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Catalyst deactivation during steam reforming of acetic acid over Pt/ZrO_2

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Abstract

Steam reforming of acetic acid as a model compound present in bio-oil over Pt/ZrO_2 catalysts has been investigated. Pt/ZrO_2 yields steam reforming products (i.e., H_2, CO, CO_2) to the amounts predicted by thermodynamic equilibrium; however, conversion and yields dropped rapidly with time on course. The deactivation was due to blockage of active sites by coke/oligomer formed. This report clarifies cause of the deactivation during steam reforming of acetic acid. It was found that many products can be formed from acetic acid on ZrO_2, such as acetone. The experimental results confirmed that aldol condensation of acetone took place on ZrO_2 to give larger compounds which can easily become deposits to block active sites for steam reforming. In order to develop durable catalysts for steam reforming of bio-oil, support should be designed to enhance activation of water, minimize dehydration reactions and thus oligomer formation.

Keywords: Steam reforming; Acetic acid; Acetone; Aldol condensation; Pt; ZrO_2; Bio-oil; Hydrogen; Sustainable

1. Introduction

Currently, developments in the area of fuel and energy applications focus on the use of hydrogen in fuel cells. Tremendous interest is gained when hydrogen originates from renewable resources, e.g., biomass, to arrive at CO_2 neutral energy supply [1]. Studies on flash pyrolysis of lignocellulosic biomass have demonstrated that solid biomass can be efficiently converted to a bio-oil [2], which allows for easy transport and generation of hydrogen from this bio-oil on-site where hydrogen is needed. A combination of catalytic steam reforming and water gas shift reactions can maximize hydrogen yield from bio-oil. Bio oil is made up of aliphatic/aromatic oxygenates such as acids, aldehydes, ketones, and alcohols [3]. Acetic acid (CH_3COOH, AcOH) is one of the major components present in bio-oil (up to 32 wt.%) [3]. Therefore, steam reforming of AcOH has been investigated as a model reaction in order to understand the requirements for the design efficient catalysts for the steam reforming of bio-oil [4].

In a previous study [4], we reported results on Pt/ZrO_2 catalyst for the steam reforming of AcOH. A bifunctional mechanism was proposed wherein AcOH is activated on the Pt and H_2O is activated on the ZrO_2. The Pt/ZrO_2 catalyst was very active for steam reforming of AcOH, giving close to equilibrium yield of hydrogen. However, the catalyst showed severe deactivation even in the presence of excess amounts of steam due to blockage of active sites by coke/oligomers formed [4]. ZrO_2 is an amphoteric oxide on which both medium-strength acid and basic sites coexist [5] and catalyze various oxygenate conversions [6]. For instance, it has been reported that ZrO_2 is active for acetone (CH_3COCH_3) formation from AcOH [4,7,8]. Thus, acetone, which is formed on the ZrO_2, may influence the performance of the catalyst. Steam reforming of AcOH and acetone over Pt/ZrO_2 has been investigated in order to study the reaction pathways that lead to deactivation of the Pt/ZrO_2 catalysts and help in the design of stable catalysts.

2. Methods

2.1. Catalyst preparation

ZrO_2 (monoclinic, Daiichi Kigenso Kagaku Kogyo, RC100) was first calcined for 15 h at 1125 K. It was then crushed and sieved to give grains having diameters between 0.3 and 0.6 mm.

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0.5 wt.% Pt/ZrO_2 catalyst was prepared by wet impregnation. An aqueous solution of $H_2PtCl_6·6H_2O$ (Alfa Aesar, 0.01 g Pt per ml) and the calcined ZrO_2 grains were used. The Pt/ZrO_2 catalyst was dried and finally calcined for 15 h at 925 K. Specific surface area of the ZrO_2 and the Pt/ZrO_2 catalysts used are 21 and 20 $m^2 g^{-1}$, respectively. Pt dispersion of 0.84 (H/Pt) was determined by hydrogen chemisorption.

