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CONTENT

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PHOTOCATALYTIC PRODUCTION OF HYDROGEN ON PLATINUM DOPED TITANATE CATALYST: INFLUENCE OF ALCOHOL CHAIN LENGHT

H. Šalipur, J. Dostanić and D. Lončarević

University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia. (hristina@ihtm.bg.ac.rs)

ABSTRACT
Platinum doped titanate catalysts were synthesized via alkaline hydrothermal method, followed by incipient wetness impregnation method and temperature programmed reduction (TPR). The effects of sacrificial agents on the photocatalytic activity of platinum doped titanate catalysts were studied in water splitting/alcohol photoreforming process under simulated solar light irradiation. Mechanism of photocatalytic reactions were elucidated by additional experiments performed using temperature-programmed desorption/mass spectrometry (TPD/MS). The applied alcohols (methanol, ethanol and 1-propanol) have shown enhanced hydrogen production rate in water splitting/photoreforming. Decreasing hydrogen production rate were observed in order methanol>ethanol>1-propanol (with achieved 11.6, 12.5, and 5.9 mmol g^{-1} h^{-1}, respectively) due to the decrease in carbon atoms in alcohol carbon chain.

INTRODUCTION
Photocatalysis has been developing rapidly as potential strategy for sustainable and clean energy as a process that converts solar irradiation into chemical energy using semiconductors. In photocatalytic process, band gap excitation is followed by charge separation and transportation to the semiconductor surfaces. The generated photoexcited electrons and holes transfer to the surface-adsorbing reactants and get trapped. The trapping of excited charge carriers is a key step in photocatalytic reactions, and the adsorbates that can trap holes are called hole scavengers [1]. The hole transfer from the surface to the dissociative adsorbate is crucial for understanding the photocatalytic water splitting/photoreforming [2]. Noble metals such as Pt are well-known for accepting photoexcited electrons and lowering the overpotential of hydrogen production in photocatalysis, being responsible for the enhanced photocatalytic efficiency [3].

The photocatalytic activity of platinum doped titanate catalyst was investigated using methanol, ethanol, and 1-propanol as hole scavengers in water splitting/alcohol reforming process. The mechanistic pathways of photocatalytic reactions were proposed from alcohol decompositions and identified adsorbed and desorbed species.

METHODS
Titanate nanotubes were synthesized by a hydrothermal method. Briefly, 4 g of the P25 TiO_2 were mixed with 250 mL of 10 M NaOH solution in a Teflon-lined autoclave at 150 °C for 24 h. After hydrothermal reaction, the participate was dispersed in 125 mL of 2 M NH_4NO_3 solution for 24 h, which led to ion-exchange of Na^+ ions by $NH4^+$ ions. In order to ensure complete ion-exchange reactions the washing and redispersion steps were repeated. Precursors were obtained after drying at 110 °C for 24 h. Platinum doped titanate catalysts (0.5 wt%) were obtained using wetness impregnation method followed by reduction. Reduction of precursors and platinum doped titanate catalysts was performed under 5 vol% of H_2 in H_2/Ar mixture, 20 mL/min flow rate with heating rate of 10 °C/min for 3 h at temperature 500°C (using Thermo Finningen TPDRO 1100

apparatus, equipped with a thermal conductivity detector). The final catalysts were labeled as N doped titanate catalyst (N-TNT) and Pt doped titanate catalyst (Pt-TNT).

Temperature-programmed desorption (TPD) of the applied alcohols was performed on a Thermo Scientific 1100 TPDRO instrument coupled with a ThermoStar GSD320 mass spectrometer. The alcohol was adsorbed on a N-TNT catalyst surface before TPD experiments. The catalyst sample (0.06 g) was exposed to the alcohol containing gas (5% mixture in He, flowing at 20 mL min^{-1}) at 60 °C for 1 h. After the adsorption, the reactor was purged with Ar at a flow rate of 20 mL min^{-1} for at least 1 h to remove any residual alcohol. For TPD experiments, the samples were heated in Ar flowing at 20 mL min^{-1} at a temperature ramping rate of 10 °C min^{-1}.

The photocatalytic activity of the Pt-TNT catalysts was assessed towards the hydrogen production via photocatalytic water splitting/alcohol reforming process under simulated solar light. The photocatalytic tests were performed at 25 °C (maintained by a JULABO F25 circulation thermostat) under atmospheric pressure in a photocatalytic reactor (ACE glass) equipped with standard reaction vessel, quartz immersion well and 100 W mercury-vapor lamp. Prior to illumination, the suspension consisting of 125 mg of photocatalyst and 250 mL of 2 M alcohol/water mixture was placed in a reaction vessel and purged for 60 min with Ar flow to remove oxygen from the suspension. During illumination the concentration of effluent gas was analyzed with a constant time interval sampling by gas chromatograph (Shimadzu GC-8A).

