

Sustainable hydrogen from bio-oil—Steam reforming of acetic acid as a model oxygenate

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Abstract

Steam reforming of acetic acid over Pt/ZrO₂ catalysts has been investigated. Pt/ZrO₂ catalysts are very active, completely converting acetic acid, and give a hydrogen yield close to thermodynamic equilibrium. The catalyst deactivated by formation of oligomers which block the active sites. The mechanism of both the reaction and the deactivation was studied with kinetic and spectroscopic measurements on Pt/ZrO₂, ZrO₂, and Pt black. It is shown that Pt is essential for steam reforming to proceed. ZrO₂ is needed to activate steam. ZrO₂, on the other hand, is also active for oligomer–precursor formation under the conditions investigated. Results obtained in the study show that steam reforming takes place at the Pt–ZrO₂ boundary and that deactivation occurs when this boundary is blocked by oligomers.

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1. Introduction

Currently, there is tremendous interest in the use of hydrogen as a clean fuel, especially for power generation with fuel cells. Hydrogen production from sustainable sources, e.g., biomass, is gaining attention for a CO₂ neutral energy supply [1,2]. Recent developments in flash pyrolysis technologies make it possible to convert lignocellulosic biomass efficiently to a bio-oil, which is easier for handling and transport [3]. The bio-oil so generated contains a variety of aliphatic and aromatic oxygenates (aldehydes, ketones, acids, alcohols).

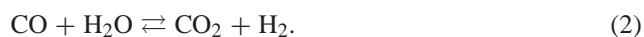
The most promising option to generate hydrogen from bio-oil is via catalytic steam reforming followed by a wa-

ter gas-shift reaction, since these reaction steps maximize hydrogen yield. Recent attempts to make hydrogen by steam reforming of bio-oil have been hindered by severe deactivation of catalysts due to coke/oligomer deposition [4] even in the presence of excess of steam (H₂O/C > 5). A lower steam/carbon ratio (< 2) is essential for economy of the process. In this study, Pt/ZrO₂ has been investigated since earlier work [5,6] has shown excellent activity and stability for Pt/ZrO₂ under conditions favorable for coke formation, for, e.g., even in the absence of steam, during CO₂ reforming of natural gas.

Bio-oil is a complex mixture of oxygenates. Thus, design of an efficient catalyst requires the use of model oxygenate components to establish structure activity correlations. Acetic acid (CH₃COOH, HAc) is one of the major components of bio-oil (up to 32 wt%) [7]. This study pertains to the steam reforming of HAc over Pt/ZrO₂ catalysts. Steam reforming and water gas-shift reactions [Eq. (2)] occur simultaneously and the overall stoichiometry is represented [Eq. (1)],

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The purpose of this study is to elucidate the reaction and deactivation mechanisms and to provide a knowledge base for the design of active and stable catalysts.

2. Methods

2.1. Catalyst preparation

Pt/ZrO₂ was prepared by a wet impregnation technique. A solution of H₂PtCl₆·6H₂O in water (0.01 g Pt/ml) was used. ZrO₂ (monoclinic, Daiichi Kigenso Kagaku Kogyo, RC100) was first calcined for 15 h at 1125 K (heating rate 3 K min⁻¹) in flowing air (30 ml min⁻¹). The support was then isostatically pressed into pellets at 400 MPa for 5 min. The pellets were crushed and sieved to give grains having diameters between 0.3 and 0.6 mm. The grains were impregnated with the H₂PtCl₆ solution to yield a catalyst with 0.5 wt% Pt. The catalyst was dried at 325 K for 2 h in a rotating evaporator followed by drying overnight at 395 K in static air. Subsequently, the impregnated grains were calcined at 925 K for 15 h (heating rate 5 K min⁻¹). Pt black powder (Acros Organics, > 97.5% (Pt)) was used as received (alkali (K, Na) < 0.4%).

2.2. Catalyst characterization

H₂ chemisorption measurements were carried out in a volumetric system with 1 g of Pt/ZrO₂ catalyst or 100 mg of Pt black. The sample was reduced at 925 K in H₂ for 1 h. After reduction the sample was degassed at 925 K in vacuum (10⁻⁶ mbar). The sample was cooled to room temperature (293 K) and the H₂ adsorption isotherm was measured by introducing H₂ to the sample. After the first isotherm the sample was again degassed at room temperature, followed by the second H₂ adsorption isotherm. The hydrogen chemisorption capacity was calculated by extrapolation of the hydrogen uptake, which corresponded to the difference of the first and second isotherms, to zero pressure [8].

Thermogravimetry (TG) (Mettler Toledo TGA/SDTA 851E) was used to determine the amount of deposits in the catalysts. The catalysts used for the reaction were heated from room temperature to 1075 K in 1% O₂/Ar.

