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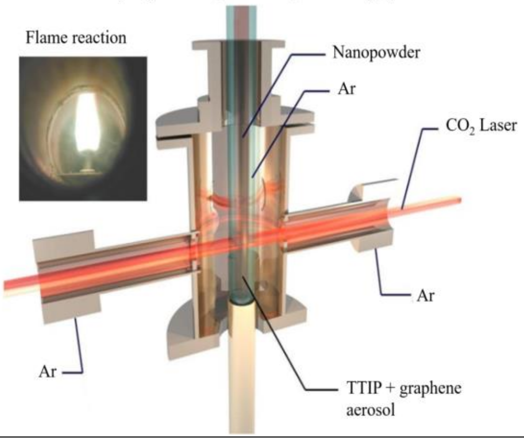
Laser Pyrolysis Set Up For Graphene/TiO_2 Synthesis



In an effort to produce alkenes in a low-cost and less energy-consuming way, this study presents the possibility of a photocatalytic process permitting to obtain ethylene from propionic acid.
To this end, TiO_2 and graphene/TiO_2 photocatalysts were successfully synthetized by an original method, the laser pyrolysis technique. Consisting on an interaction between a CO_2 laser beam with liquid/gaseous precursors, this process provides great flexibility in terms of crystallinity, nanoparticles size etc. The obtained nanocomposites were mostly composed of anatase and graphene could be detected with RAMAN spectroscopy.
TiO_2 and graphene/TiO_2 were compared for ethylene photo-production from propionic acid, and ethylene yield did not seem to be significantly improved despite graphene addition.

Alkenes, and more particularly ethylene C_2H_4, are essential organic molecules for chemical and petrochemical industries and are needed in ton quantities [1]. New ways to produce ethylene without hydrocarbons are developed. They mainly focus on ethanol dehydration reaction. However, despite the use of heterogeneous acid catalysts, these processes require high temperatures reaching 200-550°C and consequent pressures, at least 0.3 MPa and consequently correspond to significant energy consumption [2-3].

In this context, we aim to synthesize environmental-friendly and low-cost photocatalysts, which could degrade organic compounds such as alcohols and acids into alkanes and alkenes at ambient temperature and atmospheric pressure. Particularly, the outcome sought here is to promote high selectivity and yield towards ethylene photo-production using UVA as energy source.

To achieve this goal, graphene modified TiO_2 nanostructures appear to be promising photocatalysts for their high stability, excellent electron mobility and large specific surface area [4-5].

Thus, TiO_2-based photocatalysts were synthesized from TTIP (Titanium Tetra Isopropoxide) precursor by an original gas-phase method, the CO_2 laser pyrolysis technique. This one-step method consists on an interaction between an infrared laser beam with gaseous and/or aerosolized liquid precursors. Such process, existing at industrial scale, offers a great flexibility in obtaining small and homogeneous nanoparticles (5-60 nm size ranging), with controlled crystallinity and carbon content. Addition of graphene (Graphene Nano Pellets - GNP, 120-150 m^2/g) in TTIP allowed obtaining graphene-modified TiO_2 composites (from 0.04 to 2.00 wt% regarding TTIP). Nanopowders were thus synthetized with a production rate of several grams per hour.

Obtained graphene/TiO_2 nanocomposites were mostly formed of anatase (>95 wt%), indicating a low-temperature laser pyrolysis flame preserving graphene nanosheets from heat destruction. Moreover, GNP graphene could be detected by RAMAN spectroscopy. Graphene/TiO_2 specific surface area tends to increase with graphene content.

These photocatalysts were first used for photo-oxidation of formic acid solutions. At low graphene loadings, results shew slight improvements in formic acid degradation compared to bare TiO_2. Besides, the composites were also tested for alkene photo-production from 1 vol% of propionic acid photo-reduction. Subsequent photo-Kolbe reaction permits producing CO_2, ethane, ethylene, butane and H_2. Graphene/TiO_2 exhibit no significant ethylene production enhancement whatever graphene content. For both photocatalysts graphene-TiO_2 and associated TiO_2 reference, ethylene selectivities and yields remained low.

To conclude, graphene/TiO_2 photocatalysts were successfully synthetized by laser pyrolysis. Despite slight improvements for formic acid degradation at low graphene loadings, these nanocomposites presented no significant differences in results compared to pristine TiO_2 for ethylene photo-production from propionic acid.

In a further work, graphene oxide will be considered in order to promote the anchorage of TiO_2 on graphene nanosheet.

Keywords: Photocatalysis, TiO_2, Graphene, Ethylene.

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