# Valorization of Ethanol into 1,1 Diethoxy-Ethane by Photocatalysis in Presence of $TiO_2$-Based Photocatalyst

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Since more than 30$^{th}$ years, photocatalysis has been intensively investigated for degradation of water and air pollutants. However, recently, due to our important reliance on fossil fuels as our primary source of energy, several publications deal with photocatalysis for the production of energy, in particular for the production of $H_2$ from sustainable sources. H. Zhang et al. [1-3], using ethanol, an important bio-compounds easily obtained from fermentation of biomass, has showed also the possibility to generate a promising fuel additive, the 1,1 diethoxy-ethane from photocatalytic transformation of neat ethanol using noble-metal loaded $TiO_2$ under inert atmosphere and suggest that hydronium ions generated are responsible for its formation.

The objective of our work was to better understand the mechanism of the formation of 1,1 diethoxy-ethane from the photocatalytic transformation of ethanol and determine if the use of noble metal and an inert atmosphere was essential. To answer to these questions, first different experiments were done under air in presence of $TiO_2$ without noble metal. The influence of several important parameters namely: (i) water proportion, (ii) phase of $TiO_2$, (iii) presence of F and $WO_3$ on $TiO_2$ and (iv) $TiO_2$ surface is highlighted. Secondly, we have investigate the impact of the presence of Pt on $TiO_2$ rutile and anatase under air but also under inert atmosphere.

In addition to some traces of methanol and ethylacetate which are detected, acetaldehyde was the initial products formed whatever the atmosphere and the catalyst used. In all cases after stabilization of acetaldehyde formation, 1,1 diethoxy-ethane appears and increases as a function of time indicating that he comes from the acetalization reaction between acetaldehyde and ethanol occurring on the surface of the catalyst. Its formation is favored in absence of water and in presence of $F/TiO_2$, $WO_3/TiO_2$ and $Pt/TiO_2$ under air atmosphere. These observations might be related to the type of acetaldehyde adsorption in the presence or absence of water and to the acidic properties of the catalyst surface in presence of F, $WO_3$ or Pt. In the case of $Pt/TiO_2$, besides the formation of acetaldehyde, hydrogen was formed and favored on rutile phase under inert atmosphere. Moreover, whatever the atmosphere, air or inert, the formation of 1,1 diethoxy-ethane appears at a lower concentration of acetaldehyde compared to the case of $TiO_2$ without Pt.

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[2] H. Zhang, W. Zhang, M. Zhao, P. Yang and Z. Zhu, Chem. Commun., 2017,53, 1518-1521
[3] H.Zhang, Y.Wu, L. Li, and Z. Zhu, ChemSusChem, 2015, 8(7),1226-31