IR spectra were recorded in situ under vacuum by using a transmission spectrometer (Bruker, Vector 22) with a MCT detector. The catalyst reduced ex situ at 925 K was pressed into a pellet and loaded in a miniature cell, equipped with CaF₂ transparent windows. The cell can be evacuated to pressures below 10⁻⁷ mbar. The catalyst was first reduced in situ by introducing 0.1 mbar of H₂ at 725 K. After evacuation, oxygenates and steam were introduced into the system with an S/C molar ratio of 5 at a total pressure of 0.1 mbar at 725 K. Each spectrum consists of 32 scans taken at 4 cm⁻¹

resolution. More details will be described wherever necessary.

2.3. Catalytic measurements

For continuous flow experiments, 50 mg of catalysts was loaded in a fixed-bed reactor and held by quartz wool plugs. The catalyst was first reduced in 5% H₂ in N₂ at 925 K with a total flow rate of 50 ml min⁻¹. Then the gas was purged with Ar at a flow rate of 30 ml min⁻¹. An aqueous solution of HAc giving a steam to carbon molar ratio (S/C) of 5 was introduced by using a microfeeder (KD Scientific) and a syringe (Hamilton Co.). The feed was adjusted in bypass mode, prior to the experiment, to obtain constant HAc/H₂O/N₂/Ar (= 3/30/5/82 ml min⁻¹, N₂ as an internal standard). This gives weight hourly space velocity (WHSV) for HAc 9.0 h⁻¹ and total gas hourly space velocity (GHSV) 160,000 h⁻¹. The system was heated at 425 K to avoid condensation of reactants and products. After purging the catalysts with inert gas (Ar), the mixture of reactants was introduced to the reactor. For analysis, a flame ionization detector (FID) and a Hayesep Q column were used for HAc, acetone (CH₃COCH₃), ketene (CH₂CO), and hydrocarbons; a thermal conductivity detector (TCD) and a Carbosieve column were used for H₂, N₂, CO, CH₄, and CO₂.

Pulse experiments were performed with 20 mg of Pt/ZrO₂ or ZrO₂, or 10 mg of Pt black dispersed in quartz wool. After reduction at 925 K, the system was purged in Ar at a flow rate of 37.5 ml min⁻¹. Pulses of 0.2 μl of HAc or 0.61 μl of HAc aqueous solution (S/C = 5) at 293 K were introduced. Both type of pulses contained 3.5 μmol of HAc.

The hydrogen yields were calculated based on Eq. (1). For carbon-containing compounds, the yields were calculated based on C₁ equivalent values; e.g., acetone (C₃H₆O) yield was calculated as three times the number of moles produced divided by two times the number moles of HAc fed.

Thermodynamic equilibrium conversions and yields were calculated using the HSC, Outokumpu program by specifying reactants and products (H₂O, CH₄, CO, CO₂, H₂, and all possible oxygenates including acetone). However, the only products which had nonzero concentrations at equilibrium at 725 K were H₂O, CH₄, CO, CO₂, and H₂.

3. Results

3.1. Catalyst characterization

Specific surface area of ZrO₂ was 21 m² g⁻¹ after calcination at 1125 K. After impregnation and calcination at 925 K, the Pt/ZrO₂ has a surface area of 20 m² g⁻¹. Pt loading in the catalyst was 0.5 wt%. Hydrogen chemisorption capacity (H/Pt) was 0.84 after reduction at 925 K. Pt black has a hydrogen chemisorption capacity (H/Pt) of 0.001 after reduction at 925 K.

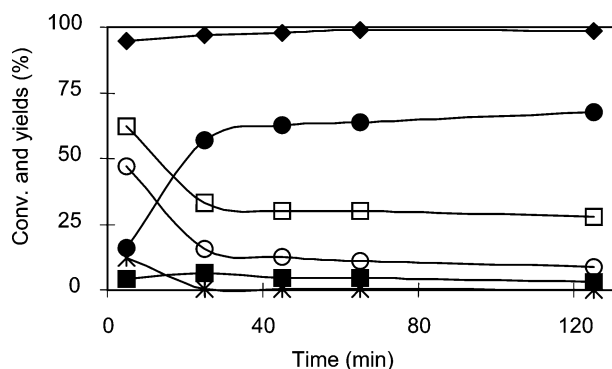


Fig. 1. Conversion and yields for steam reforming of HAc over Pt/ZrO₂ catalyst (725 K, S/C = 5, GHSV = 160,000 h⁻¹). (◆) HAc conversion, yields to (●) acetone, (□) CO₂, (○) H₂, (■) CO, (*) CH₄.

