

# Effect of Alkali Metal Cations on the TiO<sub>2</sub> P25 Catalyst for Hydrogen Generation by the Photoreforming of Glycerol

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The effect of three aqueous chloride salts, NaCl, KCl and LiCl, on the photoreforming of glycerol over TiO<sub>2</sub>, and Pt promoted TiO<sub>2</sub> catalysts, has been investigated. At concentrations between 0.01 to 0.05 M an enhancement in activity over the TiO<sub>2</sub> catalyst by a factor of ~10 can be ascribed to the presence of the cation, with the effect occurring at increasingly high concentrations of

salt in the order Li < Na < K. At salt concentrations above 0.05 the activity is strongly inhibited on the oxide surface for all the different salts but only slightly degraded on a Pt promoted catalyst, hinting that the effect of the chloride is to hinder the reduction step on the oxide surface.

## Introduction

Practical applications of photocatalysis are likely to involve water sources that are much less pure than those used in laboratories where experiments are carried out under ideal conditions. A deeper understanding of the mechanisms by which typical contaminants such as sulfates, nitrates and halides affect photocatalytic reactions such as the degradation of organic pollutants or the generation of hydrogen by photoreforming will guide catalyst designs so as to develop materials more tolerant towards these types of contaminants.

There is a particular interest in the effect of chlorides on titanium dioxide-based catalysts,<sup>[1,2]</sup> but there have been conflicting reports about their effects on the photocatalytic activity and selectivity. For example, Huang et al.'s study<sup>[3]</sup> of water splitting over TiO<sub>2</sub> showed a measurable increase in rate in the presence of low concentrations (~0.4–0.6 M) of KCl or NaCl which the authors attribute to the stabilisation of reactive oxygen states on the TiO<sub>2</sub> by the chloride. Photodegradation studies by Yang et al.<sup>[4]</sup> on the other hand, show that the rate of removal of methylene blue (MB) by photocatalysis over TiO<sub>2</sub>, decreases in the presence of chloride ions (Cl<sup>-</sup>), even at low concentrations (0.01 mol L<sup>-1</sup>) whereas, for 2-naphthol orange,


the photodegradation rate improved at 0.5 mol L<sup>-1</sup> Cl<sup>-</sup>. Wang et al.,<sup>[5]</sup> reported that Cl<sup>-</sup> did not affect the photocatalytic mineralisation of o-methylbenzoic acid, whereas Piscopo et al.<sup>[6]</sup> showed that whilst benzamide photodecomposition was strongly inhibited by the presence of chloride concentrations greater than 0.5 M, the rate of 4-hydroxybenzoic acid photodecomposition was hardly affected at all over a TiO<sub>2</sub> catalyst. Lair et al.,<sup>[7]</sup> investigated the influence of inorganic ions on naphthalene adsorption and photodegradation on TiO<sub>2</sub> and reported that by adding sodium chloride (NaCl) to the initial solution at concentrations of 0.60, 1.2 and 2.4 mol L<sup>-1</sup>, both the quantity of naphthalene adsorbed, and the reaction rate increased as the concentration of the salt increased.


One factor that may contribute to the confusion is that, for some systems, although chloride ions open up new reaction pathways and therefore accelerate conversion of the target, the products of these pathways are more resistant to photodegradation and so complete degradation is inhibited. For example, in a recent study<sup>[8]</sup> related to the photodecomposition of cinnamic acid, we found that the formation of chloride radicals created new pathways resulting in chlorine substituted products. The result was an accelerated rate of decomposition of the cinnamic acid but since the substituted products were resistant to photocatalytic decomposition, there was an overall reduction in the rate of total combustion to CO<sub>2</sub>.