RESULTS AND DISCUSSION
The effect of alcohols on the photocatalytic activity of the Pt-TNT catalysts is shown in **Figure 1a**. Maximal hydrogen production rate were observed to follow the order methanol>ethanol>1-propanol with obtained values of 11.6, 12.5, and 5.9 mmol g^{-1} h^{-1}, respectively. Regardless of small difference in maximal hydrogen production rate between ethanol and methanol (12.5 mmol g^{-1} h^{-1} and 11.6 mmol g^{-1} h^{-1}, respectively), it is evident from **Figure 1a** that the hydrogen production rate using methanol decreases slower compared to hydrogen production rate decrease using ethanol. According to the results from TPD/MS (**Figure 1b and Figure 1c**) the decrease in hydrogen production rate using ethanol is related to the greater number of intermediates on the catalyst active sites, such as ethylene and acetaldehyde. Regarding methanol, there are fewer intermediates which are more easily desorbed at lower temperatures, therefore leaving reactive sites available for the next step of reaction [4].

The decomposition pattern of methanol on N-TNT catalyst is shown in **Figure 1b**. The main products are CO, H$_2$O, CH$_4$, CH$_2$O indicating both dehydrogenation and dehydration process. Molecular methanol desorbs at 150 °C and is fully desorbing at around 450 °C which has characteristic fragments at m/z=31. CH$_2$O as main product desorbs at around 400 °C, and has fragments at m/z=30. Methane evolution is a result of C-O bond scission which needs the presence of anion vacancies. The vacancies interact with the oxygen atom in the methanol and enables C-O bond scission.
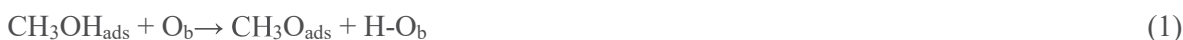
The decomposition pattern of ethanol on N-TNT catalyst is shown in **Figure 1c**. The first desorption peak at 100 °C corresponds to ethanol molecular desorption and fully desorbing at around 370 °C which has characteristic fragments at m/z= 45. The signal of desorbed water (m/z = 18) at around 440 °C**.** The sharp and intense peak at 360 °C (m/z=27) corresponds to ethylene desorption. This peak is the result of ethanol dehydration catalyzed by acid sites on N-TNT catalyst surface. The peak (m/z=44) at 420 °C corresponds to acetaldehyde desorption.

The decomposition spectrum of 1-propanol (**Figure 1d**) follows a similar dehydration pattern to that of ethanol with H$_2$O, propionaldehyde and propylene released as the main products. The sharp peak at 400 °C is ascribed to desorbed propylene (m/z=42). The propionaldehyde evolves at 350 °C with characteristic peak at m/z=58.
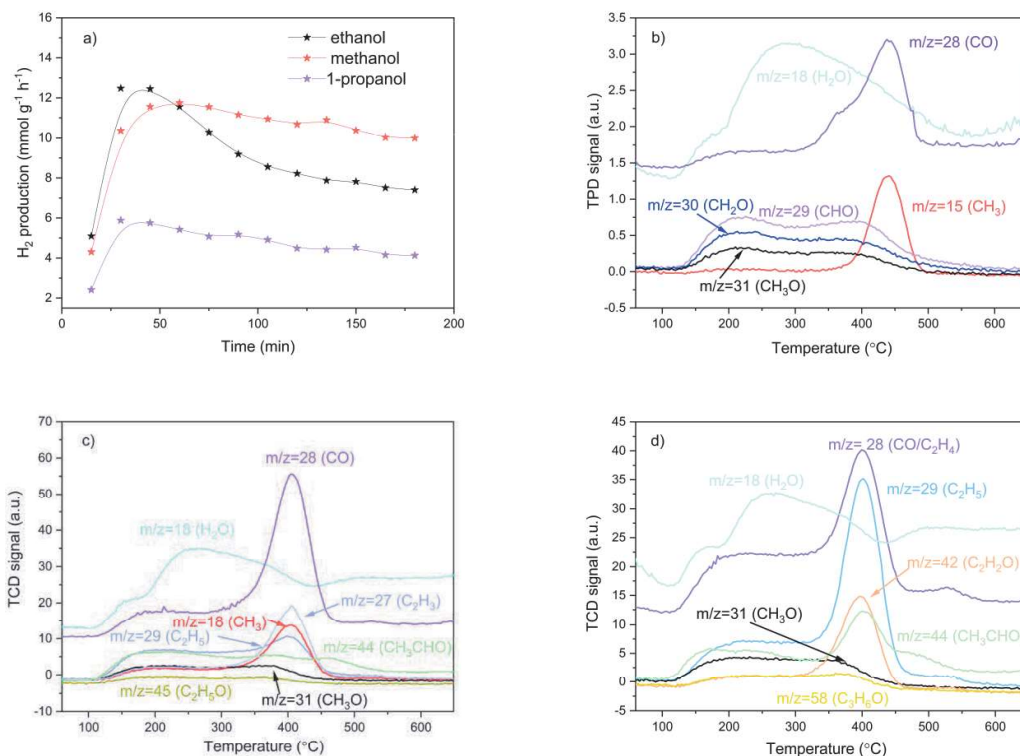
Figure 1. a) Time-dependent hydrogen production rates of Pt-TNT catalyst using different hole scavengers, and temperature programed desorption spectra of the b) methanol c) ethanol d) 1-propanol on N-TNT catalyst.

