

Decomposition of Mixed Plastics Consist of Polypropylene and Polyethylene Terephthalate into Fuel Oils over Titania/Silica Catalyst

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Mixture of polypropylene (PP) and polyethylene terephthalate (PET) were converted into oils without formation of certain kinds of phthalic acids over a $\text{TiO}_2/\text{SiO}_2$ catalyst at 698K. The product oils included large amounts of C_{12+} hydrocarbons due to aromatics from PET. Using FT-IR spectroscopy, the $\text{TiO}_2/\text{SiO}_2$ catalyst was found to have Lewis acidic sites, where PP derived hydride react with pyrolysates of PET to form oils and gas.

Introduction

While plastics are convenient materials and indispensable to our life today, the treatment of waste plastics causes many troubles and problems. For example, in the case of waste disposal, plasticizer such as phthalic acid ester and adipic acid ester, so called endocrine disrupting chemicals, leach out into soil. In the case of incineration, environmental pollutants such as dioxin are formed. In the new law for protection of sorted garbage and recycling of containers and packaging, the Japanese government decided on the guideline for plastics containers (with exception of PET bottles) to convert into fuel oils after the year 2000. The reason for the exception of PET bottles is that pyrolysis of PET forms large amounts of carbon and/or phthalic acids, which choke up reactors or pipes and prevent continuous operation. However, it is next to impossible to remove PET bottles completely from a large quantity of municipal plastic waste. In addition, it is estimated that the amount of waste PET will increase gradually with the introduction of 500ml PET bottles since 1996.

In previous paper [1], we reported polyethylene (PE), polypropylene (PP) and polystyrene (PS) were converted into light oils, gasoline and kerosene respectively, over TiO_2 catalyst supported on silica beads having macropores. On active sites in the pores macromolecules such as pyrolysates of plastics can be trapped and adsorbed. The aim of the present work is to study the decomposition of mixed plastics consisting of PP and PET over $\text{TiO}_2/\text{SiO}_2$ catalyst and to investigate which operating conditions influence product composition.

Experimental

Preparation of catalyst

Silica beads with mean pore diameter of about 50nm (Fuji Silysia Chemical Co.; 2.8~3.3mm in diameter and $86\text{m}^2/\text{g}$ in BET surface area) were impregnated with a mixture of titanium tetraisopropoxide (Katayama Chemical Co.) and isopropanol (Ishizu Seiyaku Co.) (molar ratio; 1:2) and left overnight. After hydrolysis of titanium tetraisopropoxide in humidified air, the treated

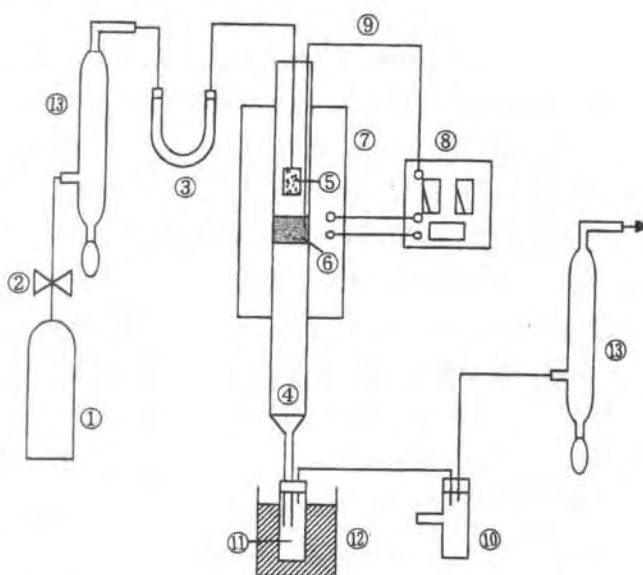
beads were calcined at 773K for two hours. In this way, a 20wt%TiO₂/SiO₂ catalyst was obtained [2, 3].

