Catalytic valorization of non-condensable pyrolysis gases derived from mixed plastic waste towards selective and sustainable propylene production

Ehsan Mahmoudi[1,2], Stavros A. Theofanidis[3], Stamatia A. Karakoulia[4], Alessandro Longo[5], Christoph Sahle[5], Dirk E. De Vos[2], Angeliki A. Lemonidou[1,4]*

1 Department of Chemical Engineering, Aristotle University of Thessaloniki, University Campus, 54124 Thessaloniki, Greece;
2 Centre for Membrane Separations, Adsorption, Catalysis and Spectroscopy for Sustainable Solutions, KU Leuven, Celestijnenlaan 200F, 3001, Leuven, Belgium;
3 AristEng S.à r.l., 77, Rue de Merl, L-2146, Luxembourg City, Luxembourg;
4 Chemical Process & Energy Resource Institute, CPERI/CERTH, 57001 Thermi, Thessaloniki, Greece;
5 European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000Grenoble, France;
**Corresponding author: alemonidou@cheng.auth.gr*

Highlights

- The effect of WO_3 loading on Al-MCM-41 in the cross-metathesis reaction was studied.
- Ethylene/1-butene ratio and residence time played a crucial role in this reaction.
- By adjusting the reactants' partial pressure, 97.1% of 1-butene conversion and 73.3% propylene selectivity were obtained on the 20%WO_3/Al-MCM-41(30) catalyst.

1. Introduction

Mixed plastic waste (MPW), instead of traditional energy recovery, incineration or landfill can be valorized into valuable chemicals and fuels. This aligns with the European plastics industry's current transition toward net-zero carbon emissions and circularity goals by 2050 [1]. Pyrolysis is a promising method for valorizing MPW to value-added products and has advantages, such as flexible feed, simple operation and low-cost technology. Pyrolysis is a thermal decomposition method at high temperatures (300-700°C) in an inert atmosphere which yields three main products: solids (chars), liquids (pyrolysis oil) and non-condensable pyrolysis gases (NCPGs). NCPGs mainly contain light olefins such as ethylene, propylene, and butenes; nevertheless, they are commonly used for their calorific value [2]. On the other hand, propylene as a major commodity chemical plays a leading role in the market. However, the inequality between supply and demand created the so-called 'propylene gap', which highlights the necessity for on-purpose propylene production [3]. The propylene gap in Europe has been estimated at 347 kt in 2021. This work aims at valorizing the NCPGs, produced via MPW pyrolysis, through the catalytic cross-metathesis. Employing 1-butene as a challenging feed, the goal is to isomerize it to 2-butene (Eq.1) and subsequently react it with ethylene to produce propylene (Eq. 2).

$$1\text{-}C_4H_8 \rightleftharpoons 2\text{-}C_4H_8 \qquad \text{(Eq. 1)}$$
$$C_2H_4 + 2\text{-}C_4H_8 \rightleftharpoons 2C_3H_6 \qquad \text{(Eq. 2)}$$

2. Methods

WO_3-based catalysts were prepared by the wet impregnation method. Upon the addition of the custom-made Al-MCM-41 support to the $((NH_4)_6W_{12}O_{39}\cdot xH_2O)$ solution, the water was evaporated at 80°C under continuous stirring and the resulting powder was dried at 120°C and calcined under airflow at 600°C for 4h. The catalysts were designated as xWO_3/Al-MCM-41(Si/Al) where x is the wt% of WO_3 (5, 10, 20 or 25), while the Si/Al is the molar ratio (i.e. 30 or 60) of the Al-MCM-41 supports.

Catalytic activity measurements were conducted, using a quartz reactor, in a continuous flow unit (101.3 kPa). Typically, 0.6g (WHSV = $3.2h^{-1}$, W_{Cat}/F^0 = 29.4 $kg_{Cat}\cdot s\cdot mol^{-1}$) of catalyst (180-320 μm) mixed with an inert SiC (1:1) were placed in the fixed bed reactor. Initially, the catalyst was pretreated under Ar flow at 550°C for 2h. Afterward, ethylene and 1-butene were introduced into the reactor. Products and unreacted reactants were detected by an Agilent® 7890A GC. The key performance indicators (KPIs) e.g. reactants' conversion and products' carbon-based (C-based) selectivity were calculated.

A comprehensive ex-situ and in-situ characterization techniques of XRD, Raman spectroscopy, TEM, BET, FTIR, TPO, TPR, MeOH-TPSR and EXAFS were applied to the fresh and used catalysts.

