CARBON CIRCULARITY IN PLASTIC WASTE: CROSS-METATHESIS OF ETHYLENE AND 1-BUTENE OVER WO₃/Al-MCM-41 CATALYST TOWARDS PROPYLENE PRODUCTION

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ABSTRACT

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]. Chemical recycling of MPW contains a range of methods, all aim at converting MPW into valuable monomers (carbon circularity). 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 C_4 alkenes; 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. The propylene gap in Europe has been estimated at 347 ktn in 2021 [3]. This work aims at valorizing the NCPGs, produced via MPW pyrolysis, through the catalytic cross-metathesis reaction between ethylene and 2-butene to produce propylene. A series of WO₃/Al-MCM-41 catalysts with different Si/Al ratios were synthesized and ex-situ and in-situ characterization techniques (XRD, Raman spectroscopy, TEM, BET, FT-IR (study of pyridine adsorption), TPO, TPR and EXAFS) were applied to the fresh and used catalysts. A comprehensive parametric study on the effect of temperature, Si/Al ratio, WO₃ loading, residence time (W_{cat}/F^0), feed ratio (ethylene/1-butene) and reactants' partial pressures were investigated. The 20%WO₃/Al-MCM-41 catalyst, with a Si/Al ratio of 30, attained a promising performance at 550°C and 101.3 kPa, with a carbon-based propylene selectivity of 73.3% at ethylene and 1-butene conversions of 28.3% and 97.1%, respectively. Therefore, the upgrading of NCPGs via the cross-metathesis reaction not only narrows the propylene gap but also advances sustainable management of MPW.

**KEYWORDS:** Plastic Recycling, Pyrolysis, Propylene Production, tungsten oxide catalyst, Cross-metathesis.

INTRODUCTION

The European plastics industry is in a transition period to achieve net zero greenhouse gas emissions and circularity by 2050 [1]. Nevertheless, Europe's plastic production in 2021 reached 57.2 million tons (Mt), representing 15% of the 390.7 Mt global plastics production capacity. In 2020, Europe generated a staggering 29.5 Mt of post-consumer MPW. Only a mere 34.5% of those MPW

underwent recycling, while 42.3% and 23.2% were sent to energy recovery and landfill, respectively [4, 5]. Recycling can be categorized into mechanical and chemical processing. Mechanical recycling involves physical processes to retrieve and reuse plastic materials and it is limited since the polymer quality decreases due to degradation [6]. On the contrary, chemical recycling of MPW involves a range of methods including pyrolysis [7], gasification, solvolysis [8], and enzymatic degradation [9], all aimed at converting MPW into valuable monomers, known as carbon circularity [10].

Pyrolysis of MPW is a process where plastics are heated in a temperature range of 300-700°C in the absence of oxygen (inert atmosphere), leading to the breakdown of the plastic polymer chains into simpler chain blocks providing a practical solution to address MPW management via carbon circularity [11, 12]. Pyrolysis yields three primary products: char, pyrolysis oil and non-condensable pyrolysis gases (NCPGs). NCPGs have not been considered a valuable stream, even though they contain C_1-C_5 hydrocarbons along with CO, CO_2, H_2, N_2 and H_2O, the calorific value of NCPGs from the pyrolysis of MPW is often taken into account [2]. Notwithstanding, the makeup of the NCPGs depends on the conditions and the composition of MPW in the feedstock employed in the pyrolysis process [13]. However, it is important to note that the presence of valuable light olefins, such as ethylene, propylene and C_4 alkenes, offers an opportunity to utilize them directly or to valorize into high-value chemicals. These olefins are highly sought after in the industry as essential chemical commodities and can be further processed to create a range of valuable products [2, 14].

The "propylene gap" – a shortage of propylene relative to demand – emerged at the beginning of the new millennium and has experienced significant growth over the past two decades and it is estimated to reach 165 Mt per year by 2030 [15]. Approximately 50% of the world's propylene production is derived from steam cracking (SC), followed by fluid catalytic cracking (FCC) which accounts for around 39% of global propylene production. The remaining propylene is produced through on-purpose processes such as propane dehydrogenation (PDH), the cross-metathesis of olefins and methanol-to-olefins (MTO)[16]. Given the current higher demand for propylene compared to ethylene and C_4 alkenes, the incorporation of the NCPGs in the cross-metathesis process could offer a practical solution to shrink the propylene gap [3]. Cross-metathesis reaction involves the reaction of ethylene with another olefinic substrate (e.g. 2-butene and 2-pentene for propylene production) [17]. Conventionally, ethylene and 2-butene (-cis or -trans) are converted to produce propylene via the cross-metathesis reaction (Eq. 1). Nonetheless, 1-butene can serve as a challenging feedstock since it initially undergoes isomerization to 2-butene (Eq. 2), subsequently reacts with ethylene to produce propylene (Eq. 1).

