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Research Note

Steam reforming of biomass based oxygenates—Mechanism of acetic acid activation on supported platinum catalysts

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ABSTRACT

The activation of acetic acid during steam reforming reactions over Pt-based catalysts has been probed by decomposing CH_3COOD over Pt/C. The product mixture contained CO_2, CH_4 and its D-analogs ($CH_{4-x}D_x$, $0 \leqslant x \leqslant 4$), H_2, HD and D_2. CO_2, CH_3D and D_2 are typically primary desorption products whereas the rest originate from hydrogen redistribution reactions and H–D exchange. The bifunctional mechanistic pathways suggested earlier [K. Takanabe, K. Aika, K. Seshan, L. Lefferts, J. Catal. 227 (2004) 101–108; K. Takanabe, K.-i. Aika, K. Inazu, T. Baba, K. Seshan, L. Lefferts, J. Catal. 243 (2006) 263–269] for the steam reforming of acetic acid over Pt/ZrO_2 are substantiated.

1. Introduction

Sustainable routes to hydrogen, a future energy carrier, are of much interest currently. Steam reforming of biomass is one such option; however, development of efficient and stable catalysts is a bottleneck [1–4]. Knowledge on a reaction mechanism is an essential point for the catalyst improvement. In this context, we proposed in previous studies [1,2], on biomass based oxygenates reforming, that a bifunctional mechanism, where both Pt and support participate in the catalytic reaction, is involved for the steam reforming of acetic acid (AcOH) over Pt/ZrO_2. The role of the support, ZrO_2, is in the activation of water forming reactive hydroxyl groups. Unlike metals such as Ni [5], Re [6], Fe [7], dissociation of water on Pt is improbable at the reaction conditions used in this study [8,9]. We, however, showed that the presence of Pt was essential for steam reforming and suggested that AcOH decomposed on Pt forming CH_x ($1 \leqslant x \leqslant 3$) type surface species [1,2]. It was further suggested, that this CH_x species on Pt reacted with hydroxyl groups at the periphery between Pt and ZrO_2 forming hydrogen and carbon oxides. However, it was not possible to provide experimental evidence for the existence of intermediate surface CH_x species under reaction conditions because of their high reactivity with OH groups. In order to establish the formation of such CH_x species on Pt it is essential to (i) carry out experiments preventing presence of hydroxyl groups, e.g., using a hydrophobic support such as graphite and (ii) use deuterated acetic acid which allows us to follow redistribution reactions of intermediate surface hydrocarbon species.

In this study, we report on the activation of CH_3COOD over Pt/C (graphite) catalysts. Use of graphite allows us to disperse Pt and provide for measurable activity under our experimental conditions, in comparison to pure Pt. It is well established that activation of hydrocarbons is facile over Pt [10], independent of the support [1]. It has been shown by Zaera [11] that by cofeeding CH_3I and D_2 over Pt single-crystals, CH_x species were formed. They observed that (i) CH_3I decomposed over Pt to give CH_3^* and I^* (ii) CH_4 originated from the hydrogenation of CH_x (iii) H–D exchange resulted in the formation of D-substituted analogs such as CH_3D, CH_2D_2, CHD_3.

It was proposed by us that acetic acid decomposes during steam reforming over Pt/ZrO_2, to gas phase CO_2 and sorbed CH_x^* and H^* species. Thus, if CH_3COOD is used, reactions between CH_x^* and D^* can be expected. Occurrence of D-substituted analogs such as CH_3D, CH_2D_2, CHD_3 (as above [11]), allows us to establish if CH_x species [1,2] are relevant during steam reforming of acetic acid.

The objective of the present study is to suggest the reactive intermediate species involved when activating AcOH over Pt and to complete the mechanistic pathways suggested earlier [1,2] for the steam reforming of acetic acid over Pt/ZrO_2 catalysts.