3.2. Steady-state catalytic tests

First, blank experiments (no catalysts) with inert quartz chips did not show any conversion of HAc. Fig. 1 shows HAc conversion and yields of products during steam reforming of HAc over Pt/ZrO₂ at 725 K. The HAc conversion was 100% during the whole experiment. During the test, in addition to typical steam-reforming products (CO, CO₂, H₂), also methane and acetone were observed. Carbon balance throughout the experiment was 100 ± 3%. During initial times on stream, hydrogen yield (47.0%) was lower than that calculated from thermodynamic equilibrium (56.0%). Under thermodynamic equilibrium conditions all the possible oxygenates that are formed (including acetone) in this reaction are completely steam-reformed at 775 K. Under our experimental conditions, acetone is observed, and thus part of the possible hydrogen yield is lost in the acetone that remains unconverted.

It can be seen from Fig. 1 that yields of products changed with time. In the beginning (5 min), H₂ and CO₂ were the main products, and CH₄ and CO were observed in small quantities. However, after 25 min time on stream, H₂ and CO₂ yields decreased drastically, and a corresponding increase in acetone was observed. Acetone is known to form easily from HAc and the reaction is catalyzed by a variety of oxides [9,10]:

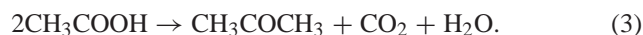


Fig. 1 also shows that the steam-reforming activity of Pt/ZrO₂ catalyst was lost after an initial period of time; however, the route to the formation of acetone was not affected and hence HAc conversion remained complete.

Fig. 2 shows HAc conversion and yields of products during HAc/H₂O reaction over ZrO₂ (without Pt). HAc conversion was close to 90%. However, no steam-reforming activity (H₂ and CO) was observed; only acetone and CO₂ were observed as products. Further, no methane was formed in this test. The stoichiometry of the products (acetone and CO₂) corresponded to the ketonization reaction [Eq. (3)]. The conversion of HAc and yields of the products were constant for 3 h.

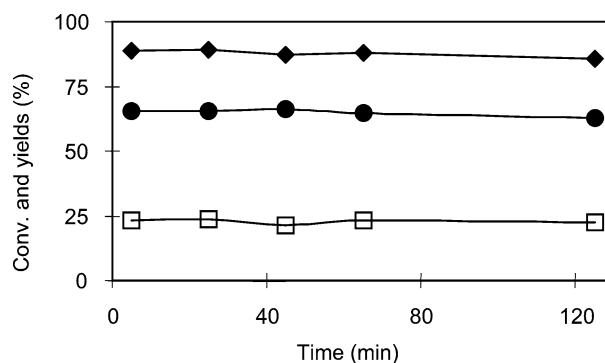


Fig. 2. Conversion and yields for steam reforming of HAc over ZrO₂ catalyst (725 K, S/C = 5, GHSV = 160,000 h⁻¹). (◆) HAc conversion, yields to (●) acetone, (□) CO₂.

It is seen from Figs. 1 and 2 that both Pt/ZrO₂ and ZrO₂ are very active for HAc conversion. However, H₂ and CO, i.e., steam-reforming products, were produced only over Pt/ZrO₂ and not over ZrO₂. This implies that the presence of Pt is essential for steam reforming. ZrO₂ shows acetone yields similar to those observed over Pt/ZrO₂ after 25 min time on stream (Fig. 1), indicating that even after the active sites for steam reforming were deactivated, the accessible ZrO₂ sites still provided the activity to form acetone and CO₂. It is important to recall here that in the Pt/ZrO₂ catalyst, Pt covers only about 5% of the ZrO₂ surface available. For Pt/ZrO₂ and ZrO₂, TG experiments showed approximately 1.2 and 0.8 wt% deposits, respectively, after a 3-h test.

3.3. Pulse catalytic tests

The results so far indicate an essential catalytic role for Pt during steam reforming; however, if ZrO₂ is required for steam reforming is not evident. In order to establish this, three catalysts, Pt/ZrO₂, ZrO₂, and Pt black were studied. Experiments were carried out in pulse transient mode since the steam-reforming activity of Pt/ZrO₂ catalyst decreased rapidly during steady-state experiments. The pulse size of HAc used (3.5 μmol) is much larger than the amounts of Pt-surface atoms available in Pt/ZrO₂ (0.43 μmol) and Pt black (0.05 μmol). On the basis of amounts of HAc, the reactant pulse size in these experiments corresponded to the first 2 s in the steady-state experiments.