$C_2H_4 + 2\text{-}C_4H_8 \rightleftharpoons 2C_3H_6$ *(Eq. 1)*
$1\text{-}C_4H_8 \rightleftharpoons 2\text{-}C_4H_8$ *(Eq. 2)*
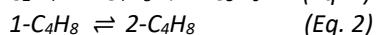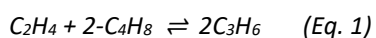
In this work, the production of propylene through the cross-metathesis of a sustainable feed comprised of ethylene and 1-butene, the main constituents of NCPGs, derived from MPW pyrolysis at 600°C, was investigated. A comprehensive parametric study was performed to identify the optimum operating window during the cross-metathesis reaction, aiming at maximizing the technical key performance indicators (KPIs): ethylene and 1-butene conversions and propylene carbon-based selectivity. The catalytic reactions were conducted using xWO_3/Al-MCM-41(Si/Al) catalysts, which were thoroughly characterized prior to and after the experimentation.

METHODOLOGY

Catalyst synthesis
WO_3 catalysts were prepared by wet impregnation method on Al-MCM-41 support using an aqueous ammonium metatungstate hydrate solution. Upon water evaporation at 80°C under

continuous stirring, the resulting white paste was dried at 120°C overnight and subsequently calcined under continuous air flow at 600°C for 4h. The impregnated catalysts are designated as **xWO₃/Al-MCM-41(Si/Al)** where x is the nominal wt.% of WO_3 (x = 5, 10, 20 or 25) and (Si/Al) the molar ratio (30 or 60) of the synthesized Al-MCM-41 supports.

Catalyst characterization

The crystallographic phases of fresh and used catalysts were analyzed using XRD with a Bruker D8 Advance diffractometer. The XRD patterns were generated using CuKa radiation (λ = 0.15406 nm) over a 2θ range of 10° to 70°, with a scan rate of 0.5 s/point and step of 0.02°. The Scherrer formula was utilized to determine the crystallite size of the WO_3-based catalysts.

The Raman spectra were taken by a micro-Raman Renishaw, Qontor, Gloucestershire, UK in Via Instrument coupled with a 785 cm^{-1} laser and ×50 and x100 Leica lens at 10 mW power.

All the experiments were carried out in a JEOL 2011 High Resolution Transmission Electron Microscope, operating at 200 kV, with a point resolution of 0.23nm and Cs = 1.0 mm.

N_2 adsorption-desorption at -196°C was performed on an Automatic Volumetric Sorption Analyzer (Autosorb-1, Quantachrome) for the determination of surface area (BET method).

The type and strength of acid sites were determined with pyridine adsorption monitored by Infrared Spectroscopy (IR).

Catalyst performance

Catalytic activity measurements were performed in a continuous flow, lab-scale unit at atmospheric pressure. Initially, the catalyst was diluted with an inert SiC for improved heat conductivity and placed in the quartz fixed bed reactor with an internal diameter of 10 mm, which was placed inside an electric furnace equipped with three independently controlled temperature zones. The temperature of the catalyst bed was measured with a K-type thermocouple placed inside the quartz thermowell located in the catalyst bed (middle heating zone). A fritted quartz disk was placed in the center of the reactor to hold the bed material. For a typical activity test, 0.6g (WHSV = 3.2 h^{-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, resulting in approximately 3.0 cm (GHSV = 882 h^{-1}) of catalyst bed length. The inlet gas flow rates were controlled using calibrated mass flow controllers (Brooks, 5850E series) and pre-mixed before entering the reactor. Initially, the catalyst was pretreated under Ar flow at 550°C for 2h. Afterward, for the cross-metathesis reaction, a mixture of ethylene and 1-butene, with varying feed ratios was fed through the reactor, while 1-butene partial pressure was kept constant (0.073 bar). In addition, helium (He) was used as a diluent, while argon (Ar) served as an internal standard. The total flow rate (F^0) was set to 30 ml/min. The products (methane, ethane, propylene, 2-butene, n-butane, isobutylene and 1,3-butadiene) and unconverted ethylene and 1-butene were detected using an Agilent® 7890A GC system for online analysis, equipped with a TCD detector and two columns: Porapaq Q and Molecular Sieve 5A in-series configuration.