Experimental operation

A schematic diagram of the apparatus is shown in Fig. 1. A vertical tubular Pyrex reactor (28mm in diameter) was encased by an electric furnace with a temperature controller. A TiO₂/SiO₂ catalyst was packed in the reactor below the sample holder which was packed with a mixture of PP and PET. The nitrogen stream was set at a flow rate of 40ml/min. At 698K, pyrolysis gas of mixed plastics passed through the catalyst bed, was liquefied and stored in a condenser immersed in an ice bath. The product gas and liquid were analyzed by gas chromatographic equipment with FID (Perkin Elmer Co., Model Auto System) and TCD (Yanaco Co., Model G-2800). 'Sample holder residue' which was left in a sample holder, 'reactor wall residue' which was attached to reactor wall and 'adsorption substance' which was adsorbed on the catalyst, were estimated by measuring their mass before and after the reaction. Characterization of the catalyst was made utilizing FT-IR (Perkin Elmer Co., Model 1600 series) spectroscopic data from the adsorption by pyridine on the catalyst.

Result and Discussion

PET itself did not convert into oils over TiO₂/SiO₂, but formed milk-white colored solid considered to be certain kinds of phthalic acids. The reason for the result may be explained due to the fact that pyrolysates of PET contain aromatic compounds and oxygen but lack in hydrogen. We thought it would be able to decompose them when the



① N₂ gas bomb ② Needle valve ③ Silica gel dryer
④ Reactor ⑤ Sample holder ⑥ Catalyst
⑦ Electric furnace ⑧ Temperature controller
⑨ Thermocouple ⑩ Sampling tee ⑪ Condenser
⑫ Ice bath ⑬ Soap-film flow meter

Fig. 1 Schematic diagram of the apparatus

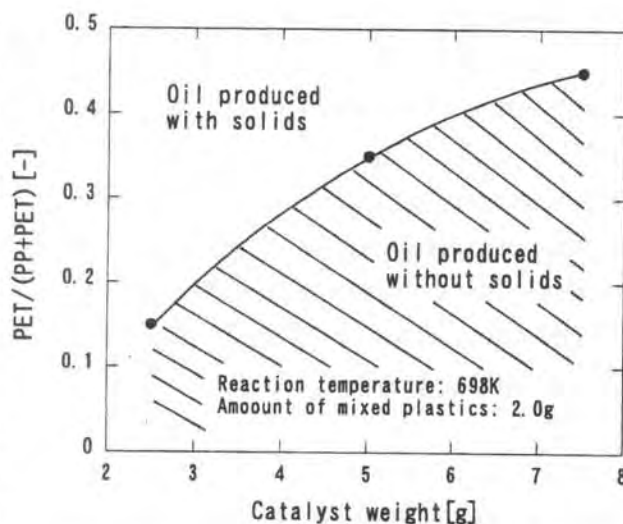


Fig. 2 Operating conditions that produce oil without solid

PP pyrolysates, having the higher hydrogen content, were mixed with them over $\text{TiO}_2/\text{SiO}_2$. As we had expected, PET could be decomposed into oils completely under the conditions shown by the area of oblique lines in Fig. 2. Outside of this area, solid materials were produced in the oil. Comparison of the carbon number fraction of the oily products from the PP and the PP and PET mixture under the conditions of PET/(PP+PET) ratio (we call this the PET ratio) of 0.15 can be seen in Fig. 3. It was found that oil produced from PET contains less amounts of $\text{C}_5\sim\text{C}_{10}$ hydrocarbons and larger amounts of C_{12+} hydrocarbons compared with the oil from PP. As the PET ratio increased, this tendency becomes more remarkable because C_{12+} fractions are due to aromatics from PET.

Yield of oil for 0.15 PET ratio and with various amounts of catalyst can be seen in Fig. 4. At PET ratio of 0.15 and the catalyst weight at 2.5g, the yield of oil was about 70%, but decreased with increasing catalyst weight. The greater the catalyst weight, the lighter the fraction of oils, because the heavier components were decomposed on the catalyst surface into lighter oils. We then characterized the surface of the catalyst to clarify the decomposition mechanism. The acidity of the catalyst was characterized using FT-IR spectroscopy of the adsorbed pyridine. In general, pyridine combines with Lewis acidic sites to form coordinated pyridine (PyL) and pyridinium ion (PyB) with Brønsted acidic sites [4, 5]. The peaks were found to be at 1446, 1490 and 1608 cm^{-1} in the FT-IR spectra of adsorbed pyridine on the $\text{TiO}_2/\text{SiO}_2$ catalyst as shown in Table 1. They correspond to the peaks of coordinated pyridine. No peak was found for Brønsted