Fig. 3 shows the comparison of conversion/yields obtained by contacting pulses of HAc/H₂O (S/C = 5), at 725 K, over the three catalysts, Pt/ZrO₂, ZrO₂, and Pt black. Table 1 shows conversion of HAc and selectivities for the first pulse toward carbon-containing products. Background tests in an empty reactor under these conditions did not show any conversion. As expected from the initial part of the continuous catalytic test (Fig. 1), Pt/ZrO₂ showed high HAc conversion (99%) and the main products were CO₂ and H₂ (Fig. 3a). CO and acetone was observed only in traces. The catalyst did not show any deactivation even after 5 pulses, indicating that the results shown here were in the region

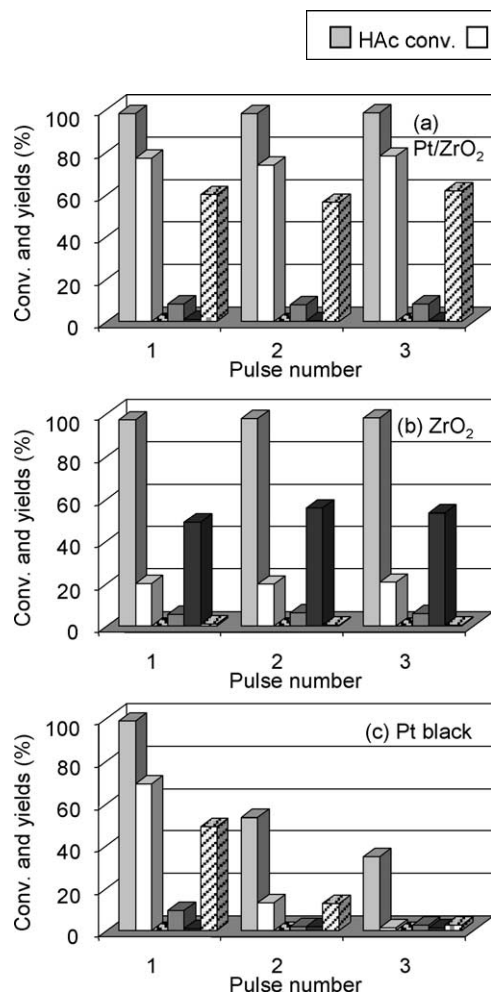


Fig. 3. Product distribution during HAC/H₂O pulsing over (a) Pt/ZrO₂, (b) ZrO₂, and (c) Pt black at 725 K.

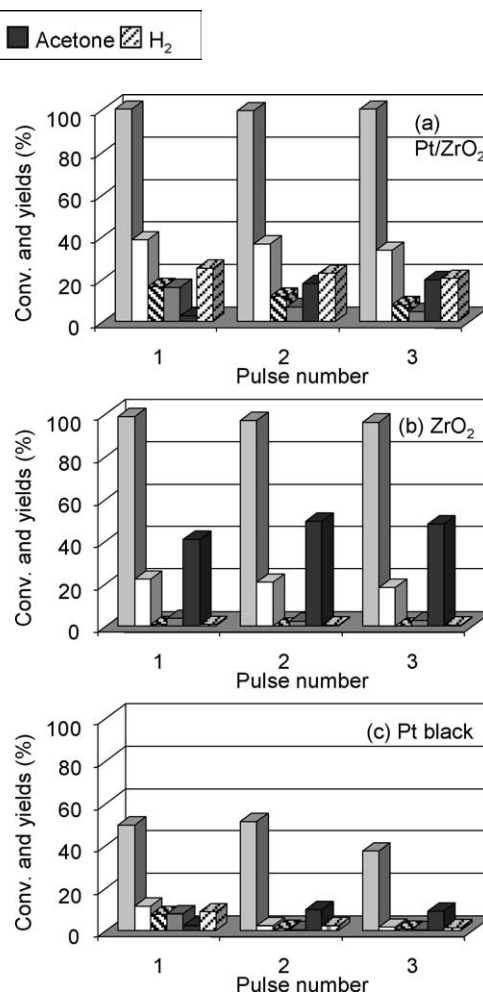


Fig. 4. Product distribution during HAC pulsing over (a) Pt/ZrO₂, (b) ZrO₂, and (c) Pt black at 725 K.

where steam-reforming activity was high and not yet affected by deactivation. However, carbon balance was around 90%, suggesting that accumulation on the catalysts occurred during these pulses.

Further, over ZrO₂ (Fig. 3b, Table 1), the conversion and product distribution were similar to the steady-state tests (Fig. 2), i.e., high amounts of acetone and CO₂, and low amounts of CO and H₂. Unlike in steady-state tests, also methane (12.8 mol%) and ketene (3.3 mol%) were observed

here (Table 1). Conversion and yields did not change during the five pulses, as expected from Fig. 2. Carbon balance was approximately 75%, suggesting that accumulation occurred on ZrO₂.