2. Experimental

A 10 mg sample of 5 wt% Pt/C (graphite) (commercial, Alfa Aesar, EG-nr.: 231-955-3) diluted with quartz particles (1:5) was

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loaded in a fix-bed reactor and held by quartz wool plugs. The catalyst was first reduced in situ under 5% H_2/Ar flow (50 $ml\,min^{-1}$) at 500 °C for 30 min. After purging the reactor with Ar for 15 min, the temperature was lowered to 320 °C [2], in order to prevent any homogeneous decomposition of acetic acid as well as Pt metal sintering. CH_3COOD (Aldrich, 99 at% D) or CH_4 pulses (17.5 µmol each) were injected into the reactor, using a microsyringe. Outlet composition was measured online with a mass spectrometer (Balzers QMS 200 F). Unconverted acetic acid was delayed from the gas-mixture using a cold trap. This helped to avoid overlapping of the MS-signals of the gaseous products formed, with those from acetic acid. Blank experiments indicated no decomposition of acetic acid at this temperature. Correspondingly, delayed broad signal corresponding to acetic acid was only observed. All gaseous products were determined semi quantitatively.

3. Results and discussion

Fig. 1 shows the spectra obtained during three subsequent pulses (I, II and III) of CH_3COOD over Pt/C (graphite) at 320 °C. Contacting CH_3COOD (m/z 43) over the catalyst resulted in the formation of the following species: CO_2 (m/z 44), CH_4 (m/z 16), CH_3D (m/z 17), H_2 (m/z 2), CH_2D_2 (m/z 18), HD (m/z 3), CHD_3 (m/z 19) and D_2 (m/z 4).

CO_2 is formed when acetic acid decomposes over Pt, as shown by us earlier [1] and here it should come from CH_3COOD according to Eq. (1),

$$CH_3COOD + 2^* \rightarrow CH_3^* + CO_2(g) + D^*, \qquad (1)$$

where the symbol $*$ denotes a metal site. CH_3D and D_2 (Fig. 1) can be primary desorption products assuming recombination on the catalyst surface of the species formed in Eq. (1) (CH_3^* and D^*). The other gaseous products observed (CH_4, CH_2D_2, CHD_3, H_2 and HD (see Fig. 1) cannot originate directly from the decomposition of CH_3COOD according to Eq. (1). Further, if the direct recombination of CH_3^* with D^* was facile, these deuterated gas products would not have been observed.

The following routes can be proposed, in agreement with Zaera [11] and Kemball [12], concerning methane formation, i.e., (i) hydrogen redistribution—via dehydrogenation/hydrogenation reactions—among CH_x ($1 \leqslant x \leqslant 3$) species (e.g., $CH_{3(ads)} \rightleftarrows CH_{2(ads)} + H_{(ads)}$; $CH_{3(ads)} + H_{(ads)} \rightarrow CH_{4(g)}$, etc.) or (ii) hydrogen/deuterium redistribution among $CH_{4-x}D_x$ and surface H^* or D^* species (e.g., $CH_3D_{(g)} + H_{(ads)} \rightleftarrows CH_{4(g)} + D_{(ads)}$). In the former case a Langmuir–Hinshelwood and in the latter Eley–Rideal-type mechanisms are involved as at least one of the species is in the adsorbed state. The possibility of this Eley–Rideal-type exchange is also reported by Guczi et al. [13] who observed exchange of D_2 with CH_4 over pure platinum in the temperature range from 300 to 400 °C. In both cases the presence of H atoms on the platinum is essential, supporting partial dehydrogenation of CH_x species formed in Eq. (1). Further, it is important to recall that gas phase (noncatalytic) H–D exchange (e.g., between CH_3D and D_2) is not probable under the experimental conditions reported here [14–17].

From a pool of surface species such as CH_x ($0 \leqslant x \leqslant 3$), H and D, all species such as $CH_{4-x}D_x$ (e.g. CH_3D) can be formed. Comparison of the amounts of "C" based products based on elementary statistical probability calculation with those from our experiments showed that the amount of CH_4 formed experimentally was larger than would be expected if H–D redistribution was the only route for CH_4 formation. CH_4 (Expt.—45%, Stat.—32%), CH_3D (33% vs 42%) and CH_2D_2 (16% vs 21%) were observed in different amounts than predicted by statistical calculations. Deviations from statistics in our kinetic experiments may indicate that scrambling is not the only pathway for the formation of $CH_{4-x}D_x$ ($0 \leqslant x \leqslant 4$) species.