2.2. Catalytic measurements

For catalytic measurements, 50–200 mg of catalysts were loaded in a fixed bed reactor and held by quartz wool plugs. The catalyst was first reduced in 5% H_2 in N_2 at 925 K for 1 h with a total flow rate of 50 ml min^{-1}. For reactions with water in the feed, an aqueous solution of AcOH or acetone giving a steam to carbon molar ratio (S/C) of 5 was introduced using a micro feeder (KD Scientific) and a syringe (Hamilton Co.). For reactions without water in the feed, AcOH or acetone was fed using a saturator. In both reactions with and without H_2O, AcOH and acetone were fed giving a vapor pressure of 2.5 and 1.7 kPa, respectively. The space velocity (SV) of 40,000–160,000 h^{-1} was achieved with argon as a carrier gas. N_2 was added as an internal standard. Analyses were carried out by using a gas chromatography (Varian 3400), equipped with a Hayesep Q column connected to a flame ionization detector; and a Carbosieve column connected to a thermal conductivity detector.

In the case of AcOH conversion, steam reforming (Eq. (1)), and water gas shift reactions (Eq. (2)) occur simultaneously and the reaction stoichiometry is represented

$$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2 \quad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

Similarly, in the case of acetone reforming, the reaction stoichiometry is (Eq. (3))

$$CH_3COCH_3 + 5H_2O \rightarrow 3CO_2 + 8H_2 \quad (3)$$

The hydrogen yields were calculated based on Eqs. (1) or (3). For carbon containing compounds, the yields were calculated based on C_1 equivalent values [9].

2.3. Quantification of deposits

Thermogravimetry (TG) (Mettler Toledo TGA/SDTA 851E) was used to determine the amount of deposits on the catalysts. The catalysts used for the reaction were heated from room temperature to 1075 K in $1\%O_2/Ar$ and weight changes recorded.

3. Results

Blank experiments with inert quartz chips showed negligible conversions of AcOH and acetone under the conditions investigated. Thus, homogeneous decomposition of AcOH or acetone was not significant.

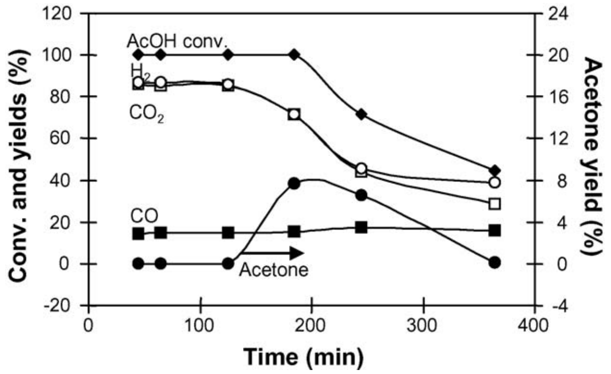


Fig. 1. Steam reforming of AcOH over Pt/ZrO_2 (875 K, $H_2O/C = 5$, GHSV = 40,000 h^{-1}, AcOH = 2.5 kPa).

3.1. Steam reforming of acetic acid and acetone over Pt/ZrO_2 catalysts

Fig. 1 shows conversions and yields obtained during steam reforming of AcOH over Pt/ZrO_2 catalyst at 875 K. Products observed were H_2, CO_2 and CO, and hydrogen yield (87.0%) was nearly at thermodynamic equilibrium (91.3%). However, a sharp drop in conversion was observed after 3 h time on stream. H_2 and CO_2 yields decreased correspondingly, while the CO yield remained constant. Notably, acetone was observed as deactivation set in. Carbon loss (<15%) was observed throughout the catalytic test, indicating that deposits remained on the catalyst surface. After 6 h time on stream, yields of acetone, H_2 and CO_2 decreased whereas the yield of CO remained constant in smaller amounts.