Whilst the role of the chloride ions has been discussed extensively, there has been very little consideration of whether the associated cations affect the catalysis. There is some evidence that this could be the case, Huang et al.'s study for example,<sup>[3]</sup> showed that potassium chloride (KCl) promoted a higher H<sub>2</sub> evolution rate than NaCl (1.70 vs. 1.30 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, respectively), with maximum activities occurring at different salt concentrations (6 × 10<sup>-3</sup> M KCl and 4 × 10<sup>-3</sup> M NaCl) but did not consider that the cations might be affecting the catalyst directly. It's well known that cations can affect the activity of thermal catalysis, Na<sup>+</sup> and K<sup>+</sup> have been shown to affect the selective catalytic reduction of NO over TiO<sub>2</sub> catalysts for example<sup>[9]</sup> but this question has not as far as we are aware been considered in photocatalysis.

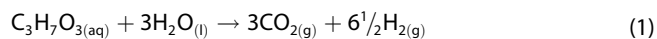
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 Supporting information for this article is available on the WWW under <https://doi.org/10.1002/slct.202304301>

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Therefore, in the present paper we report the effect of three chloride precursors (NaCl, KCl and LiCl) on the photocatalytic activity of P25 TiO<sub>2</sub> – with and without Pt (0.2 wt.%) – toward H<sub>2</sub> generation by the photo-reforming of glycerol. Glycerol is a side product of biodiesel production and readily degraded by photocatalysis generating a high volume of hydrogen, Eq. 1,<sup>[10]</sup> via a number of intermediates such as glyceraldehyde, lactic acid, and glycolic aldehyde.<sup>[11]</sup>



This makes it an ideal probe molecule for kinetic studies. Both catalysts responded to the salt solutions in very different ways and the results allow us to speculate on the nature of the interactions of the chloride and cations ions with the catalysts.

## Results

### Synthesis and Characterisation

Titanium (IV) oxide (Aeroxide® P25, Sigma Aldrich), which comprises ~70% anatase (A), ~25% rutile (R) with minor amounts of an amorphous phase,<sup>[12]</sup> was used without any further modification as photocatalyst. The 0.2 wt.% platinum (Pt) modified catalyst was prepared via a modified impregnation method:<sup>[13]</sup> a stock solution of platinum acid was prepared and heated in an oil bath from room temperature up to 60 °C and stirred at 800 rpm, followed by the addition of TiO<sub>2</sub>. After stirring for a few minutes, the temperature was increased up to 95 °C and keep it for 16 h -to evaporate the water. The final catalytic powders were crushed, sieved (53 μm Fisher brand stainless steel test sieve) and reduced in 5% H<sub>2</sub>/Ar at 200 °C for 4 h (heating rate: 2 °C min<sup>-1</sup>).

XPS spectra were recorded using a Kratos Axis Ultra-DLD photoelectron spectrometer with a monochromatized Al K $\alpha$  x-ray source in the “hybrid spectroscopy” mode with an analysis area of 700×300 μm. A pass-energy of 40 eV was used for high-resolution scans and 60 eV for survey scans. CasaXPS<sup>[14]</sup> (version 2.3.24) was used to analyse the spectra with binding energies referenced to the largest Ti<sup>4+</sup> (2p) peak at 458.5 eV with an uncertainty of ~0.2 eV. Raw spectra were modified using Wagner sensitivity factors, as supplied by the instrument manufacturer after the subtraction of a Shirley background. Because the platinum concentration in the 0.2 wt% Pt catalysts is too low for detection with XPS, a 2 wt% Pt catalyst was examined. Powder X-ray diffraction (XRD) data were obtained over the range 10° < 2θ < 80°, Figure S1., using a PANalytical X'Pert Pro diffractometer with a monochromatic Cu K $\alpha$  source (λ = 0.154 nm) operated at 40 kV and 40 mA. The surface areas were measured using a Quadrasorb (Automated Surface Area and Pore Size Analyzer).

### Photocatalytic H<sub>2</sub> Evolution Measurements

The experimental procedure for photocatalytic H<sub>2</sub> tests was reported by Bahruji et al.,<sup>[15]</sup> 100 μL glycerol (Sigma Aldrich, ≥ 99.0%) and 0.1 g of the catalyst were added to 40 ml distilled water in a 100 ml Pyrex flask with 2 mm thick glass. The mixture was purged with Ar gas in the dark for 30 minutes to remove dissolved oxygen.

