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COMMUNICATION

Photo-thermal reactions of ethanol over Ag/TiO_2 catalysts. The role of silver plasmon resonance in the reaction kinetics.

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Photo-thermal catalytic reactions of ethanol over Ag/TiO_2 were conducted in order to probe into the role of plasmonic resonance response in the reaction kinetics. In the 300-500K temperature domain the increase in reaction rates is found to be mainly due to changes in the activation energy while above this temperature the increase was due to the pre-exponential factor. These results might be linked to the role of plasmonic Ag particles to polarise the reaction intermediates and therefore increase the reaction products at temperatures up to about 500K.

While elevated temperatures are not needed in photo-catalytic reactions because of their low activation energy recent reports indicate an enhancement in chemical reaction rates when both light and heat are used.[1-5] To date, there is a lack of understanding and probably consensus on how or even whether photo-excited electron transfer rates can be enhanced by thermal reactions over a semiconductor. Several explanations were provided depending on the type of the catalyst and reaction studied. For example, Upadhye and co-workers demonstrated that the localized surface plasmon resonance (LSPR) increases the reverse water gas shift reaction (RWGS) rate ($CO_2 + H_2 \rightarrow H_2O + CO$) on Au catalysts.[1] A light to chemical efficiency of up to 5% was computed. The authors proposed that the LSPR changes the intrinsic reaction kinetics on the catalyst surface via either "hot" electron generation mechanism or LSPR mediated adsorbate polarization mechanism. Tan and co-workers observed that, despite being a weak thermal ethanol oxidation catalyst, Au/TiO_2 displayed considerable increases of its catalytic performance upon excitation with visible and UV light.[2] The enhancement under UV illumination was attributed to congruent roles of the photo- and thermal- catalysis, while that under visible light illumination was due to plasmonic-mediated electron charge transfer from Au particles to the TiO_2 support (the so-called "hot" electrons). Kennedy and co-workers investigated the photo-thermal catalytic oxidation of ethanol over non-plasmonic catalysts: TiO_2 and 1 wt. % Pt/TiO_2. The photo-thermal enhancement of CO_2 production (70% at 100 °C) appeared to be caused primarily by increased levels of acetaldehyde produced by photo-oxidation over TiO_2 and its subsequent migration to Pt metal leading to CO_2 production by thermal reaction.[3] Chanmanee and co-workers studied alkane reverse combustion under photo-thermal conditions.[4] They observed an increase in productivity of liquid hydrocarbons with temperature but with a very weak incident photon quantum yield (IPQY) of 0.02-0.05% on a per electron stored basis. Hu and co-workers studied the temperature-induced visible light photocatalytic hydrogen production from water and methanol using black TiO_2.[5] They found an enhancement in the reaction rate that was attributed to visible light photo-catalysis due to the presence of Ti^{3+} states in TiO_2. At elevated temperatures, the injection of electron, into Ti^{3+} states, was proposed to be behind the increase in the relative population of adsorbed methanol molecules in "vibrationally" excited states, which lead to improved reaction rates.

In this work, we have found that ethanol photoreaction rate increases with increasing reaction temperature. The experiments were conducted in an UHV chamber with TiO_2 and 3 wt. % Ag/ TiO_2 (anatase-88% + rutile-12%) catalysts. Details of the experimental set-up and procedure are provided in the supplementary information. UV-VIS, XRD and XPS analyses of 3 wt. % Ag/TiO_2 catalyst are presented in Fig. 1. In the case of UV-Vis spectrum, relatively sharp absorption edges at 415 nm and 387 nm are consistent with the intrinsic band gap absorption of TiO_2 rutile and anatase phases, respectively. The rise in the background in the visible region that extends into UV region is attributed to the surface Plasmon absorption of Ag particles.[7, 8] XRD patterns show Ag_2O (111) diffraction in addition to diffraction peaks at 25.3 and 27.5 due to TiO_2 anatase (101) and rutile (110), respectively. The average crystallite sizes calculated using Scherer equation were 31, 44 and less than 10 nm (mean particle size) for anatase, rutile and Ag particles, respectively.

