Catalytic hydrogenation of chlorated oxyanions in water with Pt-catalysts

Antonio .Eduardo Palomares[1], Adrián Pla-Hernández[1], Nadia Benmebirouk-Pareja[1]
[1]*Instituto de Tecnología Química (Universidad Politécnica de Valencia - Consejo Superior Investigaciones Científicas), 46022 Valencia, Spain*
**apalomar@iqn.upv.es*

Significance and Relevance

Catalytic hydrogenation is used to remove chlorate ions from water streams at room temperature and atmospheric pressure by using supported platinum catalysts. The catalysts have been supported on different materials as γ-Al_2O_3 and TiO_2 and a second transition metal (vanadium) has been added in order to improve the reaction rate. The catalytic studies showed an important influence on the support, being the catalysts supported on TiO_2 the most actives indicating that the photochemical and acid properties of this material enhances the catalytic activity of the platinum centers. The main novelty of these results is that the catalyst has been tested in natural polluted water obtaining interesting results.

Preferred for the topic: Water treatment
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Introduction and Motivations

Water is an essential resource for life and it is necessary to ensure its quality, mainly when it is used for human consumption. An emerging pollutant that may be present in water is the chlorate ion that could be generated during the disinfection treatment of natural water using oxidizing agents, such as chlorine dioxide or ozone. Chlorates are harmful to health, as they can oxidize haemoglobin, leading to haemolytic anaemia. Additionally, some research has shown that chlorates can interfere with iodine uptake by the thyroid gland and negatively impact both the quantity and quality of sperm. Due to these health risks, the World Health Organization (WHO) has set a provisional limit of 0.7 mg/L for chlorates in drinking water[1].

As a result of this, there is a necessity of sustainable methods able to remove this pollutant from natural water. Catalytic hydrogenation has been suggested as a potential solution for treating this pollutant as it can be reduced to innocuous chloride according to:

$$ClO_3^- + H_2 \rightarrow Cl^- + H_2O$$

Van Santen et al[2]. patented a method to remove chlorate from solutions using monometallic catalysts based on noble metals supported on SiC, ZrO_2, Al_2O_3, activated carbon and graphite, among others. The results of this patent establish the following sequence of activity against chlorate reduction: Rh > Pt > Pd. Despite these results, most studies have focused mainly on catalysts based on Pd supported on different carbonaceous materials. Ren et al.[3] used Pd/C catalysts with immobilised MoO_x as a promoter for chlorate reduction. They found that at pH = 3, the MoO_x-Pd/C catalysts showed activity comparable to the activity of monometallic Rh. Another way to improve the catalytic activity is by using vanadium promoters dissolved in water. Gao et al[4]. have used Pd/C composite catalysts together with a vanadium promoter dissolved in water for the reduction of ClO_3^-.

Hereby, we continue our previous study with monometallic materials[5], studying the performance of different bimetallic Pt-V catalysts supported on different oxides for the hydrogenation of chlorate at room temperature and atmospheric pressure.

Materials and Methods

The catalysts were prepared by incipient wetness impregnation of Al_2O_3 and TiO_2 in order to have catalysts with different Pt/V ratios. The support was initially impregnated with a solution of $VOSO_4$, dried and calcined at 773 K. After that, a solution of $PtCl_4$ was added and the catalyst was dried and calcined again at 623K. The catalysts were reduced with hydrogen at 473 K for 4 h before the reaction. The experiments were made in a batch-stirred tank reactor at room temperature and atmospheric pressure, using hydrogen as a reducing agent. The typical experiments used 1 g of catalyst and 0,6 L of water with 50 ppm of chlorates. The analysis of the reactants and products was made by ionic chromatography. The catalysts were characterised through different techniques such as ICP, XRD, TPR, N_2 adsorption and IR and UV spectroscopies.

Results and Discussion

The catalytic studies were made using mono and bimetallic catalysts with different Pt:V ratios. As it can be seen in Figure 1 left the bimetallic catalyst supported on Al_2O_3 has a significant increase of the activity compared to the monometallic ones indicating a synergic effect of Pt and V that results in an important increase of the catalyst activity. The influence of the support was studied by comparing the results obtained with catalysts supported on Al_2O_3 with those with the same composition but supported on TiO_2. It is again observed that the bimetallic catalyst is more active than Pt-monometallic catalysts, whilst V-catalyst is not active. Nevertheless, catalysts supported on TiO_2 are much more active than those supported on Al_2O_3. As can be seen in Figure 1 right, the 5%Pt/TiO_2 catalyst reduces 80% of chlorate in 15 minutes and the 5%Pt-5%V/TiO_2 bimetallic catalyst achieves the same conversion in 2.5 minutes. It was also observed that catalyst activity decreases in darkness, indicating that together with the hydrogenation, a photocatalytic reaction is occurring. The combination of the photocatalytic properties of titania, its acidic properties and the synergic effect of Pt-V metals results in the high activity obtained with this catalyst for the chlorate reduction. This catalyst has been used in natural polluted water and in these conditions, the reaction rate decreases probably because there is a competitive adsorption of the other ions present in natural water on the active sites. Even that, the catalyst is active indicating that Pt/V bimetallic catalysts are active in the removal of chlorates in aqueous phase using H_2 as a reduction agent.

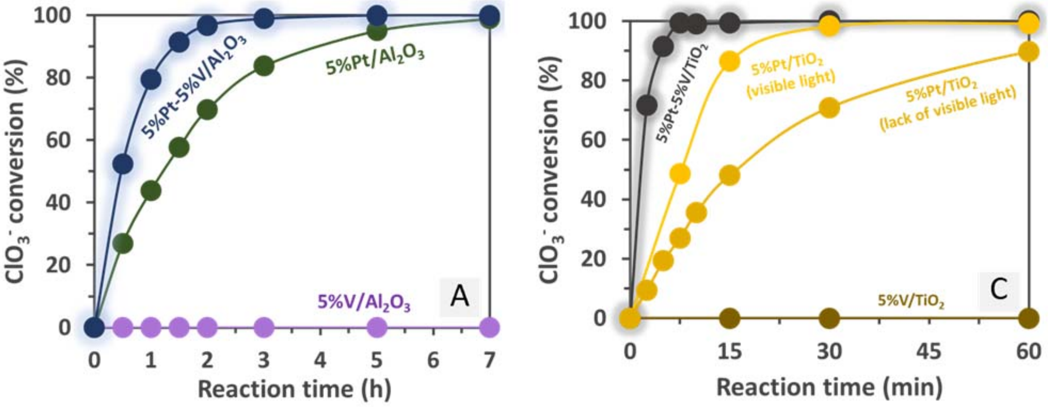

Figure 1 Conversion of Pt-catalysts supported on alumina and titania for the catalytic reduction of chlorates.

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