A xenon arc lamp (LOT Quantum Design Model LSU106, λ: 750–1000 nm), enclosed in an arc lamp housing (LOT Quantum Design Model LSH102) connected to a power supply (LSN 150/2). The distance between the lamp and the Pyrex flask was 15 cm. 200 μL gas samples were extracted every 30 min from the overhead space of the reactor using a 500 μL Thermo Fisher Scientific, gas tight syringe with a removable needle and injected into a GC (Clarus 400/480) with a thermal conductivity detector (TCD) and a 2MX1/8SilicoStol Molecular Sieve 5A 80/100PE 800NCCI SS column. The temperature in the reaction flask increased slightly by 5–10 K during exposure to the light source.

### Catalyst characterization

The surface areas of the TiO<sub>2</sub> and Pt/TiO<sub>2</sub> catalysts were measured to be 63 m<sup>2</sup>/g and 52.5 m<sup>2</sup>/g respectively using a Quadrasorb (Automated Surface Area and Pore Size Analyzer). No evidence for Pt particles was observed in the XRD data (Figure S1) consistent with the small particle size evident in SEM images of the catalyst.<sup>[16]</sup>

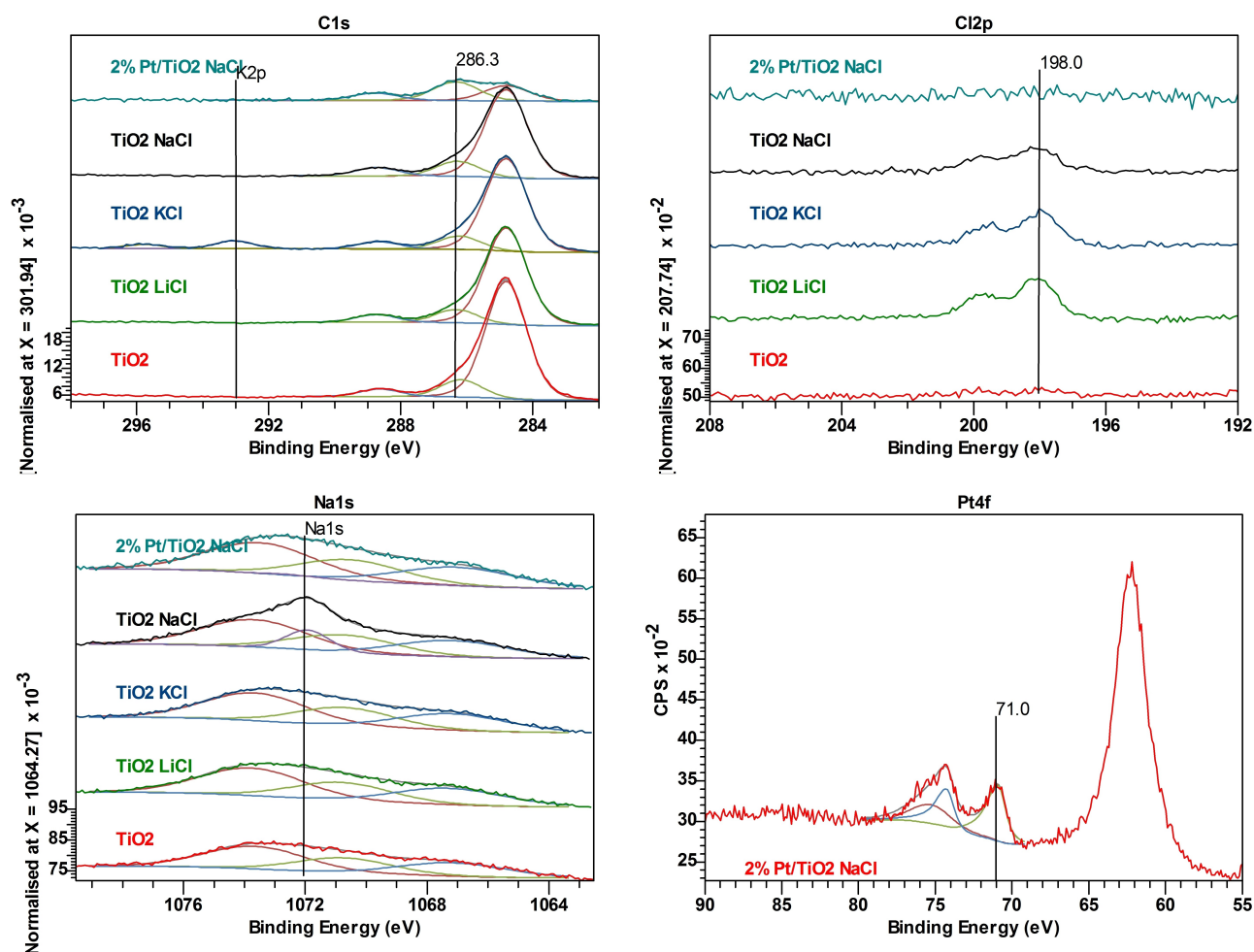
XPS analyses of the fresh and spent catalyst (Figure 1) show evidence of both chloride and alkali metal adsorption during reaction, lithium isn't observed but the relative sensitivity of the Li1s is ~45 times lower than for the K2p.