The chemical nature and atomic % of Ag in the near–surface region determined from XPS Ag3d core–level peak areas are given in Fig. 1 and Table 1.

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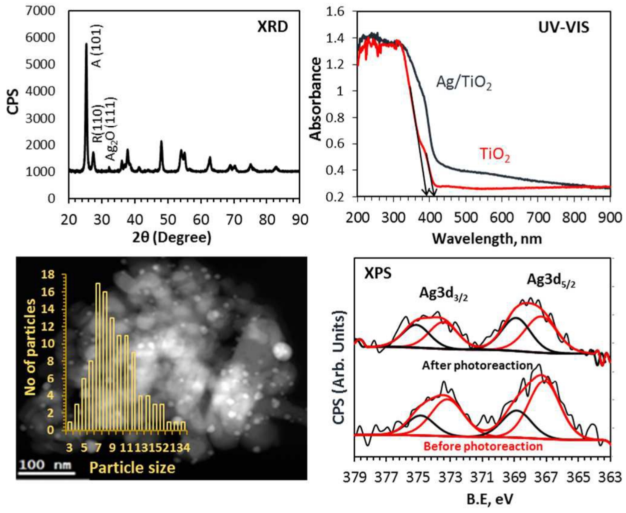

Figure 1. XRD, UV-Vis, TEM (dark field) and XPS Ag 3d of 3 wt. % Ag/TiO_2

Both Ag metal and Ag^+ were present as evidenced by the $Ag3d_{5/2}$ binding energy values of 368.8 eV and 367.4 eV corresponding to Ag^0 and Ag^+, respectively.[10] An increase in Ag/Ag^+ ratio is noticed and attributed to in situ reduction of Ag^+ during photoreaction. XPS core levels of Ti and O were also collected and found consistent with typical TiO_2 (not shown).[10, 11]

Table 1. XPS results of 3 wt. % Ag/TiO_2 before and after photoreaction.

Chemical	Core level	Peak position (eV)	FWHM (eV)	ΔE (eV)	at. %	
					Before	After
Ag	$Ag3d_{5/2}$	368.8	2.1	6.1	0.6	0.6
	$Ag3d_{3/2}$	374.9	2.2			
Ag_2O	$Ag3d_{5/2}$	367.3	2.3	5.9	1.0	0.7
	$Ag3d_{3/2}$	373.2	2.4			

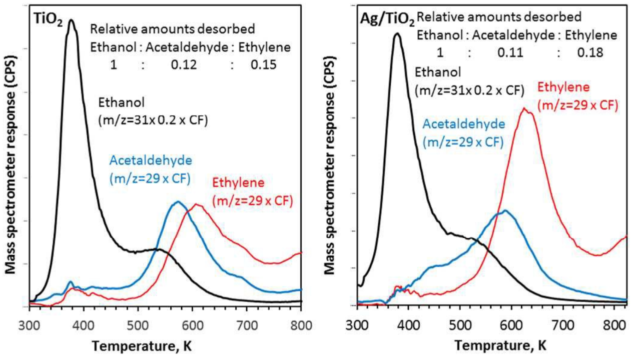

Figure 2. Ethanol-TPD of the main carbon containing products after adsorption at 300K on TiO_2 and Ag/TiO_2 catalysts. CF stands for mass spectrometer correction factor.

Ethanol is dissociatively adsorbed on TiO_2 at 300K, equation 1.

$$CH_3H_2OH + \mathbf{O}_{(s)} \rightarrow CH_3CH_2O_{(a)} + \mathbf{O}H_{(s)} \qquad (1)$$

A fraction of ethanol starts to desorb at 310 K followed by a second desorption together with other products from ca. 500 K (Fig.2). The desorption profiles are multiplied with their appropriate mass spectrometer correction factor to reflect the accurate amounts of products.[12] Ethanol desorption profile (310–700 K) is de-convoluted into two peaks. The low temperature peak centred at 380 K is attributed to molecular and re-combinative desorption (of ethoxides with OH(a)) adsorbed on non-defected surfaces. The high temperature peak centred at about 540 K is attributed to re-combinative desorption of ethoxides on oxygen-defect sites.[13]
On both catalysts, ethylene and acetaldehyde are the main products, desorbed with a combined carbon selectivity of ca. 30%.

