Review of: "Test study and molecular dynamics simulation of Fe3+ modified TiO2 absorbing automobile exhaust"

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Potential competing interests: The author(s) declared that no potential competing interests exist.

Object: Post-publication review of the manuscript "Test study and molecular dynamics simulation of Fe^{3+} modified TiO2 absorbing automobile exhaust", which has been published in PLOS ONE journal.

OVERALL COMMENTARY

This manuscript deals with the potential role of a modified TiO2 matrix in the photocatalytic oxidation of regulated automotive exhaust emissions. The paper addresses the degradation of automotive pollutants in a complementary manner through: i) experimental measurements performed in a reaction chamber and ii) numerical simulations performed using a molecular dynamics model. Nevertheless, the article suffers from several limitations in terms of both form and content. On the form, the readability of the article could be greatly improved, for example by correcting the English and the multiple editing errors or by rephrasing/deleting vague sentences or statements not supported by direct evidence. As for the content, there are problems with the methodology employed in the reaction chamber experiments, the uncertainties in the data, and the nature and description of the reactions taking place. The resulting lack of perspective on the results is a symptom of this. In addition to these problems, there are questions about the assumptions and choices made about the molecular dynamics model and, consequently, about the representativeness of the simulations (see below).

Overall, the authors have provided interesting results. However, the reader should be aware that these results are surrounded by many assumptions or uncertainties. The data acquired should therefore be used to encourage research on these modified TiO2 materials but not to provide quantitative figures concerning their catalytic performance.

SPECIFIC VIEWS ON THE ARTICLE CONTENT

Title

The title fits well to the content of the manuscript.

Abstract

The abstract presents, like the manuscript itself, several vague and poorly written sentences. It needs to be rewritten in a more concise and factual way, focusing on the innovative aspects of the research and key numerical data and results obtained. Complex and poorly worded sentences such as “In this study, this paper attempts to use Fe3+ to modify the TiO2, which is one of the main photocatalytic materials, to expand the range of light reaction band and to improve the degradation effect of automobile exhaust.” fill the manuscript and hinder its readability.

1. Introduction

To begin, the manuscript should undergo a thorough review of English and sentence structure, which should include an editorial screening. Reformulate or remove vague terms such as “In addition to... a new direction”.

A lot of research has been done for decades on vehicular exhaust emissions and their negative effects on the environment and health have been known for a long time (i.e. especially from the middle of the 20th century). It would be good if the authors evoke these reference studies first instead of mentioning more recent research (Hong et al., 2018, Wang et al. 2019,...).

Authors should indicate that the pollutants addressed herein are primarily regulated gaseous pollutants. Several key terms (i.e. like bandgap, conduction band, annealing or photocatalyst, etc.) could also have been defined the first time they were used. Additional references and bibliographic material must be added in the second and third paragraphs of the introduction. Overall, the introduction is unevenly written and gives the impression of having been done without much care.

The introduction does not present the question asked nor the elements of answer proposed by the article. It does not introduce the strategy employed, the structure of the article or the novelty of the research. It also does not evoke the insight that molecular simulation provides or justifies its necessity.

2. Preparation of modified TiO2 powder

The first paragraph should have been rewritten in a more readable manner and a schematic view of the procedure used to prepare the Fe2O3-TiO2 matrix added to Figure 1. In addition, the size distribution and specific surface area of the initial TiO2 and the modified Fe2O3-TiO2 powders could have been provided.

Is there any information on the toxicity of the tested catalytic materials?

3. Test study

Many questions surround the reaction chamber. First, more information is needed about the characteristics of the reaction chamber: its size, the type of material, the chemical reactivity of the compound of interest on the walls, potential sources of contamination or leakage or the degree of uniformity of the concentration of gases. Are there memory effects between series of experiments? In addition, the characteristics of the exhaust gas source are currently unknown, as are the emission conditions: engine characteristics, type of fuel burned, engine speed or power.

As for the operation of the reaction chamber, it is not clear how and in what form the gaseous pollutants and TiO2 substrates were added and dispersed. It would also have been a plus to know the S/V ratio: total surface of the photocatalyst divided by the volume of the reaction chamber. One can also wonder what are the values of other critical parameters such as the temperature of the exhaust gases in the reaction chamber, the dilution factor used and if it varies during the test or if it is compatible with that of the air at road level. I also question the wavelength and intensity of the light used and how the authors handled the interactions between the different pollutants or pollutant phases.