Chlorine is observed at the catalyst surface after reaction except where Pt is present. Due to the low Pt content, any adsorption of chloride on the metal is unlikely to be picked up by the photoelectron spectroscopy, but the Pt 4f<sup>7/2</sup> peak, at 71 eV is typical of Pt<sup>0</sup> and argues against the presence of Cl-containing Pt compounds.

### Photocatalytic H<sub>2</sub> evolution

Figure 2 shows the rate of the H<sub>2</sub> production (mmol g<sub>Cat</sub><sup>-1</sup> h<sup>-1</sup>) on TiO<sub>2</sub> and Pt/TiO<sub>2</sub> for different NaCl, KCl and LiCl concentrations (M). It is observed the rate of the H<sub>2</sub> evolution from the anaerobic photocatalytic decomposition of glycerol on both catalysts is strongly affected by the presence of salts in the reaction, as well as by the nature of the Cl<sup>-</sup> precursor.

The Pt modified catalyst exhibits a decrease in activity in the presence of the salts at very low concentrations, but that decrease is not continued as the salt concentration increases and the rate never declines to the level seen for the TiO<sub>2</sub> catalyst. On the other hand, the bare TiO<sub>2</sub> catalyst shows an increase in H<sub>2</sub> production rate by as much as a factor of 10 at salt concentrations lower than ~0.06 M. This improved activity



**Figure 1.** XPS of the photocatalysts post-reaction in the presence of 0.05 M of three different alkali metal chlorides. On pure  $\text{TiO}_2$ , the adsorption of Na and K is evident on the relevant samples; Li is not observed because of the very low Li(1s) photoionisation cross section. However, chloride adsorption is apparent in all three samples. In the presence of the Pt, there is no adsorption of Cl. The Pt 4f region is shown post reaction in the presence of 0.05 M NaCl for a 2.0 wt% Pt samples because at lower concentrations, the Pt peaks are too weak to be distinguished from the  $\text{TiO}_2$  background. Survey scans and other regions are available in Figure S2).

is not maintained and at concentrations above 0.06 M there is a decrease in rate until almost no  $\text{H}_2$  is produced at chloride concentrations exceeding 0.1 M. Interestingly the maximum in activity occurs at slightly increasing salt concentrations in the order  $\text{Li} < \text{Na} < \text{K}$ .