$$CH_3CH_2O(a)+\mathbf{O}_{(s)} \rightarrow CH_3CHO+\mathbf{O}H_{(s)} \qquad \text{(on 5 fold Ti atoms)}^{14} \qquad (2)$$
$$CH_3CH_2O_{(a)} \rightarrow CH_2CH_{2(\uparrow)} + OH_{(a)} \qquad \text{(on oxygen defects)} \qquad (3)$$

Ethylene selectivity is higher in the case of Ag/TiO_2 when compared to that of TiO_2 alone. This is opposite to our previous work on Au/TiO_2. Earlier, we have noticed that ethylene is the dominant product desorbed from TiO_2 followed by acetaldehyde but the ratios decreased with an increase in Au metal loading.[12, 15, 16] Because Ag is far easier to oxidize when compared to Au and because its work function is similar to that of TiO_2; it may contribute in C-O bond dissociation at its vicinity which in turn may increase the dehydration reaction of ethanol.

Photoreactions of ethanol on metal supported on TiO_2 has been studied in some detail over the last decade and it has been found that ethanol is mainly converted to H_2 and acetaldehyde. The later further reacts to produce CO, CO_2, and CH_4.[9,17] Ethanol photoreaction on metal supported on TiO_2 under UV radiation occurs via either two photons – two electrons mechanism[10, 11] or through a one photon – two electron transfer mechanism (current doubling effect).[18-20]

The effect of temperature on ethanol photoreaction rate is presented in Fig.3. Each line represents a separate run as explained in experimental section.

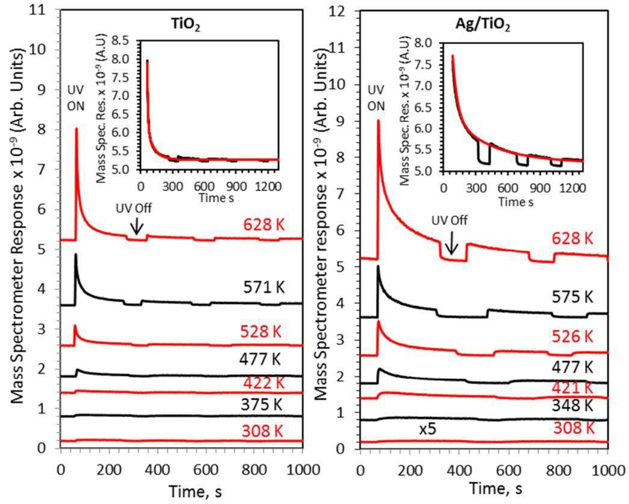

Figure 3. Production of acetaldehyde from ethanol pre-dosed TiO_2 and Ag/TiO_2 catalysts upon UV irradiation as a function of time at the indicated temperatures. Insets indicate the exponential fitting of acetaldehyde photo-production at 628K.

These set of experiments were all done at the same initial surface coverage as indicated in the experimental section and therefor one can directly relate the product desorption to catalytic activity. As shown in figure 4 other products were also observed. Concurrent hydrogen desorption is shown in Fig. S1. Because the UHV chamber

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pressure was *ca.* 5 × 10^{-10} Torr before reaction, O_2 and water background would be in the low 10^{-11} to high 10^{-12} Torr range. An increase in acetaldehyde desorption (Fig. 3), at all investigated temperatures, together with other products with increasing the surface temperature give evidences of a synergism between heat and radiations. All experiments were performed several times and were found to be reproducible. At all investigated temperature Ag /TiO_2 was more active than TiO_2 alone. The wider peak in the case of Ag/TiO_2 upon UV excitation, at all investigated temperatures, is linked to the presence of Ag, making more heterogeneous additional sites.