4. Test method and molecular dynamics simulation method

As I am not a specialist in the field of numerical simulation of molecular dynamics, I will therefore approach the relevant parts of the paper either from a formal or a geochemical point of view.
In general, it would have been useful to have more information about the assumptions made and the functioning of the molecular dynamics model. For example, it is not clear how the transition from 2D to 3D is made by adding a vacuum layer or how the quality of the simulations evolves with the size of the supercells (why did the authors choose 5,7,1 repetitions among other values?)

How did the authors account for ambient air and nanoparticles in their simulations? In addition, how were the numerical ratios used in the simulations determined, and how is it that the initial concentrations of CO2 and CO are similar in the experiments (about 4.5%) when, in most gasoline vehicle exhaust, CO2 levels

typically exceed those of CO?

What exactly are the organic gaseous compounds and what do the authors mean by inorganic TiO2? Does this differ from TiO2 or the modified Fe3+-TiO2 groups in the catalyst matrix?

The definition and rationale for 100 PS is missing. The authors also state that simulations were performed at 298°K and 333°K, but data from simulations performed at 333°K are not presented.

Looking at Figure 6, I wonder why Fe3+ ions are distributed (uniformly) only on the surface of the TiO2 channels, and not in depth of the modified matrix. Does the absence of gaps or Fe3+ ions in the molecular matrix lead to differences in reactivity with the data obtained experimentally? Furthermore, the mean approach distances of the relevant exhaust molecules are not given, which does not help to evaluate the degradation efficiency based in MD simulations.

5. Results and discussion

Since many chemical and physical reactions are probably occurring at the same time in the reaction chamber, it is not obvious to link the observed variations in concentrations to the added TiO2 powders. From this point of view, the measurement of degradation products followed by mass balance calculations could have been performed (for example for the CO2/CO system) in order to better understand the mechanisms involved.

In addition, in order to judge the significance of the variations in Figures 6, the uncertainties on the measurements (in the form of error bars, typically 2-10%) and the labels could have been displayed. The minimum y-axis value in the panels of Figure 7 should also be zero.

I think that r(t) rather accounts for the average position or the distance from the starting point (i.e. r(0)) than for the displacement of the particles at time t.

Based on MD numerical simulations, the authors have provided interesting results. However, the reader should be aware that these results are, by construction and due to the many assumptions surrounding the molecular simulations, only indicative. The data acquired should therefore be used to encourage research on the role of modified TiO2 materials in the reduction of exhaust gas pollution but not to provide quantitative figures concerning their catalytic performance.

Fig. 10: Currently, the precise percentage of Fe3+ on the surface of the TiO2 channels is unknown. It is

therefore difficult to judge the actual effectiveness of powder samples prepared with 1% Fe2O3 / 99% TiO2: the difference in efficiency is likely to become minimal or even non-existent. Thus, it is difficult for me to accept the extrapolation of the trends resulting from the molecular model with TiO2 surfaces loaded with Fe3+ (up to 50% or even 100%) to the macroscopic mechanisms which occur at low Fe3+ contents (of the order of 1%). This is in addition to the fact that uncertainty in the modeled data was ignored.

I also wonder about the existence and characteristics of channels in the molecular matrix of the modified TiO2 powder. Has their existence been demonstrated? How? What are their size and surface properties? Additional information or bibliographic references are required.

The uncertainties on the parameters used in equations (e.g. C, r(t), E_total,...) must be evaluated and displayed.

Fig 11: Data for the modified Fe2O3-TiO2 catalyst should also be displayed. It would also be helpful if the authors could provide information on the duration of the catalytic efficiency. Indeed, on the basis of the current data, it is not possible to evaluate how long a high level of efficiency can be maintained as a function of temperature, mechanical stresses on the pavement, loading of the substrate with various pollutants or chemical / particulate compounds present in the atmosphere, etc.

6. Conclusions

The conclusions are too assertive. Because of issues related to the representativeness of the simulations and uncertainties in the experimental measurements, I find it difficult to justify the existence of a significantly increased efficiency of the modified TiO2 sample. I therefore recommend that the authors moderate their conclusions and that the readers consider the proposed results only as conditional or even indicative.