

Using tungstophosphoric acid ($H_3PW_{12}O_{40}$) immobilized on Ce_2O_3 , TiO_2 , and SiO_2 to produce BTEX and p-cymene via waste tire pyrolysis

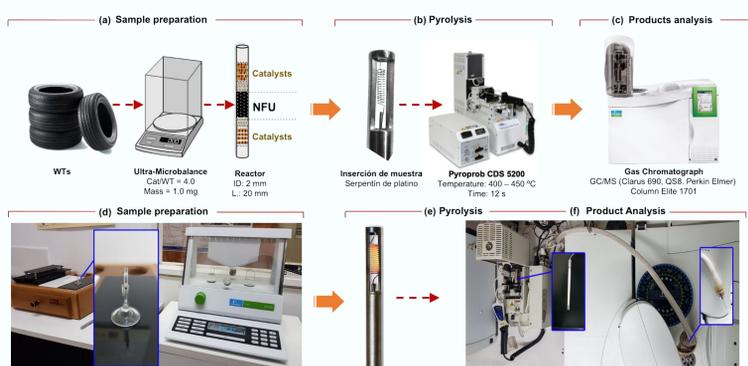
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Abstract

In Chile, about 117.000 tons of waste tires (WTs) are discarded without control, leading to increasing environmental concerns. The need for valorizing this waste has provided an opportunity to implement pyrolysis plants to convert the WT into fuels, functional liquids, or additives. The present study reports a systematic analysis of the effect of the immobilization of tungstophosphoric acid (TPA, $H_3PW_{12}O_{40}$) in three different supports (Ce_2O_3 , TiO_2 , and SiO_2), on the selective formation of benzene, toluene, xylene, and ethylbenzene (BTXE) and p-cymene during the pyrolysis of NFU. The experiments were carried out in a micro-pyrolysis system coupled to chromatography/mass spectrometry (Py-GC/MS). The results suggest that TPA/ TiO_2 catalysts are active in converting NFU into a pyrolytic oil enriched with BTXE and p-cymene. The catalysts with 1% TPA/ TiO_2 mainly favored the formation of p-cymene with high selectivity (56.3%), while the catalyst with the highest content of TPA (10%) had a selectivity towards BTXE, 8 times higher, relative to the uncatalyzed reaction. On the contrary, the immobilization of TPA on SiO_2 promoted the formation of alkenes to a greater extent, regardless of the acid load used. While TPA/ Ce_2O_3 did not witness a significant catalytic effect. The results suggest that the catalysts participated in the secondary reactions of dehydrogenation, isomerization, cyclization, and dealkylation, which lead to a greater formation of these compounds, compared to the uncatalyzed reaction.

Materials & methods



Catalysts: 1, 10%, TPA on commercial supports SiO_2 , Ce_2O_3 and TiO_2 . (Sigma, Chile).
Impregnation for 24 h in an ethanol solution and drying at low temperature. Followed by calcination at 500 °C.

Characterization

- (i) FTIR-ATR
(ii) FTIR-Pyr, (iii) RAMAN

Activity tests: measured in a micro-pyrolysis reactor (CDS5200, CDS Analytical Co Ltd.) coupled to a gas chromatograph (Clarus 690, Perkin Emer) equipped with a quadrupole mass detector (SQ8, Perkin Emer).

Temperature: 400 < T (°C) < 500

Catalyst-to-tire: 2:1

time: 12 s

Catalysts: TPA, TPA/Support, Support, Non-catalytic.

Characterization of Catalysts

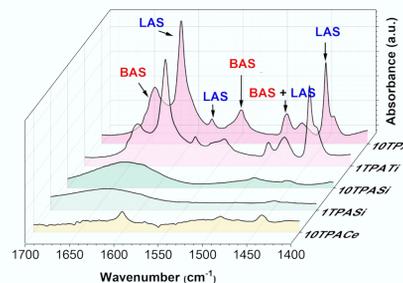
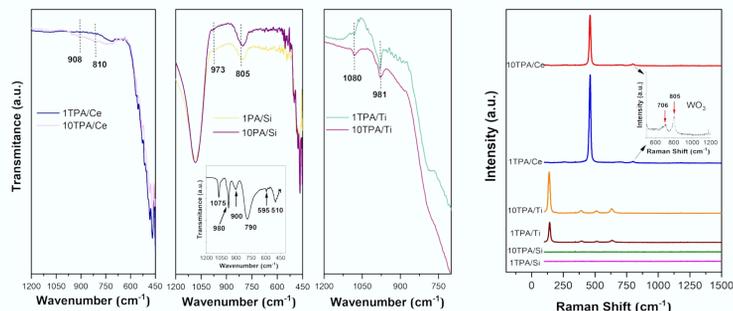


Table 1. Concentration of acid sites and its nature.