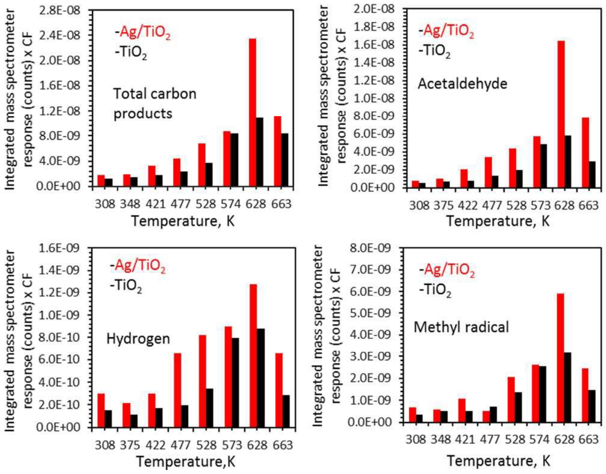

Figure 4. Ethanol photoreaction products over TiO_2 and Ag/TiO_2 upon UV radiations as a function of temperature. Surfaces were flashed to 628 K before each run to ensure constant coverage, then cooled to the indicated temperature. The complete process of correction factor (CF) and product yield calculation from area under mass spectrometer response is explained in ref.[12]

Figure 4 presents products desorbed from TiO_2 and Ag/TiO_2 catalysts upon UV radiation as a function of temperature. The total product yield increased with increasing temperature. The decrease at 663 K is due to decrease in the initial surface coverage as seen in figure 2 and in refs. [15, 16]. Methyl radicals are also produced and follow acetaldehyde production patterns. This has been noticed earlier from acetone [21] as well as acetaldehyde [22] and proposed to involve thermal reaction of acetaldehyde with adsorbed oxygen to form a photoactive acetaldehyde–oxygen complex.[22] This is followed by a substrate mediated photodecomposition mechanism that induces the fragmentation of the acetaldehyde–oxygen complex into gas phase methyl radical and surface adsorbed formates.[22] In a recent work on TiO_2(110) rutile single crystal we have found similar results (CH_3 radical production from ethanol[23]). This was not the case for anatase (101) single crystal.[24] The TiO_2 P25 used in this work contains both phases; it is possible that CH_3 radical formation is predominantly linked to the rutile phase.

Figure 5 presents the Arrhenius plots for ethanol reactions on TiO_2 and Ag/TiO_2. The activation energies extracted from the plots are indicated together with the pre-factors. There are a few points that are worth pointing out in the figure. First, both catalysts have a discontinuing reaction rate with temperature (at ca. 500K = 0.002 K^{-1}) and this is more pronounced in the case of TiO_2. It is worth indicating that the reaction is purely function of the incident photons at the indicated temperatures, in other words in the absence of photons no reaction takes place.

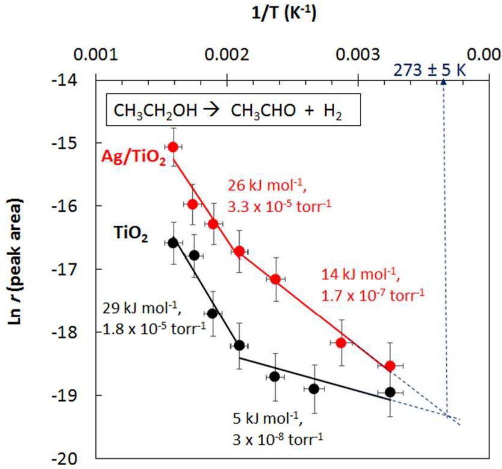

Figure 5. Ln reaction rate for acetaldehyde production from ethanol in photo-thermal conditions over TiO_2 and Ag//TiO_2 catalysts.