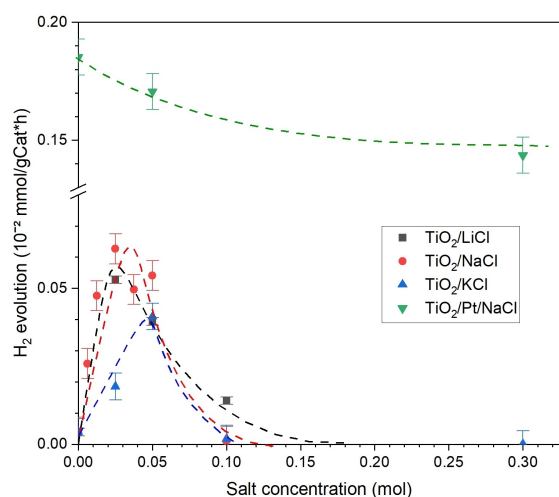
## Discussion

The addition of the chloride salts has measurable but contrasting impacts on the photocatalytic activity of the  $\text{TiO}_2$  and Pt/ $\text{TiO}_2$  catalysts, and whilst in practical photocatalysis one would tend to use the metal promoted catalyst in order to get the highest productivity, the contrast between behaviour of unpromoted and promoted materials offers an insight into the catalytic mechanism in each case.

The effect on the Pt/ $\text{TiO}_2$  photocatalyst is relatively straightforward; activity is unaffected at halide concentrations of  $\sim 0.05$  M but is reduced by  $\sim 25\%$  at concentrations of 0.1 M and above, similar effects have been discussed in connection

with the photocatalytic degradation of phenol<sup>1</sup>. In contrast, the effects of the salts on the photocatalytic activity of the unmodified  $\text{TiO}_2$  are more complicated with a 10 fold enhancement of activity in the presence of low concentrations of salts, followed by effective suppression of activity at concentrations greater than  $\sim 0.06$  M to the extent that at 0.1 M salt the activity of the catalyst is half of the halide free rate and a factor of 10 lower for concentrations of 0.3 M.

Photocatalytic reaction rate enhancements have been reported in the presence of chloride ions previously and attributed to a variety of different mechanisms including: adsorbed  $\text{Cl}^-$  enhancing the lifetime of the active species  $\text{O}_2^-$ ,<sup>[17,18]</sup> chloride ions enhancing the adsorption of the target molecule at the catalyst surface,<sup>[4,6,7,19]</sup> and the formation of chlorine radicals from the oxidation of chloride ions by  $\text{h}^+$ , (Eq. 2.)<sup>[20]</sup> which, Lei et al. report is more efficient than the formation of  $\text{HO}^\bullet$  radicals from  $\text{OH}^-$  (Eq. 3).<sup>[21]</sup> Bouleghlimat et al.,<sup>[8]</sup> showed that chlorine radicals formed in this way accelerated the rate of removal of cinnamic acid from an aqueous solution although this also generated chlorine sub-



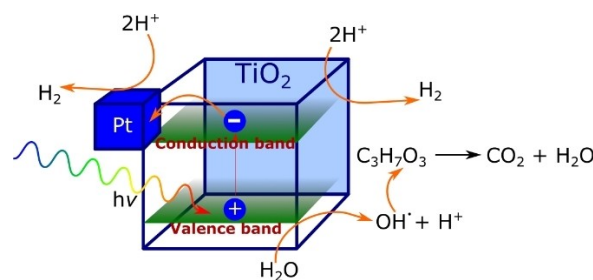
**Figure 2.** Comparison of rates of the  $\text{H}_2$  production in the presence of different concentrations of the salts LiCl, NaCl and KCl and between the  $\text{TiO}_2$  and 0.2 wt% Pt/ $\text{TiO}_2$  catalysts. Dotted lines are drawn as guidance only. Experimental conditions: catalyst 0.1 g, 40 ml of a water-glycerol (0.25 vol.%) solution under visible light (Xe arc lamp,  $\lambda$ : 750–1000 nm). Note: The rate of  $\text{H}_2$  production on  $\text{TiO}_2$  without salts or Pt present is  $3.93 \times 10^{-4} \text{ mmol gCat}^{-1} \text{ hour}^{-1}$ .

stituted side products which were more resistant towards photodegradation, similarly, Yuan et al.,<sup>[20]</sup> reported the formation of toxic chlorinated byproducts after the photocatalytic decomposition of azo dyes in saline solutions.