The catalyst activity could be regenerated with oxygen at 875 K (Fig. 2), suggesting that deactivation was caused by carbonaceous deposits which blocked active sites. Sintering of Pt particles was excluded from Pt dispersion measurements. TG analysis of deactivated catalyst showed that the deposits (amounting to 1.56 wt.% after 3 h test) could be removed by combustion in air below 700 K.

Fig. 3 shows acetone conversion and H_2 yield for steam reforming of acetone over Pt/ZrO_2 catalyst at 875 K; results for AcOH are given in the same figure for comparison. In order to be able to make proper comparison, feed rates for carbon,

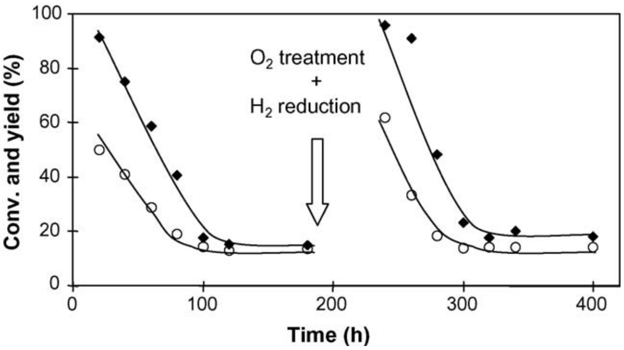


Fig. 2. Regeneration of Pt/ZrO_2 for steam reforming of AcOH. The catalyst was treated in flowing air at 875 K, then reduced in H_2 at 925 K (875 K, $H_2O/C = 5$, GHSV = 160,000 h^{-1}, AcOH = 2.5 kPa) (♦) AcOH conversion, (○) H_2 yield.

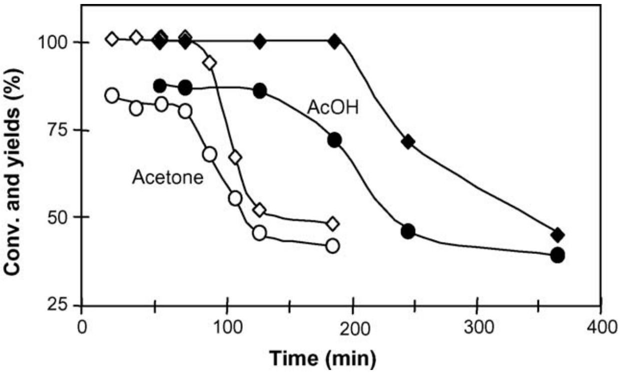


Fig. 3. Comparison of conversions and H_2 yields between steam reforming of AcOH and acetone over Pt/ZrO_2 catalyst (875 K, S/C = 5, GHSV = 40,000 h^{-1}, AcOH = 2.5 kPa, acetone = 1.7 kPa)) (◆, ◇) Conversion, (●, ○) H_2 yield, closed symbols for reforming of AcOH, open symbols for reforming of acetone.

Table 1
Conversion, selectivity for carbon containing materials, and hydrogen yields for steam reforming of AcOH or acetone over Pt/ZrO_2 catalyst (875 K, 200 mg-cat, SV = 40,000 h^{-1})

Reactant	Conversion (%)	Selectivity (mol.%)[a]			Yield (%)
		CO_2	CO	CH_4	H_2
AcOH/H_2O	100	85.5	14.5	0	87.0
Acetone/H_2O	99.8	71.1	28.1	0.5	83.7

[a] Selectivity for carbon containing compounds calculated excluding carbon loss.

steam to carbon ratios and space velocity were kept identical. It is seen from Fig. 3 that, in the beginning of the reaction, acetone could also be steam reformed. However, the Pt/ZrO_2 catalyst showed more rapid deactivation as compared to steam reforming of AcOH (85 min versus 3 h). The catalyst experienced 1.47 wt.% of deposits after 3 h test.

