

Thermal Reformation of Polystyrene Using Metal Oxide as Redox Catalyst

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While plastic has been regarded as a useful and cost-effective material, there is growing global concern about its disposal. Chemical recycling presents a promising solution to this issue. This study explores the utilization of vanadium oxide as a redox catalyst to effectively decompose polystyrene into industrially useful CO. By heating polystyrene with V₂O₅ under an inert gas atmosphere, CO was successfully produced accompanied with CO₂ as the primary by-product. Adding 5 wt% iron to V₂O₅ improved the selectivity of CO production without compromising gas yield. X-ray diffraction analysis indicated that V₂O₅ acted as an oxygen source and turned into V₂O₄ and V₆O₁₃ after the reaction. This process enables polymer reformation at lower temperatures than conventional methods, making it an energy-efficient chemical recycling strategy. Additionally, V₂O₄ and V₆O₁₃ generated during the process were easily oxidized to V₂O₅ through heating under atmospheric conditions. As both polymer reformation and oxidation are exothermic reactions, the proposed reaction scheme can be used as a thermally efficient chemical recycling process.

1. Introduction

Plastic is extensively utilized in diverse fields due to its exceptional versatility and cost-effectiveness. However, in recent years, the issue of plastic waste has emerged as a pressing environmental challenge (Yang et al.), which requires efforts to reduce plastic production and disposal through chemical, mechanical, physical, biological, and thermal recycling (Shamsuyeva and Endres, 2021). Chemical recycling, in particular, is a highly anticipated and versatile approach, given its ability to generate other substances from the resulting products (Lee and Liew et al.) However, most plastic is currently processed via incineration or landfill (Prajapati et al., 2021). For instance, the recycling rate for polystyrene (PS), recognized as one of the most versatile plastics, remains at only 0.9 % in the USA (Rahimi and Garcia, 2017). An innovative recycling method for PS is necessary to solve this global problem.

Most of the chemical recycling methods for PS reported so far have used high-temperature reformation reactions. For example, A. Demirbaş (2005) reported a chemical recycling method without a catalyst at around 400-500 °C to convert PS into a liquid hydrocarbon consisting mainly of styrene. Patrick et al. (2006) proposed a method to convert PS into styrene at high selectivity using a fluidized bed reactor at 520 °C, which was then further recycled into a biodegradable polymer. Achilias et al. (2007) demonstrated the reformation of PS into high-purity styrene at 510 °C using a fluidized bed reactor, which can be recycled as a raw material for PS. Park et al. (2020) showed that PS could be thermally decomposed into aromatic compounds at 780 °C and used as fuel. Although these studies all showed high selectivity and usefulness of the obtained products, the reaction temperature was relatively high, at 400 °C or higher. High-temperature processes have low thermal efficiency, making it difficult to downsize the process and resulting in high implementation barriers in terms of both initial and operating costs.

In this study, we investigated polystyrene (PS) reformation at low temperatures (300-400 °C) in light of the growing concern over plastic waste. To efficiently decompose PS, we employed V₂O₅ as a redox catalyst to provide an appropriate supply of oxygen to PS and aimed to decompose it into gases mainly composed of CO and H₂O. These gases can be converted to hydrogen via the water-gas shift reaction and are expected to be utilized for producing various materials through C1 chemistry. By lowering the operating temperature, we can reduce the barriers to introducing the process and expect to utilize it as a versatile chemical recycling process.

2. Experimental

2.1 Materials

Polystyrene (PS, Mw 260,000) and vanadium oxide (V₂O₅, purity > 99 %) were purchased from Kanto Chemical Co., Inc., Japan. All chemicals were used without further purification.

2.2 Thermal reformation of polystyrene

The mixture of PS and V₂O₅ (total of 0.55 g) was placed in the reactor made of an SUS tube (I.D. 19.9 mm, length 100.0 mm), and 0.15 MPa of N₂ was introduced as an inert gas. The reactor was sealed and heated by a furnace and controller (SU12, Chino Corporation, Japan) from room temperature to operating temperature (300 to 400 °C), which takes 30 min. After leaving the reactor in the furnace for a certain period (30 to 150 min), the reactor was air-cooled to room temperature. After cooling, the gas inside the reactor was collected and analyzed by gas chromatography (8860 GC System, Agilent Technologies, Inc., USA). Since the amount of N₂ in the reactor is known, the amount of product gas can be calculated. The remaining solid was analyzed by X-ray diffraction (XRD) to characterize the compound in the residue using MiniFlex II (Rigaku Corporation, Japan). The angle was scanned in the range of 2θ = 5 to 100° at the rate of 5° min⁻¹. The weight change of the vanadium oxide during the reaction was measured by thermogravimetry (TG) analysis (TG/DTA 6200, Seiko Instruments, Inc., Japan). 30 mg of sample was placed in a sample pan and heated from room temperature until 350 °C at 10 °C min⁻¹ under atmospheric conditions. After reaching 350 °C, the sample was kept at this condition for 5 hours.

