

Mechanistic study of the aqueous phase reforming of ethanol over Ru/TiO₂ catalysts by in situ ATR-IR spectroscopy under working conditions

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Abstract: Attenuated total reflection IR spectroscopy (ATR-IR) has been applied for monitoring surface species occurring during aqueous phase reforming (APR) of ethanol on Ru/TiO₂ with different loading and particle size of Ru at 200°C and 20 bar. The reaction was earlier found to be structure sensitive. On catalysts with smaller particle size (mean size d_p , 1 nm), undesired C-O cleavage was suppressed leading to enhanced H₂ production. On catalysts with larger particle size (d_p , 5 nm), formation of intermediate acetylide was detected corroborating the enhanced C-O bond cleavage leading to prevalent methanation and lower H₂ production.

Keywords: Aqueous phase reforming, ethanol, ATR-IR, structure sensitivity, Ru/TiO₂.

1. Introduction

The production of hydrogen as a clean energy carrier from bio-renewable sources is considered to be one of the most promising ways to minimize the global environmental impact associated with fossil fuel combustion. Among bio-renewable liquid feedstocks for producing hydrogen, ethanol (EtOH) is one of the most promising candidates because of its non-toxicity, facile storage and safe handling. Aqueous phase reforming (APR) of oxygenated hydrocarbons, pioneered by Dumesic's group, has attracted considerable attention due to beneficial features, such as cost reduction and H₂ generation with lower level of CO.¹

Recent studies² of APR of EtOH on Ru/TiO₂ revealed a significant dependence of the catalytic performance on the Ru loading, as shown in Figure 1. Catalysts with 5wt% Ru loading and a mean Ru particle size of 5 nm showed prevalent formation of methane and lower efficiency of hydrogen production compared to catalysts with lower loading (0.5 wt%) and smaller particle size (1 nm). On 0.5wt% Ru/TiO₂ the main product was H₂ with a relatively small amount of CH₄ and CO₂. These results indicated that APR of EtOH over Ru/TiO₂ is a structure sensitive reaction and that undesired methanation can be suppressed with catalysts of small particle size.

Here, to gain a deeper understanding of this catalytic behavior we have applied ATR-IR spectroscopy to monitor the fate of species at the catalytic solid-liquid interface during APR of EtOH.

2. Experimental

TiO₂ supported Ru catalysts (0.5 and 5 wt%) were prepared by a conventional impregnation method. The APR reaction was carried out in a stainless-steel autoclave (volume: 400ml) with a reflux condenser connected to online TCD and FID gas chromatographs. After the reduction of the catalyst (0.5g) with H₂ at 350 °C, aqueous solution of EtOH was introduced into the reactor under nitrogen atmosphere and the reaction was started at 200 °C under 2.5 to 3.0 MPa. For the ATR-IR study, a catalyst layer (12 mg) was deposited on an in situ IR cell suitable for monitoring the fate of surface species under working conditions of the catalyst.

3. Results and discussion

Figure 2(A) shows in situ ATR-IR spectra during APR of EtOH with H₂O (10 vol% EtOH in H₂O; total volume of 5 mL) on 5 wt% Ru/TiO₂ at 200 °C and 20 bar under stirring at 20 rpm. Since the background was taken when the reaction temperature of 200 °C had been reached, the IR spectra only show the species that changed over time. Species that were formed emerge as positive IR bands while those which were consumed (decomposed) appear as negative IR bands. During 2h reaction, catalytic transformation/decomposition of EtOH occurred as indicated by changes in the spectra acquired in intervals of 5 min. At initial stage of the reaction (0-20 min), a band at 1043 cm⁻¹ assigned to C-O stretching vibration of ethoxy groups emerged, associated with negative bands at 2916 and 2848 cm⁻¹ assigned to C-H stretching vibrations. Since when taking the background, ethoxy groups already existed on the catalyst surface, changes in the IR bands for C-O and C-H bonds are considered to originate from partially dehydrogenated ethoxy species: CH₃CH₂O_(a) → C₂H_{5-x}O_(a) + xH_(a). However, after 20 min the C-O band at 1043 cm⁻¹ started disappearing gradually accompanied by further decrease in the C-H bands at 2916 and 2848 cm⁻¹, indicating further dehydrogenation and cleavage of C-O bonds. In line with this process new sharp bands emerged at 3016 and 1303 cm⁻¹, assignable to C-H and C-C stretching vibrations of acetylide (μ³-η²-CCH). The formation of acetylide rationally accounts for further dehydrogenation and cleavage of C-O bonds according to:

