Pyrolysis of Waste Tires over Bi-metallic USY for the Production of Hydrogen

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This study investigates the catalytic effects of transition metals (Ni, Cu, Fe) supported on USY zeolite for the pyrolysis of waste tires, along with the synergistic effect of incorporating metal promoters (Cu, Fe, Zn, Ce) for maximizing hydrogen and light gas yields. The heterogeneous catalysts were synthesized and characterized to assess thermal stability, metal support interaction and determine surface properties (e.g. surface area, pore size). Pyrolysis experiments were carried out and the liquid and gas products were analyzed using gas chromatography, and TGA/XRD were implemented on the spent catalysts to determine carbon formation rate and type.

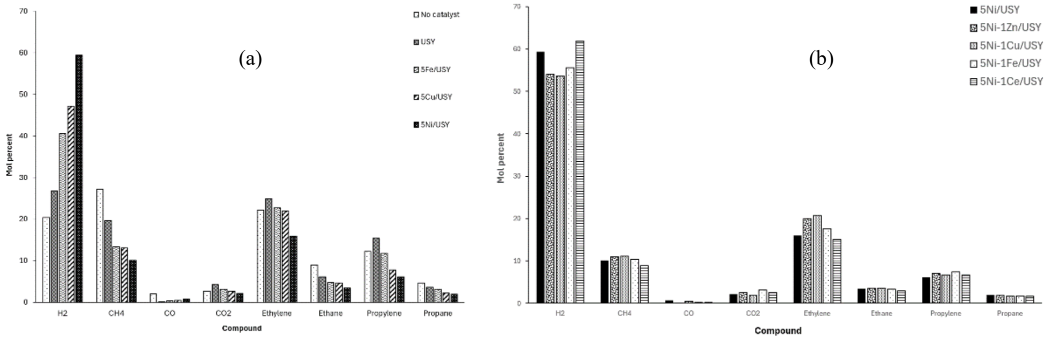

Figure 1 Distribution of product gases from tire pyrolysis under: (a) various transition metals, (b) with promoted 5Ni/USY.

The gases generated included H_2, CH_4, CO, CO_2, along with C_2–C_3 alkanes and alkenes, where these light hydrocarbons were produced due to the depolymerization of tire rubber and secondary cracking reactions occurring at high operating temperatures. CO and CO_2 are resultant from the decarbonylation and decarboxylation reactions [Czajczyńska, 2017]. It is noted that the use of USY catalyst resulted in more hydrogen being produced than from the thermal pyrolysis sample. This is because hydrogen gas is produced by secondary reactions during waste tire pyrolysis such as aromatization and dehydrogenation [González, 2001], and the Lewis acid sites on zeolites have been shown to enhance dehydrogenation reactions [Qu, 2024]. Moreover, the hydrogen formation capability of the USY is further highlighted by the fact that there are more olefins formed with the use of the catalyst than without, since the acid sites of the zeolite promote C-H bond cleavage, yielding hydrogen and carbenium ions which subsequently form alkenes via back donation of a proton to the zeolite [Rahimi, 2011]. Addition of transition metals on USY resulted in a change in the composition of the gas samples. For instance, it can clearly be seen that either of the 3 tested metals resulted in drastically increased hydrogen production than with the parent USY alone, likely due to the increased dehydrogenation activity of the Lewis acidic sites introduced by the transition metals [Yu, 2019]. Conversely, the methane production appears to decrease with the incorporation of metals, probably since the use of transition metals have been reported to catalyze the methane cracking reaction, which also produces hydrogen [Hamdan, 2022]. The use of transition metals also suppressed the production of C2 and C3 hydrocarbons, likely due to the increased cracking capability of transition metal-impregnated zeolites [Zhang, 2015; Elbaba, 2012].

Promoting the 5Ni/USY with Cu and Zn reduced the hydrogen formation capacity of the catalyst, while favoring the formation of heavier compounds such as ethylene and propylene, further proving that the use of these metals as promoters has an adverse effect on the catalytic performance. However, the use of cerium promoter enhanced hydrogen production slightly from 59.37% to 61.93% at the expense of heavier olefins, indicating that cerium acts as a suitable promoter when paired with nickel. This could be due to the fact that the addition of cerium enhances the lattice oxygen content, which absorbs reactant intermediates and then help to break chemical bonds, leading to the formation of lighter hydrocarbons [Wu, 2022]. Additionally, the addition of cerium increased the amount of nickel in the supercage of the zeolite relative to the 5Ni/USY according to the TPR data, where it has been shown that the active metal particles in the supercages are especially catalytically active compared to the surface metal particles [Smeets, 2007]. Moreover, the XPS results showed a negative shift of the Ni2p peak for the Ni-Ce catalyst compared to its monometallic counterpart attributed to a reduction in the electron density of the d orbital in the Ni metal, and this has been found to increase catalytic activity [Ni, 2019]. The relatively poor performance of the other promoted Ni catalysts highlights the detrimental effects of excessive weak metal-support interactions causing excessive carbon buildup.

This study contributes valuable insights into designing cost-effective, high-performance catalysts for waste tire recycling, where the Ni-Ce bimetallic catalyst in particular shows promise for industrial-scale applications, supporting circular-economy initiatives by converting waste tires into hydrogen and valuable hydrocarbons.

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