3. Results and discussion

3.1 Thermal reformation of polystyrene using redox catalyst

CO and CO₂ generation from the PS/V₂O₅ mixture was confirmed at 360 – 400 °C by GC analysis. To evaluate the efficacy of thermal reformation, the carbon yield (X_C) and CO selectivity (S_{CO}) were calculated by the following equations:

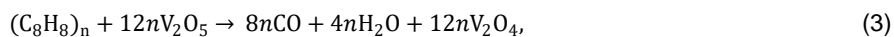
$$X_C = \frac{n_{C, \text{gas}}}{n_{C, \text{polymer}}}, \quad (1)$$

$$S_{CO} = \frac{n_{CO}}{n_{CO} + n_{CO_2}}. \quad (2)$$

X_C and S_{CO} at various operating temperature and time were presented in Figure 1. Since the reactor was heated from room temperature to operating temperature during the first 30 min of operation, no significant gas production could be observed at this point ($X_C < 10\%$). On the other hand, gasification drastically proceeded after the reactor reached the operating temperature (i.e., after 30 min). X_C increased with temperature because of the high reaction rate. Notably, no hydrocarbon or hydrogen was confirmed at any conditions, and therefore, the main product of the reaction should be CO, CO₂, and H₂O. Since the gas was sampled at room temperature in this work, the amount of water generated by the reaction could not be measured.

At the beginning of the reaction (30 min), S_{CO} was sufficiently high (40 %), although it significantly decreased with increasing operating time. For example, 95 % of the product was CO₂ when the reformation was conducted at 400 °C for 150 min. Before the reaction, the mixture was orange, and it turned dark blue (or black) after the reaction, suggesting that V₂O₅ (orange color) changed into another compound during the reaction. The residue was analyzed by XRD to confirm the loss of V₂O₅ during the reaction (Figure 2a). As expected, the sharp peaks of V₂O₅ could not be seen in the reaction residue, and V₂O₄ seems to be the most dominant product.

From the observation above, we concluded that the following two reactions mainly occur during the process:



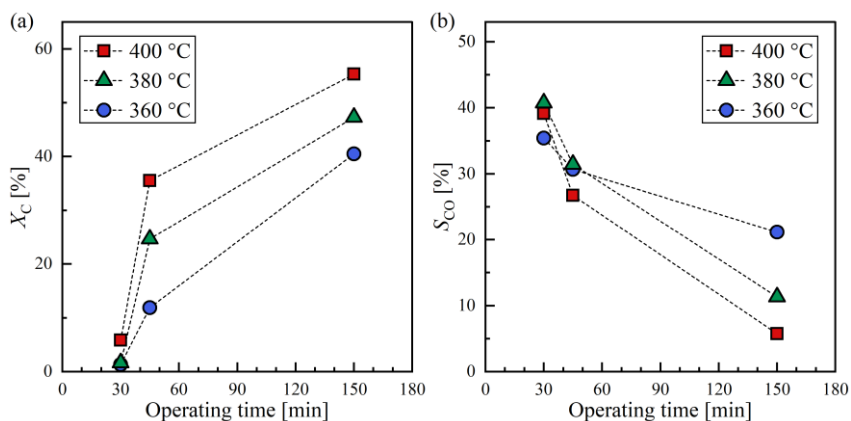
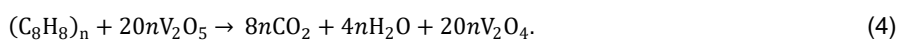


Figure 1: The carbon yield (a) and CO selectivity (b) of the reaction at various operating temperature and time