$$CH_3OH_{ads} + O_b \rightarrow CH_3O_{ads} + H\text{-}O_b \tag{1}$$
$$CH_3O_{ads} + O_b \rightarrow CH_2O_{ads} + H\text{-}O_b \tag{2}$$
$$2CH_3O_b \rightarrow CH_4 \ (gas) + CH_3OH \ (gas) + O_v \tag{3}$$
$$CH_3O_b + H\text{-}O_b \rightarrow CH_3 + H_2O \ (gas) + O_v \tag{4}$$

where O_b is basic oxygen site, O_v is oxygen vacancy.

During the thermal dissociation of CH_3OH, CH_3O and thermal hydroxyl group (HO_b) are formed in the reaction between molecularly adsorbed CH_3OH and a basic oxygen site (O_b) (Eq. 1). Formaldehyde (CH_2O) was formed from thermally dissociated CH_3OH which was initiated by O_b sites, but not by O_v sites (Eq. 2). Possible two reaction for CH_4 formation is presented by Eq. 3 and Eq. 4. Eq. 3 presents dominant reaction for CH_4 formation, since there is an increase in CH_4 TPD peak (m/z=15) and absence of the H_2O TPD peak increase.

The proposed mechanism of methanol decomposition over N-TNT catalysts yield important insights into general steps in alcohol decomposition. The reaction with the acidic hydrogen of the alcohol with basic oxygen sites on the surface lattice of the titania leaving adsorbed alkoxy species and hydroxide species. The monomolecular dehydration is likely to occur via surface anion vacancies forming alkene. The vacancies that are formed are excellent oxygen abstractors and recover their oxygen during the overall reaction cycle [2]. The proposed mechanism of the thermal decomposition

of the investigated alcohols on N-TNT catalyst can be represented with next steps: 1) dehydration of the combined adsorbate–adsorbent system to yield adsorbed alkoxy groups and vacancies and 2) decomposition of the alkoxy group by oxygen abstraction back into the vacancy site which requires C-O bond dissociation.

The obtained results indicate that hydrogen production rate decreases with the decrease in carbon atoms in alcohol carbon chain. The alcohols with longer carbon chains form stronger hydrogen bonding with surface hydroxyls, which results in the increased amount of adsorption on the hydroxylated surface [5]. However, the hole scavenging ability is affected by: redox potential and diffusivity, adsorption and desorption rate of the hole scavenger on the surface of the catalysts, and stability of the radical species generated via hole scavenging [6]. Thus, hole scavenging ability of alcohols is probably a trade-off between their adsorption/desorption rate of intermediates/products and alcohol radical stability.

CONCLUSION

Alcohols used as hole scavengers in photocatalytic water splitting/photoreforming process have shown enhanced hydrogen production rate. The hole scavenging ability of alcohols is a trade-off between their adsorption rate and radical stability. Ethanol has demonstrated the highest maximal hydrogen production rate due to higher adsorption/desorption rate and low stability of generated alcohol radical. Methanol captures the holes more rapidly than ethanol or 1-propanol therefore has highest efficiency in hydrogen production. Alcohol adsorption on the titanate nanotube surfaces leads to dissociation and the formation of an alkoxide, followed by dehydration to an alkene and/or dehydrogenation to an aldehydes.

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