Over Pt black with HAC/H₂O (Fig. 3c), the conversion was high (~100%) only for the first pulse. H₂ and CO₂ were main products and CH₄ was observed in around 10% yield. The distribution of the products was similar to that for Pt/ZrO₂ catalyst (Figs. 3a and 3c, Table 1). However,

Table 1
Conversion of HAC and selectivities for the first pulse toward carbon-containing products observed

Reactant	Catalyst	Conversion (%)	Selectivity (mol%) ^a				
		HAc	CO ₂	CO	CH ₄	Acetone	Ketene
HAc/H ₂ O	Pt/ZrO ₂	98.2	89.9	0.0	9.8	0.4	0.0
	ZrO ₂	97.1	46.1	0.0	12.8	37.8	3.3
	Pt black	98.6	87.3	0.0	12.2	0.4	0.0
HAc	Pt/ZrO ₂	99.9	53.2	22.7	22.5	1.3	0.3
	ZrO ₂	98.6	50.3	1.3	8.0	31.1	9.3
	Pt black	49.6	40.6	26.3	27.2	2.8	3.0

^a Calculated excluding carbon loss.

Pt black deactivated rapidly as additional pulses were introduced, compared to the other catalysts (Fig. 3c). For the second pulse, conversion of HAc reached only 50%. H₂ and CO₂ yields accordingly decreased. For the third pulse, conversion of HAc decreased to ca. 30% and the catalyst completely deactivated after five pulses.

In order to examine how the absence of steam affects the product yields and catalyst life, experiments with HAc only over the same catalysts were carried out and the data are shown in Fig. 4. Selectivities for carbon-containing products for the first pulse are compiled in Table 1.

Over Pt/ZrO₂ (Fig. 4a, Table 1), complete conversion was observed during three pulses. For the first pulse, CO₂ and H₂ were the main products and CO and CH₄ were also observed. Acetone was produced only in small amounts. As more pulses were introduced, CO₂, H₂, CO, and CH₄ yields decreased gradually and acetone yield increased. It should be noted that CO was observed during pulsing of HAc only, and not during pulsing of HAc with steam. This indicates that Pt/ZrO₂ is highly active for the water gas-shift reaction [Eq. (2)] when steam is present in the feed (Fig. 3a, Table 1). Correspondingly, yields of CO₂ and H₂ for HAc pulsing were lower than those in the case of HAc/H₂O pulsing. It can also be seen (Fig. 4a) that the acetone yield increased while yields of other products decreased with increasing number of pulses.

Over ZrO₂ (Fig. 4b, Table 1), HAc conversion was nearly 100%. Acetone and CO₂ were major products; CH₄ (8.0 mol%) and ketene (CH₂CO) (9.3 mol%) were also observed. The distribution of products was similar to that for HAc/H₂O pulsing. Carbon balance was ca. 75%.

Over Pt black (Fig. 4c, Table 1) only 50% conversion was obtained for the first and second pulses. Carbon balance was about 80% in these experiments. The distribution of products was different from that for HAc/H₂O pulsing. For the first pulse, CO₂, CO, CH₄, and H₂ were obtained (all less than 10% yields) and acetone and ketene were observed only in very small amounts. From the second pulse, acetone was observed more clearly. The catalyst was deactivated almost completely after five pulses.

3.4. In situ IR measurements

Fig. 5 shows in situ IR spectra of Pt/ZrO₂ during steam reforming of HAc at 725 K. Fig. 5a shows IR spectrum after the first exposition to HAc/H₂O (S/C = 5). A peak assigned to linear CO adsorption on Pt was observed at 2060 cm⁻¹. Oxygenate peaks (typical for bidentate acetate and/or carbonates) were observed in the 1300–1500 cm⁻¹ region. After evacuation (not shown), CO on Pt was completely removed, which indicated that CO adsorption was reversible. The oxygenate peaks decreased by about 70% in intensity. The HAc/H₂O exposure and evacuation cycles were repeated three times. The spectra after each adsorption are shown in Fig. 5a–5c. The CO adsorption peak became gradually weaker as the cycle was repeated. Peaks for oxy-

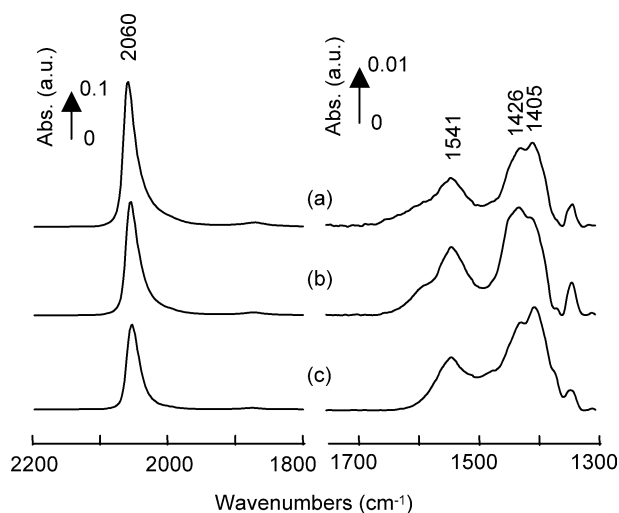


Fig. 5. In situ IR spectra over Pt/ZrO₂ at 725 K (S/C = 5, 0.1 mbar). HAc/H₂O evacuation cycles. Spectra were collected after HAc/H₂O was introduced.