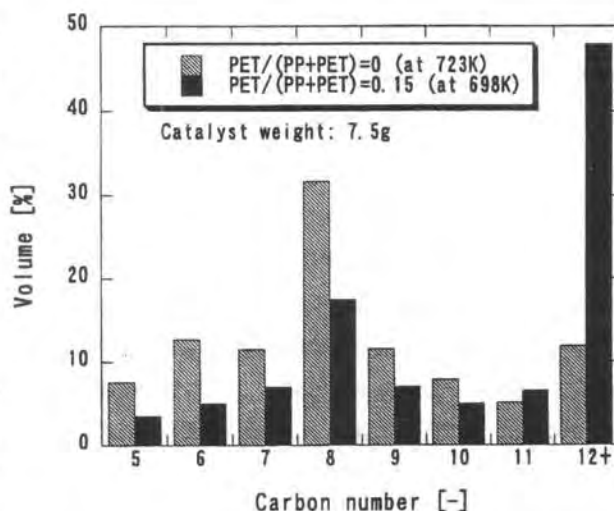


Fig. 3 Changes of carbon number fractions due to the changes of PET/(PP+PET) ratios (0 and 0.15) and reaction temperatures (723K and 698K respectively)

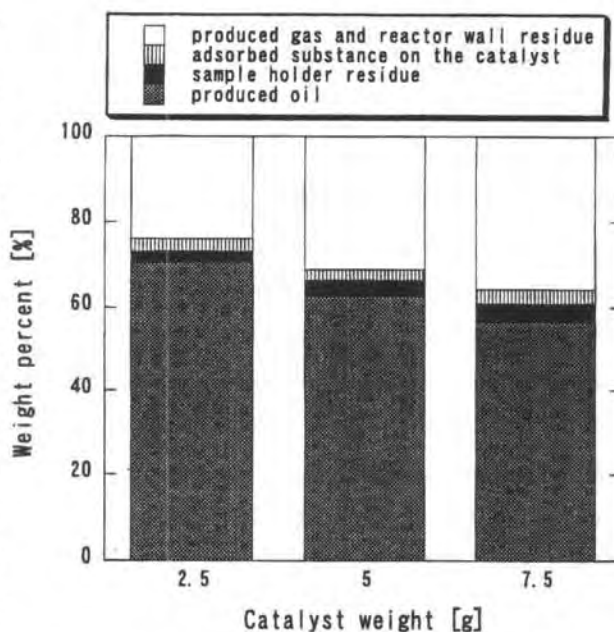


Fig. 4 Produced oil yield with changing catalyst weight

Table 1 Assignment of Infrared absorption bands of adsorbed pyridine in the range from 1700 to 1400 cm^{-1}

Vibration mode	PyB (cm^{-1})	PyL (cm^{-1})	$\text{TiO}_2/\text{SiO}_2$ (cm^{-1})
8a	1640-1634	1615-1592	1608
19a	1490-1478	1490-1471	1492
19b	1542-1525	1461-1437	1446

acidic sites, so we conclude that the acidic sites on the catalyst are the Lewis sites, which can deprive hydride from PP pyrolysates. The PET pyrolysates break down into lighter pyrolysate fraction, and the PET pyrolysate pick up the hydride moved from the PP fraction. Mobility of hydrogen on the surface was confirmed in the previous paper [1]. In addition, the oxygen in PET was found to be partly released as CO and CO₂, which were detected by gas chromatography. No oxygenated hydrocarbons could be detected in the oils produced.

Conclusion

Mixed plastics consisting of PP and PET were converted into oils using a TiO₂/SiO₂ catalyst, without the formation of phthalic acids. The reaction of PP derived hydride on Lewis acidic sites with pyrolysates of PET is the cause for the production of oil and gas. If the oil comprised of large amounts of C₁₂₊, then there will be possibility to use it as fuel after catalytic reforming. In addition, because the mass ratio of PET in actual municipal plastic waste is less than the ratio we used, and thus we expect the conditions for the reaction to be better in a full scale operation.

Acknowledgement

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