Second, the very low activation energy, at low temperatures is typical of a photo-catalytic reaction. Yet the difference between TiO_2 and Ag/TiO_2 in the 300-500K range is beyond experimental errors (5 to 14 kJ mol^{-1}) resulting in 4-fold increase of the reaction rate; the decrease of the pre-factor with decreasing the activation is to be noted, a phenomenon known as the compensation effect.[26] Third, extrapolation of the reaction rate to lower temperature shows a crossing at about 270K. In other words, at this temperature the addition of Ag does not enhance the reaction rate. The addition of a metal to a semiconductor may enhance the photoreaction rate based on a work function difference (ΔWF). The work function of Ag and TiO_2 (anatase or rutile) are actually very close[27, 28] and therefore the difference in reaction rates may not be linked to ΔWF. Scheme 1 presents the initial steps of the reaction with two electrons injected into the semiconductor as follows. Upon light excitation followed by electron transfer from the VB to the CB (step 1), ethoxide species (step 2) inject one electron into the VB, and are transformed to an oxy-radical. We have recently indicated using DFT+D computation that ethoxides are more prone to making this reaction than ethanol[29] in line with other's finding[30]. These radicals have high energy and can directly inject the second electron into the CB[31] (step 3), a phenomenon called "current doubling effect".[18-20] These two electrons in the absence of molecular oxygen, as it is this work, are taken by the two protons of surface hydroxyls to make one molecule of hydrogen. In the scheme a Ag particle is added close to the CB of TiO_2. Ag absorbs light and as a result its free electrons oscillate making the so termed "plasmon resonance (PR)". PR can increase the reaction rate of a semiconductor via either electronic or photonic effects.[32] Photonic effect of PR is either long range (light scattering) or short range to increase the local electric field (step 5). Other works have also gave evidences for the enhancement of the reaction rates due to LSPR of Ag when deposited on semiconductors.[33,34] Although at 300K this enhancement is found to be small when compared to noble metals such as Pd.[10] One would expect that long-range effect would be independent from temperature, yet the short-range effect that results in decrease of the e-h recombination may indeed increase the reaction rate if it provides enough electric field strength to change the conformation of an adsorbate in its transition state. The deviation between the reaction rate between Ag/TiO_2 and TiO_2 up to about 500K (1/T = 0.002 K^{-1}, figure 5) is explained by invoking this

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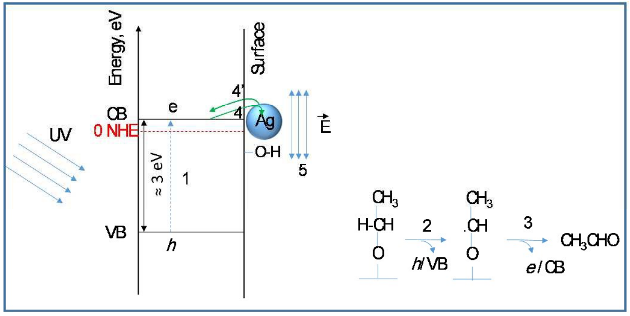
possibility. It is important to indicate that excitation with visible light alone (> 400nm) did not results in any noticeable reaction products indicating that both TiO2 and Ag need to be excited.



Scheme 1. Schematic representation of Ag/TiO_2 energetics upon light excitation. A Ag particle (blue sphere) is shown at the contact with the surface of TiO_2. Also shown are the oxidation steps of ethoxide to acetaldehyde upon light excitation. 1. e-h formation upon light absorption, 2. One electron transfer to the VB (to trap one hole). 3. One electron transfer for the oxy-radical to the CB (because it has higher potential energy level than the CB). 4. Possible excited electron transfer from the CB of TiO_2 to the Ag particle. 4'. Possible "hot electron" transfer from Ag to the CB of TiO_2. 5. Electric field generated upon light absorption by a Ag particle at the interface with TiO_2. 5 may have enough electric field strength to polarise an intermediate and increase the reaction rate.

In summary, the addition of Ag to TiO_2 resulted in the enhancement of the photo-thermal catalytic reaction of ethanol when compared to TiO_2 at all investigated temperatures but in two different temperature regimes. In the [300-500K] temperature-range, the increase seems to be mainly due to changes in the activation energy while in the [500-625K], the activation energy is found to be the same for TiO_2 and Ag/TiO_2 and the main increase is due to the pre-factor. It is thus possible that the surface plasmon resonance (SPR) of Ag induces the polarisation of reaction intermediates involved in the oxidation and/or in the desorption of final products at temperatures below 500K. Above this temperature, there is enough thermal energy and Ag nanoparticles are not needed for their SPR.

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