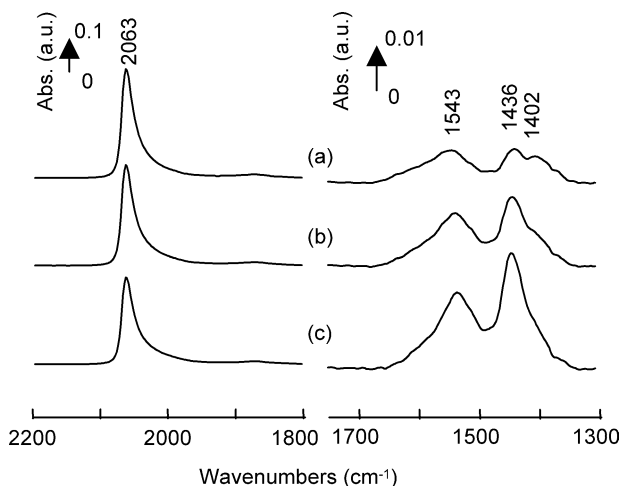


Fig. 6. In situ IR spectra over Pt/ZrO₂ at 725 K (S/C = 5, 0.1 mbar). Acetone/H₂O evacuation cycles. Spectra were collected after acetone/H₂O was introduced.

genates were almost the same in shape and intensity during the three cycles.

Fig. 6 shows IR spectra of Pt/ZrO₂ for steam reforming of acetone at 725 K. Similar to the spectra during steam reforming of HAc, linear CO adsorption on Pt was observed at 2062 cm⁻¹. Oxygenate peaks, similar to those observed with HAc, were also observed in the 1300–1500 cm⁻¹ region. As in the case of steam reforming of HAc, CO on Pt was removed and the oxygenate peaks were removed about 50% in intensity during evacuation (not shown). This cycle was repeated three times and spectra are shown in Fig. 6a–6c. The CO adsorption peak became gradually weaker as the cycle was repeated. Intensities of peaks for oxygenates increased concurrently.

In order to probe catalyst deactivation we have used in situ IR measurements. Experiments have been carried out

Table 2
Comparison of HAc conversion and H₂ yield between fresh Pt/ZrO₂ and MO-treated Pt/ZrO₂

Catalyst ^a (Pt/ZrO ₂)	HAc conversion (%)	H ₂ yield (%)
Fresh	98.2	60.0
MO treated ^b	82.4	29.1

^a 20 mg of catalyst was used.

^b MO/H₂O pulse (0.32 μmol-MO, S/C = 5) was introduced before a HAc/H₂O pulse.

under conditions simulating an accelerated deactivation test. The following text explains the background to these tests.

Acetone is known to undergo aldol-type condensation reactions over inorganic oxides [11–13] and give products such as diacetone alcohol ((CH₃)₂C(OH)CH₂COCH₃) and mesityl oxide ((CH₃)₂C=CHCOCH₃, MO). MO is known to undergo oligomerization [13,14] and form deposits on the catalysts, which can block active sites. In order to check the effect of MO on deactivation, Pt/ZrO₂ catalyst was contacted with a MO/H₂O pulse (0.32 μmol-MO, S/C = 5) before a HAc/H₂O pulse (3.5 μmol-HAc, S/C = 5). Table 2 shows HAc conversions and H₂ yields after this treatment. We observed that the Pt/ZrO₂ catalyst deactivated for H₂ formation more rapidly when contacted with MO in comparison to HAc (see Fig. 3a). In the case of HAc the catalyst did not show any deactivation during five HAc/H₂O pulses (i.e., one molecule MO deactivates the catalyst more rapidly than 60 molecules of HAc).