Contrary to the suggestions above that chloride is the “active” component of the salts, the data in Figure 2, shows a trend for the different cations, with increasing concentrations of the salts being required to achieve maximum activity going down the group from LiCl to KCl. Since at such low concentrations all the salts can be expected to be fully dissociated, we conclude that the trend in activity shown in Figure 2, indicates that it is the cations that are responsible for the increased activity at low concentrations. The effect of the cations on pH is a possible factor, since pH is known to affect photocatalytic activity and all three of the salts increased the pH when added to the reacting solution, (ESI, Table S1: Changes in pH). However, the dependence of pH change on the cation does not follow the same trend as the increase in activity, with NaCl showing a greater effect than LiCl, whereas the effect of KCl is less suggesting pH is not a direct factor in increasing the photocatalytic activity.

From the literature, an increase in photocatalytic activity over  $\text{TiO}_2$ , attributed to the presence of  $\text{Cu}^{2+}$  ions has been reported previously,<sup>[22–24]</sup> with Chen and Xu<sup>[23]</sup> observing a doubling of the rate of photodegradation of phenol which they attribute to the reduction of copper ions at the catalyst surface and subsequently a multielectron reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}_2$ . But a similar process in the present case with reduction of the alkali



**Figure 3.** Model of the photocatalytic steps involved in the photocatalytic oxidation of glycerol over  $\text{TiO}_2$  and Pt/ $\text{TiO}_2$ .

metal cations would require significantly more energy. An alternative influence could be the removal of  $\text{e}^-$  from the  $\text{TiO}_2$  catalyst reducing the extent of  $\text{h}^+/\text{e}^-$  pair recombination and increasing the rate of formation of  $\text{OH}^-$ . As the salt concentration increases, the positive influence of the cations is negated by the increasing effect of the chloride anions.

The way in which the Pt co-catalyst influences the effects of the salts is also informative. It is generally accepted that a Schottky barrier at the interface between the Pt and  $\text{TiO}_2$ , traps electrons on the Pt and significantly increases the concentration of  $\text{h}^+$  by preventing recombination of the exciton. The mechanism is summarised in Figure 3. In the present experiments, we can speculate that the approximately 100-fold increase in photocatalytic rate the Pt electron sink creates, is sufficient to swamp the smaller effect of the alkali metal cation adsorption. At higher salt concentrations this would also protect the catalyst to some extent from the effects of the chloride ions, which Delarmelina et al.<sup>[11]</sup> suggest are due to two processes on  $\text{TiO}_2$  surfaces, firstly scavenging  $\text{h}^+$  and hence preventing  $\text{OH}^*$  formation, and secondly by inhibiting  $\text{h}^+$  localisation at the surface. The higher  $\text{h}^+$  concentrations made possible by the Schottky barrier may be sufficient to overcome the chloride poisoning at least at chloride concentrations up to 0.3 M. There is evidence that at higher concentrations the reaction is more severely inhibited.<sup>[22]</sup>

## Conclusions

We have shown that alkali metal salts have dual, conflicting effects on the photocatalytic degradation of glycerol over  $\text{TiO}_2$  catalysts which we propose are due to opposite effects of the cations and chloride ions. The role of the cations has been neglected in the literature, perhaps because the effects of the chloride are so much greater. Nevertheless, the cations do provide an interesting insight into the photocatalytic mechanism and should be examined more closely.

## Acknowledgements

BBA is grateful for the sponsorship of the Nigerian government. XP spectra were acquired by EPSRC National Facility for Photoelectron Spectroscopy (HarwellXPS), operated by Cardiff Univer-

sity and UCL under contract number PR16195. SYTC was supported by the European Union – NextGenerationEU, Spanish Ministry of Universities and Recovery, Transformation and the Resilience Plan (2021URV-MS-35).

### Conflict of Interests

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are openly available in figshare at <https://doi.org/10.6084/m9.figshare.c.6775548.v1>, reference number 6775548.

**Keywords:** Photocatalysis · Cation · Chloride · Glycerol · TiO<sub>2</sub>

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Manuscript received: October 26, 2023