Table 1 summarizes the catalytic results after 5 min time on stream for the two steam reforming reactions. In the case of acetone, CH_4 was observed additionally and H_2 yield of 83.7% observed was close to thermodynamic equilibrium (88.3%) value.

3.2. Reactions of acetic acid and acetone over ZrO_2

In order to establish the role of the support, reactions were carried out on the bare ZrO_2 support. Results of the steam reforming of AcOH over ZrO_2 (without Pt) are shown in Fig. 4.

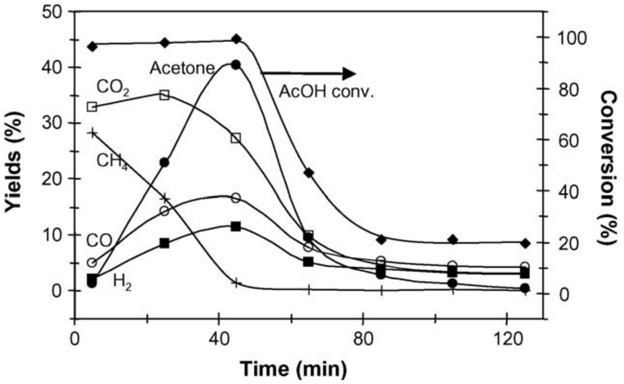


Fig. 4. AcOH conversion in the presence of water over ZrO_2 (875 K, $H_2O/C = 5$, SV = 40,000 h^{-1}, AcOH = 2.5 kPa).

The product distribution changed drastically in time. In the beginning, CH_4 and CO_2 were mainly obtained. After 45 min time on stream, CH_4 disappeared, acetone yield increased and CO_2 yield remained high. After 85 min, AcOH conversion decreased and yields of all the products decreased correspondingly. Throughout the test, H_2 and CO were observed only in smaller quantities, confirming that ZrO_2 has no appreciable activity for steam reforming (Pt is essential for steam reforming [4]). Larger carbon loss was observed throughout the catalytic test (<30%). TG analysis in air indicated 2.1 wt.% of deposits after 3 h test and the deposits could be removed below 725 K.

In the absence of water (Table 2) AcOH was extensively dehydrated over ZrO_2, producing ketene (Eq. (4)). At a lower temperature (725 K) acetone was observed according to Eq. (5).

$$CH_3COOH \rightarrow CH_2CO + H_2O \tag{4}$$

$$2CH_3COOH \rightarrow CH_3COCH_3 + CO_2 + H_2O \tag{5}$$

In the case of steam reforming acetone over ZrO_2, CH_4 and CO_2 were mainly observed (Eq. (6)).

$$CH_3COCH_3 + H_2O \rightarrow 2CH_4 + CO_2 \tag{6}$$

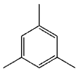
In the absence of water, in spite of the nearly complete acetone conversion, no products were observed in any significant quantities. Indeed, carbon loss was more than 90%. This suggests that the acetone conversion resulted in deposits on the catalyst. At a lower temperature (725 K), mesityl oxide and mesitylene could be observed. Lippert et al. [10] describe the formation of

Table 2
Reactions of acetic acid or acetone over ZrO_2 at 875 K with ($H_2O/C = 5$) or without H_2O at 5 min time on stream (200 mg-cat, SV = 40,000 h^{-1})

Reactant	Conversion (%)	Yield (%)						
		H_2	CO_2	CO	CH_4	Ketene	Isobutene	Acetone
AcOH/H_2O	96	4.9	32.9	2.2	28.4	0.2	1.5	1.3
Acetone/H_2O	100	4.3	22.4	3.0	40.9	0.5	3.1	–
AcOH	99	10.4	15.1	3.8	3.1	43.0	0.9	11.1
Acetone	85	2.0	1.4	1.3	0.7	2.6	0.1	–

mesitylene from acetone due to the following reactions (Eqs. (7) and (8))

$$2CH_3COCH_3 \rightarrow (CH_3)_2C(OH)CH_2COCH_3(\text{diacetonealcohol}) \rightarrow (CH_3)_2C{=}CHCOCH_3(\text{mesityloxide}) + H_2O \tag{7}$$