$$\text{C}_2\text{H}_{5-x}\text{O}_{(a)} \rightarrow \text{C}_2\text{H}_{(a)} + (4-x)\text{H}_{(a)} + \text{O}_{(a)}$$

Generally APR of EtOH should catalyze the cleavage of C-C bond to enhance the selectivity to H₂ and CO₂ formation while avoiding unfavorable methanation through the cleavage of C-O bonds. Interestingly, as shown in Fig. 2(B), in APR of EtOH over smaller Ru particles, C-H and C-O bands at 3016 and 1303 cm⁻¹ were not observed during 2 h of reaction

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4. Conclusions

ATR-IR spectroscopy of surface species occurring during APR of EtOH on the surface of Ru/TiO₂ catalysts with different Ru loading revealed significant differences corroborating the earlier found structure sensitivity of APR on these catalysts. Undesired methanation of the formed CO₂ and CO prevalent on 5wt% Ru/TiO₂ (d_p, 5nm) was suppressed on 0.5wt% Ru/TiO₂ (1 nm). We conclude that the reaction path via acetylide occurring on 5wt% Ru/TiO₂ contributes to formation of methane thereby lowering the efficiency of hydrogen generation. This reaction path can be suppressed by applying Ru/TiO₂ with small Ru particles.

References

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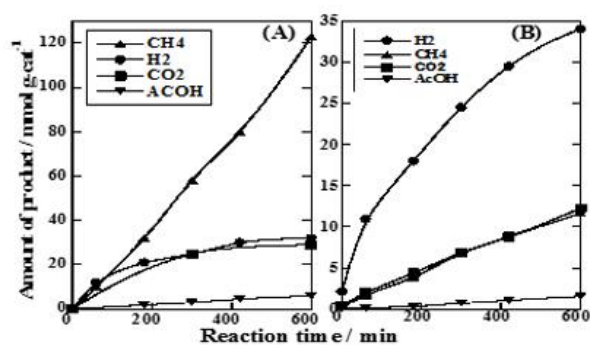


Figure 1 Time courses of APR at 200 °C

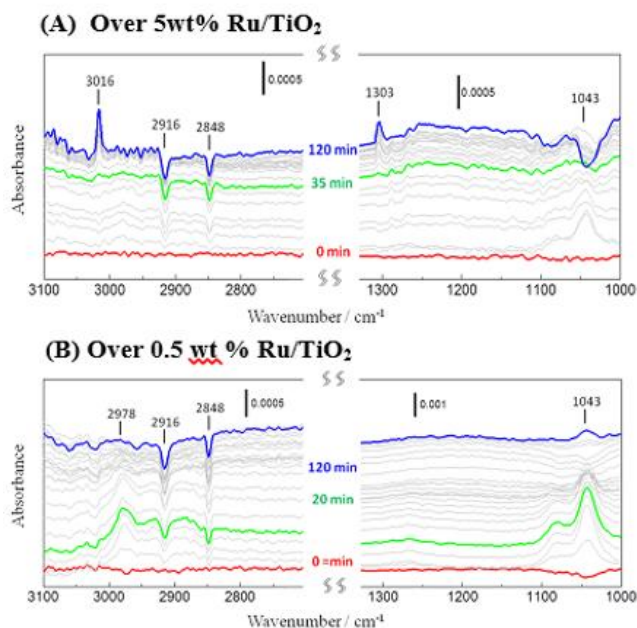


Figure 2 ATR-IR spectra taken during APR of EtOH on 0.5 (A) and 5wt% RuTiO₂ (B)