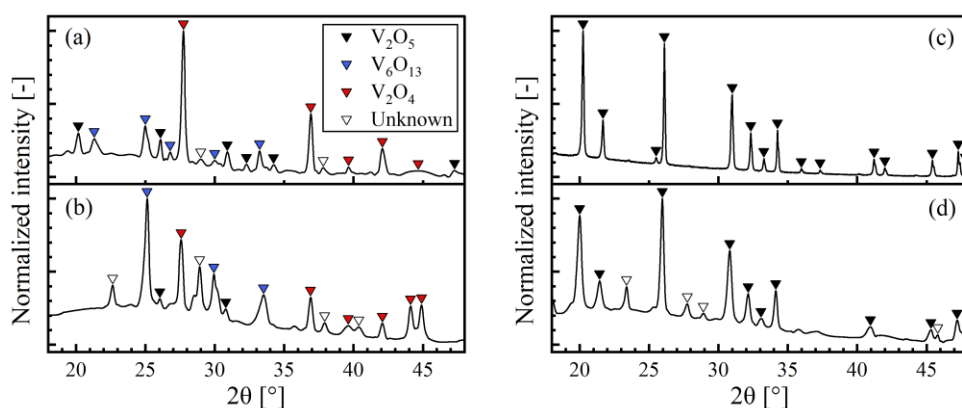


Figure 2: The XRD patterns: (a) Reaction residue (V₂O₅ + PS, at 380 °C for 150 min), (b) Reaction residue (V₂O₅ + Fe + PS, at 380 °C for 150 min), (c) pristine V₂O₅, (d) V₂O₅ after recycling.

Note that the V₂O₅/PS ratio was determined so that Eq(3) completes without any reactants left; therefore, 1.5 mol of V₂O₅ was added per 1 mol of carbon atoms in PS. If S_{CO} is small, an insufficient O atom exists in the system to gasify carbon; thus, X_C did not surpass 60 %. The ratio of V₂O₅ used during the reaction can be calculated as the following equation, under the assumption that the selectivity of Eq(3) over Eq(4) is precisely S_{CO}:

$$X_{V_2O_5} = X_C \cdot (2 - S_{CO}). \quad (5)$$

The calculated results were summarized in Table 1, along with the experimental results. As can be seen, most of V₂O₅ was consumed (X_{V₂O₅} ~ 90 %) at high temperature and a long operating time. In these conditions, most of V₂O₅ changed into V₂O₄, as suggested by XRD analysis (Figure 2a).

The effect of temperature on the reaction was investigated in the range of 300 to 400 °C; the results are given in Figure 3. X_C was clearly increased with temperature, while S_{CO} decreased. Since the mixture of CO and H₂O obtained in this reaction is variable in the engineering field, the ideal situation is that both X_C and S_{CO} should be sufficiently high. To understand the trade-off effect between X_C and S_{CO}, the following CO yield was defined:

$$X_{CO} = X_C \cdot S_{CO}. \quad (6)$$

The value is given in Table 1. Interestingly, X_{CO} decreases with operating time at 380 and 400 °C, suggesting that CO further reacted and changed into another compound during the process. Since only CO, CO₂, and H₂O were obtained in the process, the following reaction seems to proceed:



The results suggest for Eq(7) to proceed faster than Eq(3) at high temperatures. In order to establish a feasible process, the reaction Eq(7) should be suppressed.

Table 1: CO gasification results with various operating temperature and time

T / °C	t / min	X _C / %	S _{CO} / %	X _{V2O5} / %	X _{CO} / %
360	30	1.3	35.4	2.2	0.5
380	30	1.7	40.7	2.6	0.7
400	30	5.9	39.1	9.4	2.3
360	45	11.9	30.7	20.1	3.6
380	45	24.7	31.5	41.6	7.8
400	45	35.5	26.8	61.5	9.5
300	150	3.4	37.7	5.4	1.3
310	150	5.2	24.9	9.1	1.3
320	150	13.9	24.3	24.5	3.4
330	150	21.9	22.8	38.7	5.0
340	150	27.0	24.9	47.2	6.7
350	150	49.5	21.2	88.4	10.5
360	150	40.5	21.2	72.4	8.6
380	150	47.3	11.3	89.2	5.4
400	150	55.3	5.7	> 100.0	3.2