$(CH_3)_2C{=}CHCOCH_3 + CH_3COCH_3 \rightarrow$  (mesitylene) $+ 2H_2O$ (8)

Isobutene was observed over ZrO_2 in small amounts at 875 K (Table 2). Isobutene has been reported to be the main reaction product of the acid-catalyzed condensation reaction of acetone [11–13], and known to undergo polymerization to form higher hydrocarbons and aromatics which can become deposits over acidic catalysts [14]. However, in the current situation this must be a small contribution as the amounts of isobutene observed are much smaller than the other coke/oligomer precursors, ketene or mesityl oxide.

4. Discussion

In an earlier publication [4] we have shown that both Pt and ZrO_2 have a role in the catalysis of steam reforming of acetic acid; acetic acid activation occurs on Pt and water is activated on ZrO_2. Thus, the active sites are suggested to be located at the Pt–ZrO_2 boundary. It has also been established [4] from the facts (i) catalyst could be reactivated by oxidative regeneration and (ii) Pt dispersion measurements did not indicate sintering of Pt, that loss in activity during steam reforming of acetic acid is due to coke/oligomer deposition. As the active sites are located at the Pt–ZrO_2 boundary, coke/oligomer formation in these locations will deactivate the catalyst most effectively. In order to extend catalyst life, it is essential to understand how coke/oligomer formation occurs so that catalyst design can take into consideration ways to overcome this.

During steam reforming of acetic acid (Fig. 1), initially only steam reforming products are observed. Acetone is observed only after the catalyst deactivates, even though ZrO_2 is capable of catalyzing the formation of acetone from acetic acid. This implies the catalyst is able to steam reform acetone formed initially. However, during the steam reforming of acetone (Fig. 3) catalyst deactivation occurred more rapidly. This suggests that acetone can play a key role in the deactivation of steam reforming. Indeed, acetone was observed in large quantities from AcOH over ZrO_2 (Fig. 4). According to available information [9,10,15,16] most oxides catalyze this reaction (Eq. (6)). In our experiments at 875 K, over ZrO_2 (Table 2) acetic acid undergoes transformation to form CO_2, CH_4, acetone and ketene. The last three products have the potential to form coke/oligomers via consecutive reactions.

Earlier works [17,18] have shown that Pt/ZrO_2 is a very stable catalyst for the steam reforming of methane. Further, the catalyst is even stable and resistant to coke forming during the dry reforming of methane with CO_2 where coke formation is favored by thermodynamics. It is concluded from this that CH_4 itself (formed on ZrO_2) can be considered less important for deactivation here during steam reforming of acetic acid.

Ketene, on the other hand, contains two unsaturated bonds and has been proposed to be a coke-precursor [9]. However, this reaction is known to be a reversible reaction [15], so that excess of water in the feed could prevent its formation (only traces of ketene were observed during our experiments, Table 2).

Discussions so far point out fact that a route to form deposits from acetone should exist. Based on the results obtained in this study, we propose a reaction sequence that AcOH undergoes over ZrO_2 as illustrated in Fig. 5. Carbon number in a compound increases to the right of the figure. It can be noted from Fig. 5 that all the dehydration reactions are undesirable for the steam reforming because these reactions are related to the oligomerization (new C–C bond formation). This is in agreement with the fact that the presence of water in the feed significantly suppressed the rate of deposition and total amounts of deposits (Fig. 6). However, high ratio of steam to carbon of five could still not suppress the coke/oligomer deposition completely. We thus propose that the major route to deactivation is the formation of oligomers by the dehydration of acetic acid via acetone and mesityl oxide as intermediates. Separate studies indeed show that Pt/ZrO_2 catalyst could be deactivated very effectively by contacting with trace amounts of mesityl oxide [4]. Since acetone is the precursor for oligomer formation, and since acetone is formed from acetic acid by acidic or basic oxides, the more plausible way to enhance the life of the catalyst is to enhance

