid ketonisation. In particular, this concerns the acid-base properties and the surface structure of oxide materials. Nevertheless, our study demonstrates a correlation between the reactivity of oxides in the ketonisation of acetic acid and their mild basicity existing in the ketonisation system in the presence of CO2. On the other hand, no such correlation with the acid properties of oxide was observed. This is not unexpected because several reaction steps preceding the rate-limiting step of C-C coupling, namely the formation of surface acetate and enolate species, involve interaction with the catalyst base sites (Scheme 3). Our DRIFTS work provided interesting insights into the reaction mechanism. Further kinetic studies of the H/D exchange complemented by in-situ catalyst characterisation in these systems could give better mechanistic understanding and reactivity differentiation across oxide catalysts.

1. **Conclusions**

The ketonisation of acetic acid was studied using γ-alumina, titania, zirconia and ceria oxide catalysts in the gas phase. The reaction gives acetone as the primary reaction product with ≥ 99% selectivity. Catalyst activity was found to increase in the order Al2O3 << TiO2 < ZrO2 < CeO2, with specific reaction rates (105 mol m-2h-1) of 0.047, 1.1, 1.7 and 3.4, respectively, at 260 oC. These catalysts suffered from deactivation, which increased in the order TiO2 < ZrO2 << CeO2, in parallel with the amount of coke formed. TiO2 (Degussa P25) and ZrO2 exhibited the best ketonisation performance regarding the catalyst activity and long-term stability. CeO2 and ZrO2 could be regenerated by air calcination. Two mechanistically significant observations were made from our DRIFTS studies. First, facile exchange was found between the bidentate bridging acetate and co-adsorbed acetic acid on the oxide surfaces under mild conditions well below ketonisation temperatures, which demonstrates the lability of the surface bidentate bridging acetate species in the ketonisation system. This shows that various types of surface acetate species are equilibrated in the ketonisation system, which makes them kinetically indistinguishable. Secondly, we observed proton exchange between the bidentate bridging acetates and the Brønsted acid sites on oxide surfaces at typical ketonisation temperatures, which supports the intermediacy of enolate species in ketonisation of carboxylic acids.

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**Table 1.** Information about catalysts.a

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Surface areab  m2g-1 | Pore volumec  cm3g-1 | Pore diameterd  Å | Acid site densitye  mmol g-1 | B/Lf | Δ*H*g  kJ mol-1 |
| Al2O3 | 98 | 0.56 | 227 | 0.24±0.01 | ~0 | 73 |
| TiO2 | 44 | 0.10 | 90 | 0.26±0.01 | ~0 | 68 |
| ZrO2 | 117 | 0.13 | 43 | 0.23±0.01 | 0.1 | 94 |
| CeO2 | 85 | 0.22 | 104 | 0.18±0.02 | ~0 | 66 |

a For BET analysis, the catalysts were pre-treated for 2 h at 240 oC in vacuum before measuring N2 adsorption. b BET surface area. c Single point total pore volume. d Average BET pore diameter. e Total amount of NH3 adsorbed on Brønsted and Lewis acid sites at 150 oC (from TG-DSC). f The ratio of numbers of Brønsted (B) and Lewis (L) acid sites from DRIFTS of adsorbed pyridine. g Enthalpy of NH3 adsorption (±4 kJ mol-1) at 150 oC and a fractional NH3 surface coverage of 0.30 (from TG-DSC).

**Table 2.** Comparison of activity of Al2O3, TiO2, ZrO2 and CeO2 oxides in ketonisation of acetic acid.a

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalyst | Al2O3 | TiO2 | ZrO2 | CeO2 |
| Conversionb (%) | 3.1 | 48 | 73 | 100 |

a Reaction conditions: 0.20 g of catalyst, 300 oC, 3.35 kPa HOAc partial pressure, 20 mL min-1 N2 flow rate, 4 h time on stream, contact time *W/F* = 120 g h mol-1. b Average HOAc conversion between 1.5-4 h time on stream; acetone selectivity ≥ 99 mol% based on acetic acid converted.

**Table 3.** Carbon content in spent catalysts.a

|  |  |  |  |
| --- | --- | --- | --- |
| Catalyst | TiO2 | ZrO2 | CeO2 |
| Carbon content (%) | 1.2 | 1.2 | 5.6 |

a From combustion chemical analysis of spent catalysts after reactions shown in Fig. 3.

**Table 4.** Apparent activation energies (*Ea*) and reaction rates for acetic acid ketonisation over oxide catalysts.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalyst | Temperature range  oC | *Ea*  kJ mol-1 | 105 Ratea  mol g-1h-1 | 105 Ratea  mol m-2h-1 |
| CeO2 | 180-220 | 58±10 | 290 | 3.4 |
| ZrO2 | 230-260 | 106±3 | 200 | 1.7 |
| TiO2 | 270-300 | 115±5 | 47 | 1.1 |
| Al2O3 | 300-350 | 110±3 | 4.6 | 0.047 |

a At 260 oC, extrapolated using the Arrhenius equation.



