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-Al_2O_3, TiO_2, ZrO_2 and CeO_2 as the catalysts in the temperature range of 180–350 °C and ambient pressure. Catalyst activity was found to increase in the order $Al_2O_3 < < TiO_2 < ZrO_2 < CeO_2$. CO_2-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 $CeO_2 < < ZrO_2 < TiO_2$ in parallel with the amount of coke formed. TiO_2 (Degussa P25) and ZrO_2 were found to exhibit the best performance as represented by their activity and stability to deactivation. CeO_2 and ZrO_2 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 °C, 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.

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.

$$CH_3COOH \rightarrow (CH_3)_2CO + CO_2 + H_2O \qquad (1)$$
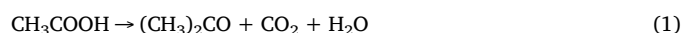
Ketonisation has long been employed as a clean method for the synthesis of ketones ([8,9] and references therein). Currently, this reaction attracts significant interest for the upgrading of biomass-derived oxygenates, for example, bio-oil produced by fast pyrolysis of biomass. Bio-oil, among other oxygenated compounds, contains lower C_1–C_4 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 °C [8–19]. The best catalytic activity have amphoteric oxides such as CeO_2, MnO_2, ZrO_2, TiO_2, etc., with CeO_2 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 [8,9,16,9–19]. 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-Al_2O_3, TiO_2, ZrO_2 and CeO_2, 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.

2. Experimental

2.1. Chemicals and catalysts

Acetic acid CH_3COOH (> 99%), CD_3COOD (99% D) and CH_3COOD (99% D) were purchased from Sigma-Aldrich. γ-Al_2O_3 catalyst was Aluminiumoxide C from Degussa; it was washed with distilled water, calcined at 400 °C and (5 °C 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. ZrO_2 and CeO_2 were prepared in-house by the literature procedures [20,21] and calcined in air, ZrO_2 at 400 °C for 5 h and CeO_2 at 500 °C for 3 h (5 °C min^{-1} ramp rate), then ground to a powder of 45–180 μm particle size.

2.2. 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 CO_2 (CO_2-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 °C in He flow for 1 h, then pure CO_2 was adsorbed at 100 °C followed by sample heating to 450 °C at a rate of 10 °C 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 °C/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 °C/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 °C/1 Pa for 1 h. Acetic acid was then adsorbed at room temperature followed by evacuation at 130 °C/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. CH_3COOH/CD_3COOD exchange on oxide catalysts was monitored by DRIFT spectroscopy as follows. First, CH_3COOH was adsorbed on a catalyst sample and the DRIFT spectrum was taken as above. Then this sample was exposed to CD_3COOD vapour at ca. 1 kPa partial pressure and a specified temperature (130–270 °C) for 0.5 h followed by evacuation at 130–270 °C/1 Pa for 1 h and the DRIFT spectrum was taken again. FTIR spectra of CH_3COOH and CD_3COOD 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 N_2.

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 °C for 1 h. Then the temperature was lowered to 150 °C and, after sample weight stabilisation (about 1 h), the measurement was performed at 150 °C by successive 2 mL pulses of pure ammonia into the N_2 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 NH_3 adsorption and the corresponding heat of adsorption were recorded, from which the enthalpy of NH_3 adsorption (ΔH) and the total amount of NH_3 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 ZrO_2 is shown in the Supporting Information (Figs. S1 and S2).

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

2.3. Catalyst testing

The ketonisation of acetic acid was carried out in the gas phase at 180–350 °C 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 × 0.32 mm × 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 N_2 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 N_2 flow rate of 20 mL min^{-1} unless stated otherwise. The downstream gas lines and valves were heated to 150 °C 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 N_2 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. CO_2 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 g$_{cat}^{-1}$ h^{-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 (g$_{cat}$ 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 TiO_2, 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.

3. 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.