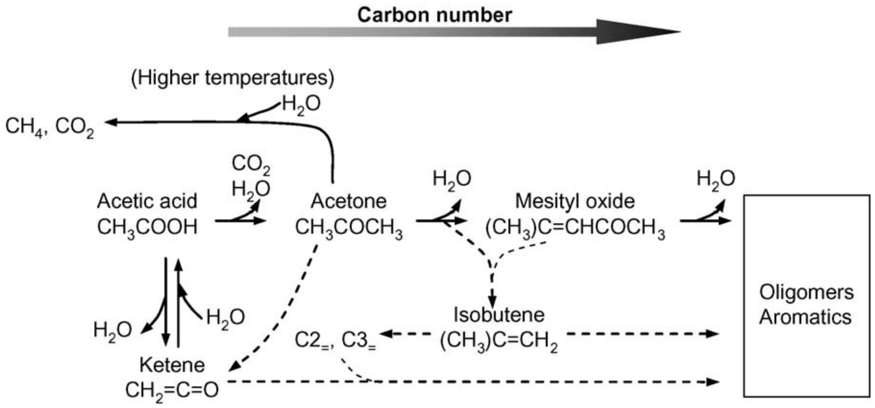


Fig. 5. Diagram for the possible reactions of acetic acid (and acetone) over ZrO_2 catalysts.

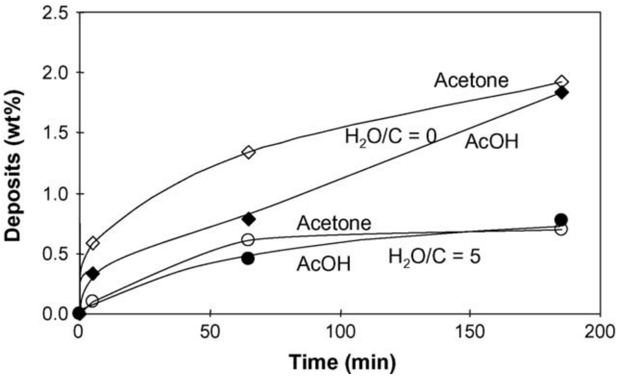


Fig. 6. Influence of reactant (AcOH or acetone) and of water on the amount of deposits on ZrO_2 catalyst (725 K, GHSV = 160,000 h^{-1}, AcOH = 2.5 kPa, acetone = 1.7 kPa) (♦, ◇) $H_2O/C = 0$, (●, ○) $H_2O/C = 5$, closed symbols for AcOH reaction, open symbols for acetone reaction.

steam reforming activity of acetone than prevent its formation. Enhancement of the ability to activate water might help in minimizing the dehydration type reactions which leads to oligomer formation.

5. Conclusions

Pt/ZrO_2 is an active catalyst for the steam reforming of acetic acid. During reaction AcOH is also converted to acetone over ZrO_2. Subsequently, acetone undergoes condensation/oligomerization reactions which result in deposits on the catalysts. The Pt/ZrO_2 catalyst is initially active to steam reform AcOH as well as all the compounds formed on ZrO_2, yielding hydrogen close to thermodynamic equilibrium. However, the catalyst is deactivated rapidly for the steam reforming after certain time on stream, due to the blockage of the Pt related active sites by the deposits. Oligomerization (new C–C bond formation) causing the deactivation is related to dehydration reactions (e.g., aldol condensation reactions of acetone), which are undesirable for the steam reforming (where C–C, C–H bond splitting is necessary). In order to develop efficient and durable catalysts for the steam reforming of AcOH, special attention should be given to the surface properties of the support to enhance activation of water which might suppress undesirable dehydration reactions.

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