**Fig. 1.** DRIFT spectra of pyridine adsorbed on γ-Al2O3 (solid line) and TiO2 (broken line).

**Fig. 2.** XRD patterns (CuKα radiation) for: (1) γ-Al2O3 Degussa catalyst air calcined at 400 oC for 2 h; (2) TiO2 P25 Degussa catalyst, 2.4:1 w/w anatase/rutile ratio; (3) CeO2 air calcined at 500 oC for 3 h, cubic fluorite structure; and (4) ZrO2 air calcined at 400 oC for 5 h, 1.9:1 w/w tetragonal/monoclinic zirconia ratio.

**Fig. 3.** Comparison of catalyst activity and stability in acetic acid ketonisation over ZrO2 (300 oC), TiO2 (300 oC) and CeO2 (250 oC) at *W/F* = 120 g h mol-1, 3.35 kPa HOAc partial pressure; acetone selectivity in all cases ≥ 99 mol%.

**Fig. 4.** Effect of regeneration of CeO2 catalyst by air calcination at 500 oC for 3 h: (1) first and (2) second run (250 oC, *W/F* = 120 g h mol-1, 3.35 kPa HOAc partial pressure; acetone selectivity in both cases ≥ 99 mol%.

**Fig. 5.** Effect of partial pressure of acetic acid on reaction rate: (1) Al2O3 (0.20 g, 320 °C), (2) ZrO2 (0.10 g, 240 °C) and (3) TiO2 (0.10 g, 270 °C); 20 mL min-1 flow rate in all cases.



**Fig. 6.** CO2-TPD in He flow: (1) CeO2 (0.294 g), (2) ZrO2 (0.432 g), (3) TiO2 (0.112 g, scaled up 2-fold), (4) γ-Al2O3 (0.403 g); pre-treatment at 450 oC/1h in He flow, CO2 adsorbed at 100oC, 10 oC min-1 temperature ramp rate.



**Fig. 7.** DRIFT spectra of acetic acid adsorbed on ZrO2 (1), CeO2 (2), TiO2 (3) and Al2O3 (4) after evacuation at 130 oC/1 Pa against pure oxide background.



**Fig. 8.** FTIR spectra of CH3COOH (1) and CD3COOD (2) in gas phase (ca. 1 kPa partial pressure).

-0.4

-0.2

0.0

0.2

0.4

0.6

0.8

1.0

1.2

1.4

Absorbance

2000

3000

Wavenumbers (cm-1)

2250

2500

2750

3250

1750

1500

1250

**1319**

**1458**

**1535**

**1718**

**2936**

**2115**

**2**

**1**

**3**

**4**

**1265**

**Fig. 9.** DRIFT spectra of CH3COOH (1) and CD3COOD (2) adsorbed on TiO2 after evacuation at 130 oC/1 Pa for 1 h. Spectrum (3) represents CH3COOH sample (1) after exposure to CD3COOD vapour at ~1 kPa partial pressure and 130 oC for 0.5 h followed by evacuation at 130 oC/1 Pa for 1 h. Spectrum (4) represents CD3COOD sample (2) treated with H2O (~1 kPa) at 130 oC/0.5 h and evacuated at 130 oC/1 Pa for 1 h.



**Fig. 10.** DRIFT spectra of CD3COOD (1) and CH3COOH (2) adsorbed on γ-Al2O3 (Degussa) after evacuation at 130 oC/1 Pa for 1 h. Spectrum (3) represents sample (2) after exposure to CD3COOD vapour at ca. 1 kPa partial pressure and 130 oC for 0.5 h followed by evacuation at 130 oC/1 Pa for 1 h.

-0.7

-0.6

-0.5

-0.4

-0.3

-0.2

-0.1

0.0

0.1

0.2

0.3

0.4

0.5

0.6

0.7

Absorbance

1500

2000

Wavenumbers (cm-1)

1600

1700

1800

1900

1400

1300

1200

1100

**1**

**2**

**3**

**4**

**1340**

**1336**

**1336**

**1717**

**1717**

**1511**

**1445**

**Fig. 11.** DRIFT spectra of CD3COOD adsorbed on TiO2: (1) CD3COOD evacuated at 250 oC/1 Pa for 1 h, (2), CD3COOD sample (1) treated with H2O (~1 kPa) at 250 oC for 0.5 h and evacuated at 250 oC/1 Pa for 1 h, (3) the same as (2) but treated with H2O and evacuated at 270 oC, (4) CD3COOD evacuated at 270 oC/1 Pa for 1 h in the absence of H2O.

0.0

0.1

0.2

0.3

0.4

0.5

0.6

0.7

0.8

0.9

1.0

1.1

Absorbance

1500

Wavenumbers (cm-1)

1400

1300

1200

1600

1700

1800

**1**

**2**

**3**

**4**

**5**

**1329**

**1333**

**1250**

**1250**

**1450**

**1560**

**1421**

**1465**

**1559**

**1717**

**Fig. 12.** DRIFT spectra of CH3COOH (1) and CD3COOD (2) adsorbed on ZrO2 after evacuation at 130 oC/1 Pa for 1 h. Spectrum (3) represents CH3COOH sample (1) after exposure to CD3COOD vapour at ~1 kPa partial pressure and 130 oC for 0.5 h followed by evacuation at 130 oC/1 Pa for 1 h. (4) represents CD3COOD evacuated at 250 oC/1 Pa for 1 h. (5) represents CD3COOD sample (4) treated with H2O (~1 kPa) at 250 oC/0.5 h and evacuated at 250 oC/1 Pa for 1 h.

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