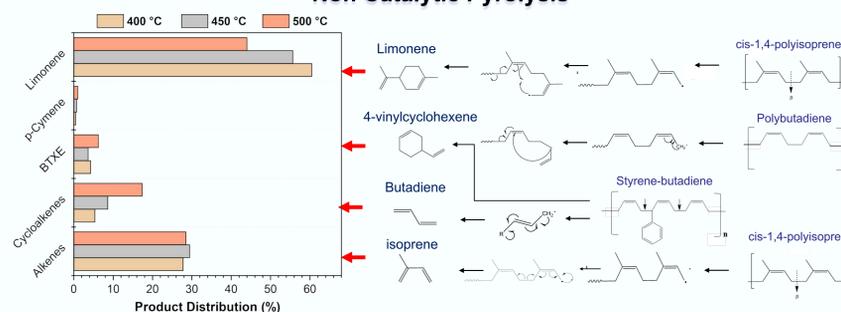
	1TPATi	10TPATi	1TPACe	10TPACe	1TPASi	10TPASi
BAS* umol/gcat	28.1	36.9	2.05	0.55	2.76	2.78
LAS** umol/gcat	73.6	47.5	4.80	28.5	7.03	3.31

* Bronsted acid sites.
** Lewis acid sites.

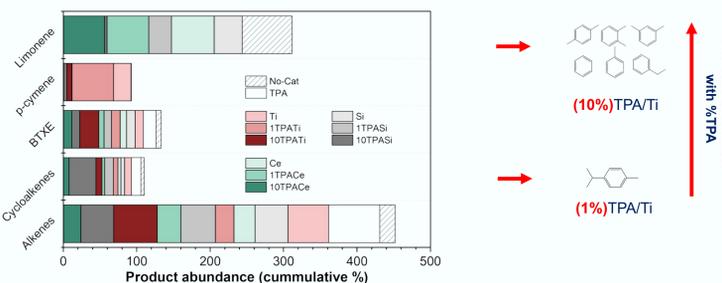
Discussion

- The weak signals at 810 cm^{-1} and 908 cm^{-1} found in the FTIR-ATR of TPA in Ce_2O_3 suggest TPA is decomposed on Ce_2O_3 , which leads to a reduction in the acidity of TPA/ Ce catalysts (Fig. 1). This was further confirmed by Raman signals corresponding to bulk WO_3 .
- The content of TPA changed the balance Lewis/Bronsted acid sites in the catalysts.
- With the immobilization of TPA on SiO_2 , the catalyst had a lower content of Lewis and Bronsted acid sites (Fig. 3 and Table 1).
- The non-catalytic pyrolysis evidenced the major presence of limonene (terpenes). For catalytic assays over TPA/Ti this terpene is converted into p-cymene and aromatics (Figs. 4 and 5).
- The BTXE were formed from dehydrogenation and isomerization reactions, promoted by acid sites (Bronsted, see Fig. 6b and 8) while p-cymene requires cooperative participation of Lewis/Bronsted sites to enhance isomerization and dehydrogenation (Fig. 6a and 8).

Non Catalytic Pyrolysis



Catalytic Screening



Role of acid sites on Pyrolysis products and reaction pathways

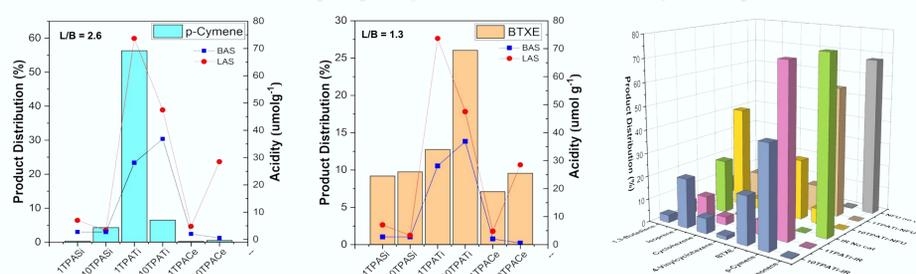
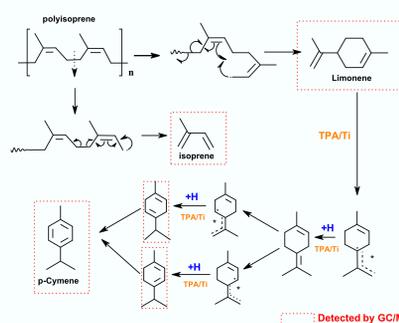
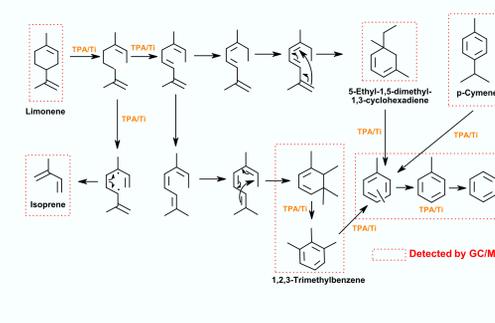


Fig. 7. Comparison of non-catalytic and TPA/Ti-catalyzed pyrolysis of WT and natural rubber.

P-Cymene from Natural Rubber in WT



Aromatics from limonene and p-cymene



Conclusions

- Adequate control of the acidity and the nature of the catalyst's acid sites is key to increasing the selectivity towards the formation of BTXE and p-Cymene during the pyrolysis of NFU. It is necessary to optimize the concentration of TPA and other parameters of the reaction that lead to an increase in the selectivity and yield of these aromatic compounds.
- The presence of active sites for isomerization could enhance the performance of these materials regarding the production of p-cymene and BTXE.
- Further, studies on the stability of these catalysts at higher scales must be carried out.

References

- Osorio-Vargas et al. *Catalysis Today*. 372 (2021) 164
- Xu et al. *Energy Conversion and Management* 175 (2018) 288–297
- Osorio-Vargas et al. *Ind. Eng. Chem. Res.* September 2021