Fig. 7 shows IR spectra of Pt/ZrO₂ during the following procedure. First, MO, in amounts similar to those used in the deactivation experiment in Table 2, was introduced with a steam (S/C = 5) (Fig. 7a). Linear CO on the Pt peak was observed at 2064 cm⁻¹, indicating that some steam reforming of MO took place. The peaks for oxygenates are similar to those obtained from HAc/H₂O. The catalyst was then evacuated (not shown). Intensities for linear CO peaks and almost all of peaks for oxygenates decreased. After evacuation,

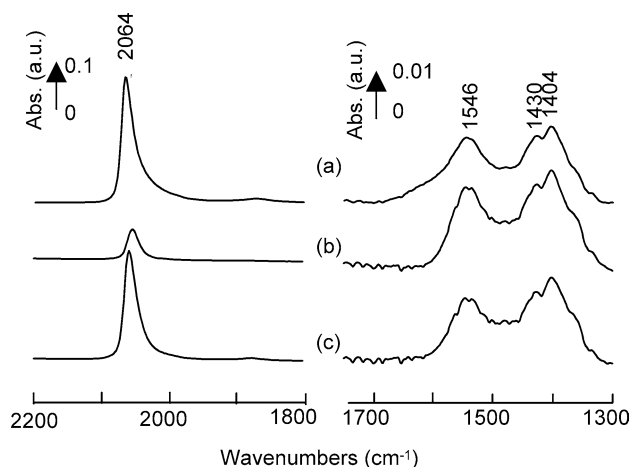


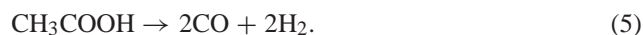
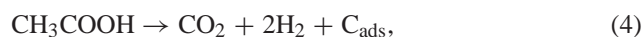
Fig. 7. In situ IR spectra over Pt/ZrO₂ at 725 K (S/C = 5, 0.1 mbar). (a) MO/H₂O, (b) HAc/H₂O (after (a) and evacuation), (c) CO (after (b) without evacuation).

HAc/H₂O was introduced (Fig. 7b). Spectrum 7b shows that CO adsorption on Pt was significantly suppressed, while the oxygenate peak showed up clearly. At this time, gas phase CO (1% in Ar, 0.1 mbar in total pressure) was introduced into the system without evacuation (Fig. 7c). Interestingly, the intensity for CO adsorbed on Pt increases dramatically. The peaks related to oxygenates remained unchanged.

4. Discussion

In general, during reaction with oxygenates, e.g., HAc and acetone, it is reported that a certain extent of homogeneous thermal decomposition is always possible [4]. However, blank experiments demonstrated the absence of significant homogeneous decomposition under reaction conditions used in this study.

In order to understand what happens on Pt, we first focus on the results over Pt black (Figs. 3c and 4c). In the absence of steam (Fig. 4c), the products observed in our experiments were H₂, CO₂, CO, and CH₄. As this happens in the absence of steam, the products must be formed from decomposition of HAc on Pt surface. Over a polycrystalline platinum surface, at temperatures between 300 and 900 K, Vajo et al. [15] observed that CH₃COOH decomposed to produce CO, CO₂, H₂, and adsorbed C according to



In our experiments, we also observed CH₄. Methane can be formed by the hydrogenation of CO_x (in separate experiments we did observe hydrogenation of CO₂ over Pt/ZrO₂ under these conditions).

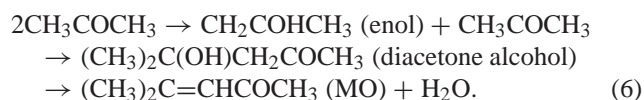
However, the significant observation was that the catalyst deactivated rapidly. After 3 pulses of HAc were introduced, the amount of deposit on the catalyst, based on C, is about 2.5 μmol. In the Pt black catalyst we have 0.05 μmol Pt available. This indicates that Pt is more or less completely covered by deposits and the resulting deactivation. During this deactivation, CO, CO₂, and CH₄ yields decreased and acetone and ketene yields increased. This could imply that the formation of ketene and acetone could occur on the deposits. This is in agreement with reported information that such oxygenates can be formed on coked Pt catalysts [15,16].

In the presence of steam, typical steam-reforming products were also observed over Pt black (Fig. 3c). However, CO was not observed and CO₂ and H₂ yields were high. This implies that a water gas-shift reaction took place, converting CO to CO₂ [Eq. (2)]. For both steam reforming and water gas shift, the activation of water is essential. In this case, we have only Pt sites in the Pt black catalysts. It is generally agreed that steam activation would hardly take place on Pt [17–20]. There is thus the possibility that the steam reforming and water gas shift activity of Pt black observed here are due to the presence of impurities, e.g., alkali (sodium and

potassium were present). Alkali metals are known to catalyze steam gasification and the products formed are similar to steam reforming [21].

ZrO₂ by itself is not active for steam reforming (Figs. 2, 3b, 4b). However, ZrO₂ is active to convert HAc to acetone. ZrO₂ is known to be catalytically active for ketonization [Eq. (3)] [22,23], and acyl and/or acetate type species are suggested to be involved in the reaction scheme [9,10,24]. IR spectra in the region of 1300–1800 cm⁻¹ at 725 K show oxygenate surface species on ZrO₂, regardless of the treatment with HAc, acetone or MO (Figs. 5–7). These bands have been attributed to species such as bidentate acetate [24,25] or carbonates [6]. On the basis of the IR spectra of oxygenate species on ZrO₂, it is not possible to pinpoint the exact nature of the species.