RESULTS AND DISCUSSION

Catalyst characterization

All the catalysts presented four diffraction peaks at 2θ = 23.1°, 23.6°, 24.4° and 34.1° attributed to the (002), (020), (200) and (202) crystal planes of the monoclinic phase of WO_3. An increase in metal loading (from 5% to 25%) resulted in more intense peaks, indicating also proportional increase in both the amount and size of WO_3 crystals on the surface of mesoporous supports.

Moreover, Raman spectroscopy reinforced XRD findings, as the results confirm the existence of the monoclinic WO_3. Furthermore, a new peak, distinct from the bulk WO_3, emerged at 970 cm^{-1}, signifying isolated surface tungsten oxide species (active sites for cross-metathesis reaction)

resulting from the interaction of WO_3 with the Al-MCM-41(30) support, and its intensity increases with higher WO_3 loading.

The morphology and structure of the mesoporous support Al-MCM-41(30) and the respective catalyst 20%WO_3/Al-MCM-41(30) were studied through HR-TEM. In the case of Al-MCM-41, a well-ordered honeycomb hexagonal pore structure was observed. HR-TEM images show that WO_3 agglomerates, with particle sizes ranging from 40 to 80 nm, are deposited on the outer surface of the tubular-shaped Al-MCM-41(30).

The BET surface area of the Al-MCM-41(30) was over 1000 m^2/g. Deposition of WO_3 on the surface of those mesoporous silicas caused a surface area decrease of more than 30% with increasing WO_3 loadings from 5 to 25 wt.%. This drop can be associated with the partial blockage of the pores by the WO_3 species on the surface of the support.

Chemisorption of pyridine followed by IR is useful to detect the number and strength of surface aprotic (Lewis) and protonic (Brønsted) acid sites on the catalyst surface. As expected, siliceous MCM-41 showed no acidity, while incorporation of Al^{3+} in the silica framework (Al-MCM-41 supports) induced the formation of both Brønsted and Lewis acidity (main active sites for isomerization reaction). An increase in Al content (decrease in Si/Al molar ratio from 30 to 60) during Al-incorporation resulted in a proportional increase in both acid types (Al-MCM-41(60) compared with Al-MCM-41(30)) keeping the B/L ratio constant at 0.4, implying the successful respective insertion of Al species into the silica framework. Moreover, it's intriguing to observe that modification of supports with WO_3 leads to an augmentation in both Brønsted and Lewis acidity.

Catalyst tests

This work presents a parametric study for propylene production through the cross-metathesis reaction, employing ethylene and 1-butene as reactants. Prior to any catalytic experiment, the contribution of the thermal reaction in the absence of any catalyst was evaluated under the same conditions as those used for the catalytic tests. The results showed that the maximum temperature for almost free of thermal effects catalytic metathesis reaction is 550°C.

In general, the tandem cross-metathesis reaction involving 1-butene and ethylene can be divided into two key steps: the isomerization of 1-butene to 2-butene and the cross-metathesis of ethylene and 2-butene to produce propylene. Enhancing the efficiency of each of these individual steps can significantly improve the overall reaction performance. The effect of support, WO_3 loading, temperature, feed ratio, residence time (W_{Cat}/F^0) and reactants partial pressure were investigated.