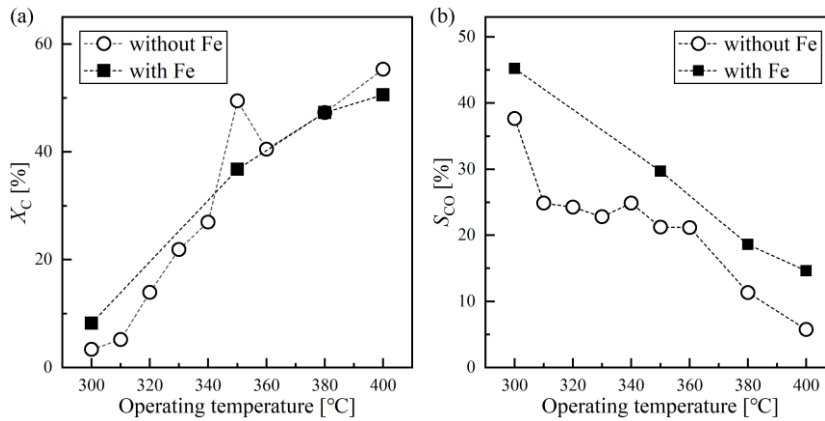


Figure 3: The carbon yield (a) and CO selectivity (b) of the reaction at various operating temperature with pure V₂O₅ or V₂O₅/Fe mixture as redox catalyst (operation time was fixed at 150 min.)

In order to produce CO efficiently, V₂O₅/PS ratio was varied. The scaled weight ratio ($w_{\text{V}_2\text{O}_5/\text{PS}}^*$) was defined as follows:

$$w_{\text{V}_2\text{O}_5/\text{PS}}^* = \omega \frac{w_{\text{V}_2\text{O}_5}}{w_{\text{PS}}} \quad (8)$$

The scale factor ω was set to 0.0477. When $w_{\text{V}_2\text{O}_5/\text{PS}}^* = 1$, Eq(3) completes without any reactants left, while an excess amount of V₂O₅ exists when $w_{\text{V}_2\text{O}_5/\text{PS}}^* > 1$. The effect of $w_{\text{V}_2\text{O}_5/\text{PS}}^*$ on X_C and S_{CO} (operating time = 45 min) was given in Figure 4. As can be seen, X_C drastically increases when an excess amount of V₂O₅ exists in the system. Intriguingly, S_{CO} was almost constant regardless of $w_{\text{V}_2\text{O}_5/\text{PS}}^*$, suggesting that the amount of O atoms and CO molecules does not affect the reaction rate of Eq(7). Therefore, Eq(7) seems to have a zero-order reaction rate in terms of the fugacity of O and CO. It should be noted that this result may be attributed to the batch-wise operation during the process. Therefore, the reaction kinetics should be carefully examined using a (semi-) continuous system to obtain a reliable conclusion.

To further facilitate the production of CO, Fe was added to V₂O₅ as a co-catalyst by 5.0 wt%. While the existence of Fe did not affect X_C, S_{CO} increased at all tested operating temperature, as demonstrated in Figure 3. Since Fe only affects S_{CO}, it is an excellent candidate to suppress Eq(7). The reaction residue was analyzed by XRD to investigate the effect of Fe (Figure 2b). As can be seen, the main product of the reaction was changed from

V_2O_4 to V_6O_{13} when Fe was added. The result implies that the existence of Fe changes the reactivity of vanadium oxide with CO and reduces the reaction rate of Eq(7).

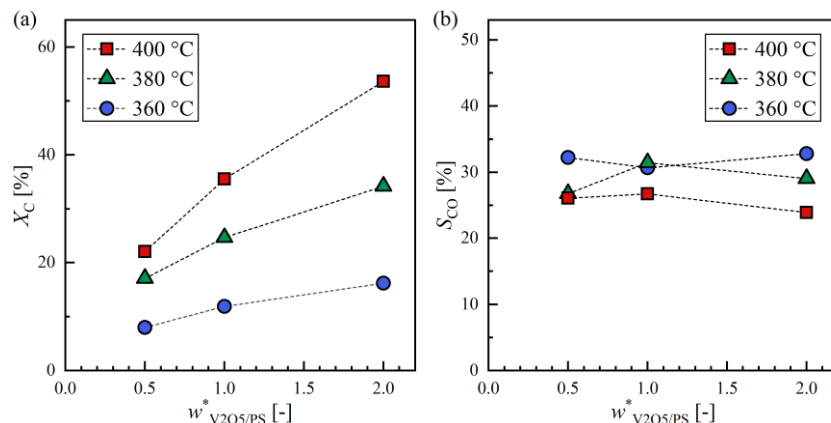


Figure 4: The carbon yield (a) and CO selectivity (b) of the reaction at various V_2O_5/PS ratios and temperature (operation time was fixed at 45 min.)