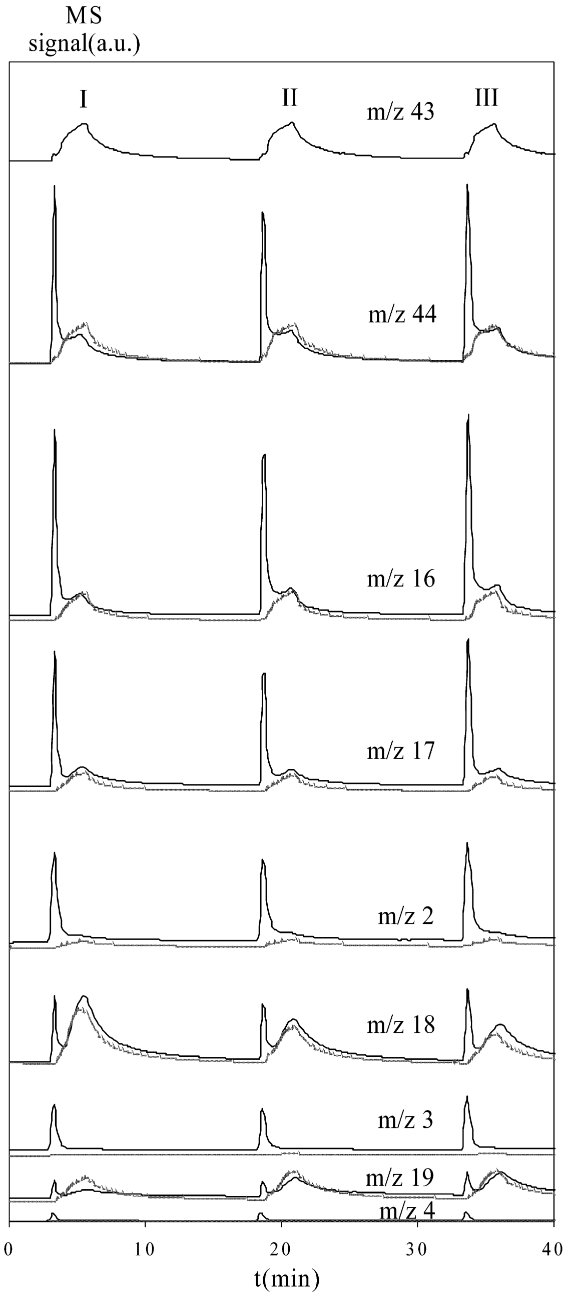

Fig. 1. Typical product distribution for CH_3COOD pulses over 5 wt% Pt/C (solid line) and over empty reactor (dash line) at 320 °C.

Observation so far supports our earlier proposition [1,2] that formation of CH_x type species on Pt was involved in the steam reforming of acetic acid over Pt/ZrO_2. In the steam reforming of methane, activation of CH_4 on metal based catalyst is a crucial step. It is known [18] that methane activation, leading to the reactive CH_x species for steam reforming, requires higher temperatures (800 °C) since it involves rupture of C–H bond (435 kJ/mol [19]). Under our experimental conditions (320 °C), pulsing of CH_4 over Pt/C (graphite) resulted in no detectable methane conversion as well as no hydrogen and coke formation, confirming that methane indeed cannot be activated at such low temperature. However, in the case of acetic acid, fragmentation of the C–C bond, which is energetically more favorable (368 kJ/mol [19]) directly results in the reactive CH_x type species. Thus, steam reforming of acetic acid follows a route similar to that proposed over Pt/ZrO_2 for methane steam reforming but can occur at milder temperatures.

4. Conclusion

Observations of deuterated analogs of methane ($CH_{4-x}D_x$, $0 \leqslant x \leqslant 4$) over Pt/C (graphite) showed that CH_3COOD activation occurred via C–C bond activation, producing CO_2 and similar to CH_4 activation, forming CH_x species ($0 \leqslant x \leqslant 3$) which could further be steam-reformed in the presence of H_2O. Presence of the $CH_{4-x}D_x$ ($0 \leqslant x \leqslant 4$) suggests that the recombination of the primary surface species formed by the scission of CH_3COOD, i.e., CH_3^* and D^*, is not exclusive and scrambling reactions occur. The fact that acetic acid activation over Pt-based catalysts directly generates CH_x species is a key point to explain why acetic acid can be steam reformed under milder conditions than methane, which requires higher temperature to activate C–H bond.

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