3. Results and discussion

The parametric study performed in this work pointed out the role of acidity on the isomerization of 1-butene to 2-butene which is the limited reactant of the cross-metathesis reaction towards propylene. The Al-MCM-41(30), with the highest content of Al, showed the highest isomerization activity. The presence of WO_3 on Al-MCM-41(30) proved to be essential for the cross-metathesis reaction towards propylene. The optimization of the WO_3 loading was carried out and showed that 20%WO_3/Al-MCM-41(30) catalyst results in the highest activity and selectivity, with the lowest carbon deposition.

The theoretical stoichiometric ratio of ethylene/2-butene according to Eq. 2 is 1/1. However, in the reaction of ethylene and 1-butene, our experimental results (Fig.1a) indicated that for optimal propylene selectivity, an excess of ethylene is necessary in agreement with literature [3]. Irrespective of the ratio, 1-butene conversion remains high at ~90% while that of ethylene decreases as expected. Propylene selectivity is greatly affected with the maximum value attained at a ratio of 4.5. Further testing of the catalyst at a longer residence time revealed the beneficial role in both the reactants' conversion and more importantly in propylene at the expense of isomerization products with a selectivity of 70.3% (Fig.1b).

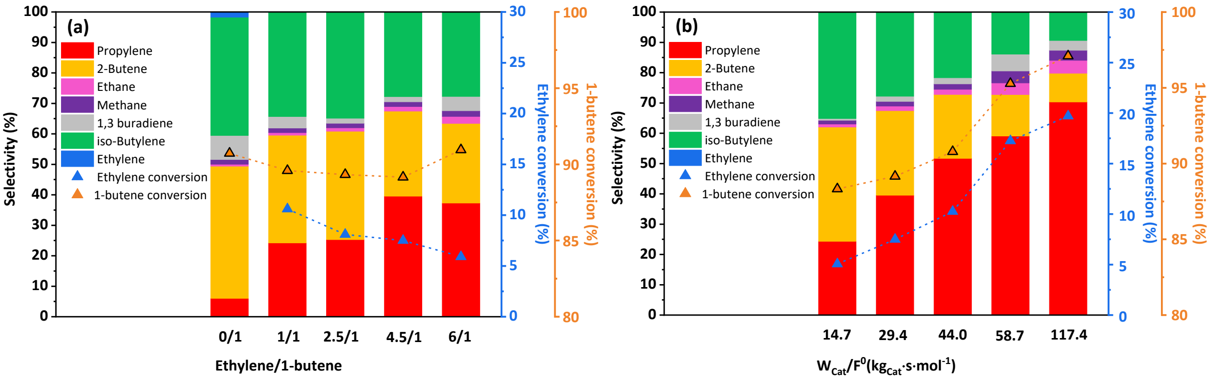

Figure 1. Cross-metathesis reaction over 20%WO_3/Al-MCM-41(30) at 550°C and 101.3 kPa: Effect of (a) ethylene/1-butene ratio (W_{Cat}/F^0 = 29.4 $kg_{Cat}·s·mol^{-1}$, 1-butene^{PP} = 0.073 atm) (b) W_{Cat}/F^0 (ethylene/1-butene = 4.5/1, ethylene^{PP} = 0.33 atm, 1-butene^{PP} = 0.073 atm), on product C-based selectivity (left axis) and ethylene and 1-butene conversion (right axes).

The impact of reactants' partial pressure (PP) was also investigated. It was found that increasing the partial pressures of both reactants, ethylene and 1-butene, by 30% is beneficial. The 1-butene conversion was relatively high, with a slight increase under the higher partial pressure. Conversely, a more pronounced improvement in ethylene conversion was noted, with an increase from 19.7% to 28.3%. A selectivity of 73.3% for propylene was achieved with the higher partial pressures applied.

4. Conclusions

With the demand for propylene exceeding that for ethylene and C_4s, NCPGs stream is a valuable feedstock to be valorized for propylene production via the cross-metathesis reaction. A series of WO_3-based catalysts were synthesized and the 20%WO_3/Al-MCM-41(30) showed the best results, attributed to the combination of Al acidity, facilitating isomerization, and the catalytic properties of WO_3. After optimizing the reaction parameters i.e., ethylene/1-butene ratio and residence time, increasing the reactants' partial pressure by 30%, the KPIs were significantly improved. Thus, ethylene and 1-butene conversions reached 28.3% and 97.1%, respectively, with a notable propylene selectivity of 73.3%.

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Keywords

Chemical Recycling; Plastic Pyrolysis; Propylene Production; Catalysis.