3.2 Chemical recycling of PS using redox catalyst

In the previous subsection, it was demonstrated that CO/H₂O mixture could be obtained by the thermal reformation of PS. Another advantage of V_2O_5 is that the residue (V_2O_4 and V_6O_{13}) can be easily reversed to V_2O_5 at mild conditions by the following reaction:



The weight change of residue over time was measured at 350 °C by TG under an atmospheric condition, and the result is shown in Figure 5. The weight clearly increases with time, confirming the reaction of V_2O_4 and V_6O_{13} with O₂ in the atmosphere. Moreover, the XRD pattern of the remaining solid indicates the complete recovery of V_2O_5 (Figures 2c and 2d). These results suggest that V_2O_5 can be a redox catalyst for the system.

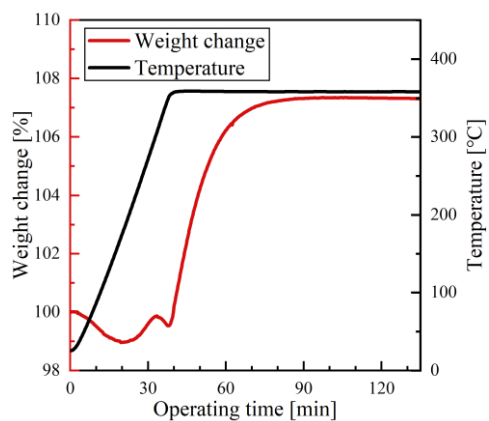


Figure 5: Weight change of vanadium oxide at 350 °C under an atmospheric condition.

PS reformation using V_2O_5/V_2O_4 as a redox catalyst is thermodynamically beneficial because the main reactions in the process are exothermic: $\Delta H = -54.5$ kJ/mol-C for Eq(3) and $\Delta H = -247.0$ kJ/mol-O for Eq(9). Therefore, with proper process design, no heat is to be added to this chemical recycling process during steady state. Moreover, the operating temperature is much lower than the conventional processes, thus, making energy efficient. These advantages make the proposed reaction system an effective chemical recycling method for PS.

4. Conclusions

The increasing severity of environmental problems caused by plastics demands a drastic solution, and developing new recycling methods is crucial. In this study, we focused on the chemical recycling of plastics and

explored a novel CO-generation process using a redox catalyst. This work demonstrated that heating a mixture of polystyrene and vanadium oxide can effectively gasify plastics at lower temperatures than conventional methods. The produced CO has potential use in various industrial applications, while mitigating by-product generation, CO₂, is identified as a challenge for this process. Our investigations into reaction temperature and time reveal a trade-off between total gas production and CO selectivity, as high temperature and CO partial pressure lead to the oxidation of CO into CO₂. We successfully increased total gas production by introducing excess redox catalyst while maintaining CO selectivity.

To enhance CO selectivity, we conducted a thermal reformation using 5.0 wt% of Fe as a co-catalyst, which successfully improved CO selectivity without compromising total gas production. XRD analysis of the residual redox catalyst confirmed an increase in V₆O₁₃ production, suggesting that Fe affects surrounding V₂O₅ and enhances polymer degradation in the system. Notably, the redox catalyst after the reaction (V₂O₄ and V₆O₁₃) was regenerated to V₂O₅ by heating in the presence of oxygen at the reaction temperature. The exothermic nature of CO production and catalyst regeneration suggests that this system presents a novel approach to producing CO without the addition of heat energy during steady state. Our findings suggest that this system could be a superior and cost-effective method for the chemical recycling of plastics in terms of initial and running costs.

Nomenclature

$n_{C,gas}$ – quantity of carbon atoms in the gas, mol	X_C – carbon yield, %
n_{CO} – quantity of CO in gas, mol	X_{CO} – CO yield, %
n_{CO_2} – quantity of CO ₂ in gas, mol	$X_{V_2O_5}$ – fraction of consumed V ₂ O ₅ , %
$n_{C,polymer}$ – quantity of carbon atom in polymer, mol	X_C – carbon conversion, %
S_{CO} – CO selectivity, %	ΔH – enthalpy of reaction, kJ/mol
w_{PS} – weight of PS, %	ω – scaling factor of $w_{V_2O_5/PS}$, -
$w_{V_2O_5}$ – weight of V ₂ O ₅ , %	
$w_{V_2O_5/PS}$ – scale weight rate of V ₂ O ₅ /PS, %	

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