In the pulse experiments with HAc over ZrO₂, ketene (CH₂CO) and CH₄ were observed in small amounts (Table 1). Ketene can be formed by dehydration of HAc (CH₃COOH → CH₂CO + H₂O) [10] or decomposition of acetone formed from HAc (CH₃COCH₃ → CH₂CO + CH₄) [25]. As excess steam is present during these experiments, the latter seems more likely. Acetone formed on ZrO₂ can also undergo an aldol condensation-type reaction scheme, according to



Both ketene and MO, which can be formed from acetone over ZrO₂, can undergo oligomerization to form deposits and deactivate the catalyst by blocking active sites. The carbon balance (70–90%) in pulse experiments (Figs. 3b and 4b) shows formation of these deposits; this is also confirmed by TG analysis of deactivated catalysts. In addition, the molar ratio of acetone to CO₂ formed is significantly lower than one (Table 1), as expected from the reaction stoichiometry in Eq. (3). Thus, it is reasonable to consider that further transformation of acetone to deposits takes place on the ZrO₂ support.

Over Pt/ZrO₂ and Pt black, typical steam-reforming products were observed at initial times on stream (Figs. 1, 3a, and 3c). As stated earlier, the product over ZrO₂ hardly contained any H₂ (Figs. 2, 3b, and 4b). These results clearly show that the presence of Pt is essential to catalyze steam reforming. However, Pt black lost its activity more rapidly (Figs. 3c and 4c) than Pt/ZrO₂. This is supported by the results from catalyst testing, where Pt/ZrO₂ catalyst was still active even after at least 1700 TON (Fig. 1, after 5 min on stream) (TON = moles of HAc introduced per moles of available Pt) while Pt black deactivated just after 136 TON (Fig. 3c, after 3 pulses). Therefore, ZrO₂ also plays an important role in maintaining steam-reforming activity.

Nevertheless, the Pt/ZrO₂ catalysts showed rapid deactivation after a certain time on stream (Fig. 1). In order to understand this, we have carried out an accelerated deactivation test by contacting the catalyst with MO. As expected, in

catalytic experiments, pretreatment with MO caused a strong decrease in steam-reforming activity (Table 2). IR experiments showed that pretreatment with MO causes decrease in the IR intensity of adsorbed CO (Fig. 7b), indicating also a decrease in steam-reforming activity. However, the intensity of the CO peak increased when CO was introduced (Fig. 7c), indicating that Pt surface was still available in this deactivated catalyst. Thus, not all Pt in Pt/ZrO₂ seems to be involved in the catalysis of steam reforming.

A bifunctional mechanism is proposed for reforming of methane over supported Ni catalysts [26,27] where methane is activated on Ni and steam on the support. For Pt/ZrO₂, also such a bifunctional mechanism is proposed for dry reforming of methane where methane is activated on the metal and CO₂ on ZrO₂ [6]. In the latter case, the reaction is suggested to occur at the periphery of the Pt particles in the proximity of ZrO₂ [6,28]. As our results suggest that only part of the Pt atoms are involved in steam reforming, we propose, in line with our earlier results [6], that steam reforming for HAc occurs probably at those Pt sites only which are in close proximity of the support ZrO₂. Studies to establish correlations between Pt periphery and catalyst activity for steam reforming are in progress.

At initial time on stream, ZrO₂ effectively activates steam; however, acetone formation as well as further oligomerization also happens on ZrO₂. Deposition of the oligomers at the periphery of the Pt particles is probably responsible for the deactivation of steam reforming.

In order to develop the durable catalysts for steam reforming of HAc, we have to avoid the condensation reactions on the support, in this case ZrO₂. Acid–base properties of the support are known to play a key role in catalyzing such transformations [13]. Thus, two aspects are to be considered while modifying the support, ZrO₂, (i) enhancing steam activation and (ii) minimizing activity toward oligomer formation.

5. Conclusions

Steam reforming of HAc was investigated over Pt/ZrO₂ catalysts. The Pt/ZrO₂ catalysts showed high activities at initial times on stream, but lost its activity for steam reforming (H₂ production) rapidly. It is revealed that Pt is essential for steam reforming, and ZrO₂ is needed to extend the catalyst life. A bifunctional mechanism is proposed for steam reforming of HAc on Pt/ZrO₂; i.e., HAc activation takes place on Pt and steam activation on ZrO₂. The reaction occurs at the Pt periphery in close proximity of ZrO₂. The catalysts deactivate due to blocking of active sites by oligomers derived from HAc/acetone on ZrO₂. In order to develop a durable catalyst, the oligomerization/condensation reactions which take place on the support need to be minimized.

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