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, by furnishing metallic W-carbene active sites on WO_3 surfaces. 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 (Figure.1(a)) 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% (Figure.1(b)). The formation of carbene requires extended contact time of ethylene and formed 2-butene with W active species.
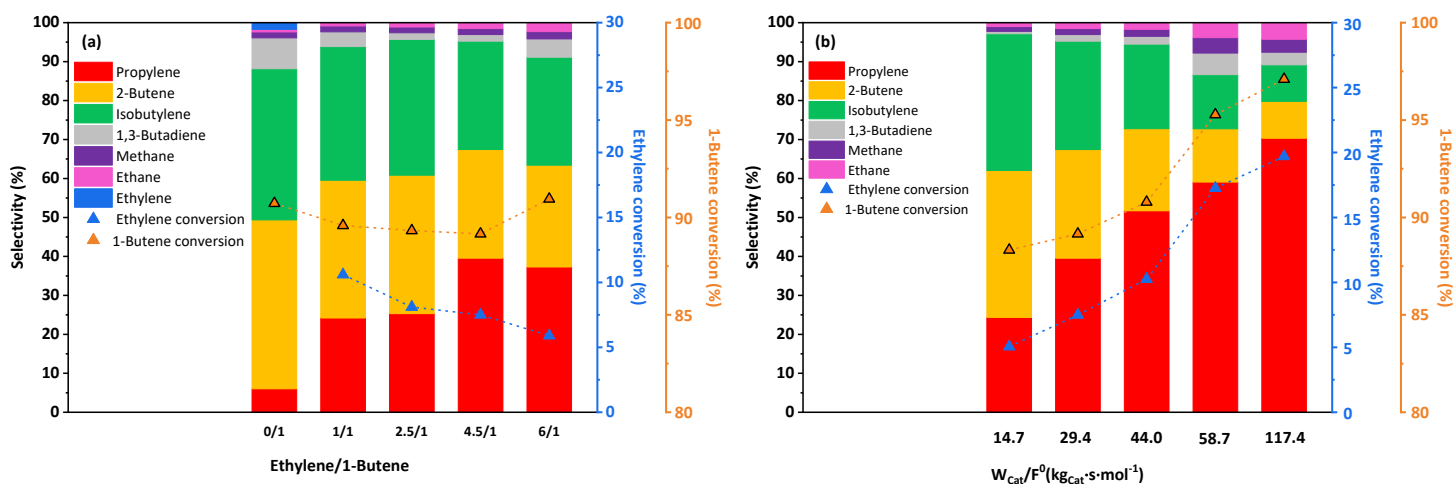

Figure 1. *Cross-metathesis reaction over 20%WO₃/Al-MCM-41(30) at 550°C and 101.3 kPa. Effect of :(a) ethylene/1-butene ratio (W_{Cat}/F^0 = 29.4 $kg_{Cat}\cdot s\cdot mol^{-1}$, 1-butene^{PP} = 0.073 atm), (b) W_{Cat}/F^0 (ethylene/1-butene = 4.5/1, ethylene^{PP} = 0.33 atm, 1-butene^{PP} = 0.073 atm), 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 (Table 1). The 1-butene conversion was relatively high. 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.

Table 1. *Effect of reactants PP on ethylene and 1-butene conversion, propylene selectivity and rate.*

W_{Cat}/F^0 ($kg_{Cat}\cdot s\cdot mol^{-1}$)	Ethylene PP (bar)	1-Butene PP (bar)	Ethylene conversion (%)	1-Butene conversion (%)	Propylene selectivity (%)	Propylene rate of production 10^{-3} mmol·s⁻¹·g_{Cat}^{-1}
29.4	0.33	0.073	7.5	89.2	39.5	1.18
29.4	0.427	0.095	9.5	91.5	42.8	1.75
117.4	0.33	0.073	19.7	96.1	70.3	0.67
117.4	0.427	0.095	28.3	97.1	73.3	1.03

CONCLUSIONS

In conclusion, pyrolysis is considered as a promising chemical recycling method for mixed plastic waste (MPW) back to monomers. On the other hand, there is an increasing urge for on-purpose propylene production. As a result, with the demand for propylene now exceeding that for ethylene and C₄ alkenes, the non-condensable pyrolysis gases (NCPGs) stream of MPW is a valuable feed to be valorized to propylene via the cross-metathesis reaction. In this work, the results indicate that the presence of Al and WO₃ loadings has a noticeable impact on the structure of MCM-41, as verified through XRD, Raman spectroscopy, TEM, BET, FT-IR (study of pyridine adsorption) and EXAFS characterizations. The introduction of aluminum leads to the presence of Lewis and Brønsted acidic sites, serving not only in isomerization but also in facilitating the interaction of tungsten oxide species with the olefins for the formation of the active carbene intermediates The 20%WO₃/Al-MCM-41(30) showed promising catalytic performance in the isomerization of 1-butene to 2-butene

in tandem with cross-metathesis reaction by actively facilitating the formation of W-carbenes of ethylene ($W=CH_2$) and 2-butene ($W=CHCH_3$). Despite the stoichiometric ratio between ethylene and 2-butene being theoretically 1/1, it is fascinating to note that an excess of ethylene in the reaction between ethylene and 1-butene has a remarkable effect on shifting the reaction towards more propylene production. Furthermore, an intriguing finding emerged when the partial pressure of both reactants was altered, increasing by 30%. These adjustments revealed an impressive synergy effect of long residence time and partial pressure, leading to a C-based selectivity for propylene of 73.3%, while the conversion of ethylene and 1-butene reached 28.3% and 97.1%, respectively.

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