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## Effect of Calcination Method on the Catalytic Degradation of Polystyrene using $\text{Al}_2\text{O}_3$ Supported Sn and Cd Catalysts

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**Abstract:** Catalytic degradation of polystyrene (PS) into liquid fuels has been carried out in a simple experimental set-up using 1% Sn/ $\text{Al}_2\text{O}_3$  and 1% Cd/ $\text{Al}_2\text{O}_3$  as catalyst. These catalysts were prepared by incipient wetness impregnation method and were subsequently calcined in a domestic microwave oven as well as using conventional method for comparison. A catalyst to PS ratio of 0.2 (w/w) was always used in the degradation reaction where the liquid product was collected and analysed quantitatively using Gas Chromatography (GC) with commercial fuel used as the standard. About 36-47% of PS was converted in the presence of 1% Sn/ $\text{Al}_2\text{O}_3$  and 1% Cd/ $\text{Al}_2\text{O}_3$  catalysts as compared to only 25% of PS converted in the absence of any catalyst. The selectivity to liquid product is between 86-97% while selectivity to gaseous product is between 3-14%. From the liquid produced, aromatic compounds are the major component in all cases, followed by isoalkanes and alkenes. Alcohol is only detected from thermal cracking of PS while n-alkane was never detected. The aromatic compounds consist of ethylbenzene as the main component and n-propyl benzene as the minor component. Styrene was never detected in all cases. It is suggested that styrene undergo hydrogenation to ethylbenzene under the experimental condition. Microwave calcinations promote the yield to diesel in the presence of 1% Sn/ $\text{Al}_2\text{O}_3$ , while the formation of diesel-like components were suppressed in the presence of microwave calcined 1% Cd/ $\text{Al}_2\text{O}_3$  catalysts.

**Key words:** Polystyrene, recycling, liquid fuel, kerosene, petrol, diesel, microwave calcined

### INTRODUCTION

Plastic waste disposal has been recognised as a worldwide environmental problem. Several methods have been proposed for recycling of waste polymers, in particular their conversion to chemicals and fuels, as a very attractive way to improve the waste disposal situation from both ecological and economical point of view. In this method, the polyolefins (polyethylene (PE), polypropylene (PP) and polystyrene (PS)) are thermally or catalytically degraded into gases and oils. However, in the thermal degradation of plastic, many hydrocarbons having a wide range distribution of the carbon atom number are formed (Sodero *et al.*, 1996). In contrast, the oils produced by catalytic degradation are known to contain a relatively narrow distribution of hydrocarbons (Bagri and Williams, 2002).

In contrast with PE, PP and PS can be thermally depolymerised at relatively low temperature to obtain the monomer styrene with high selectivity (Zhang *et al.*, 1995). On the other hand, the use of solid acid such as

zeolites, alumina and silica-alumina as catalysts produce a significant modification of the selectivity towards benzene, ethylbenzene and cumene (Audisio *et al.*, 1990). Recently, solid bases, especially BaO, were found more effective than solid acids for the degradation of PS to styrene monomer and dimer (Ukei *et al.*, 2000). Therefore, the purpose of this study is to evaluate the performance of the 1% Sn and Cd supported on  $\text{Al}_2\text{O}_3$  catalysts in the catalytic degradation of PS. To date, no publication was reported on the use of  $\text{Al}_2\text{O}_3$  supported Sn and Cd catalysts for the catalytic cracking of PS. The effect of calcinations method on the product distribution from the degradation of PS was also investigated, employing a simple batch reactor at atmospheric pressure.

### MATERIALS AND METHODS

One percent Sn and Cd supported on  $\text{Al}_2\text{O}_3$  catalysts were prepared using an incipient wetness impregnation method where the required amount of  $\text{SnCl}_4$  (Hayashi Pure Chemical Ind. Ltd) and  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  (Merck),

respectively was dissolved in a sufficient amount of deionised water in a beaker before  $\text{Al}_2\text{O}_3$  (Alfa Aesar,  $103 \text{ m}^2 \text{ g}^{-1}$ ,  $250\text{-}710 \text{ }\mu\text{m}$ ) was added to the solution. The mixtures were stirred for  $\frac{1}{2}$  h and then left to stand for 2 h before drying at  $120^\circ\text{C}$  and later calcined in a domestic microwave oven at 650 W for 5 (AB-2) and 10 (AB-3) min. The dried mixtures were also calcined using a conventional method at  $500^\circ\text{C}$  for 16 h as a comparison (AB-1). The surface area for all catalysts was determined from  $\text{N}_2$  adsorption-desorption technique using Micromeritic ASAP 2010.

Catalytic degradation of polystyrene (PS) waste (Idemitsu Petrochemicals (M) Sdn. Bhd., Pasir Gudang, Johor) into liquid fuels was carried out in a simple experimental set-up using the catalysts prepared above. A catalyst to PS ratio of 0.2 (w/w) was always used in the catalytic degradation reaction where, PS was converted into gaseous and organic liquid products. Thermal degradation of PS was also performed as a controlled reaction. Only the liquid product was collected and analysed using Fourier Transform Infrared Spectroscopy (FTIR) (Perkin Elmer GX) and Gas Chromatography (GC) (HP 5890A-Chestation HP 336GC) equipped with a TCD detector. The liquid samples were diluted 100 times with chloroform prior to analysis with GC. The chromatograms of the organic liquid were compared to those of hydrocarbons standard for  $\text{C}_5\text{-C}_{12}$  (alkanes, alkenes, isoalkanes and aromatics) (SUPELCO, USA) as well as commercial fuel (petrol, diesel, kerosene and alcohol) (SHELL, Bandar Baru Bangi).

## RESULTS AND DISCUSSION

$\text{N}_2$  adsorption-desorption isotherms for all catalysts show a hysteresis loop, which is a characteristic feature of the mesoporous materials (Li *et al.*, 2002; Pierre *et al.*, 1998), thus all catalysts are Type IV according to IUPAC classification. All samples exhibit an almost parallel and vertical adsorption-desorption branches over a wide range of P/Po showing the H1 type of the hysteresis loop. Such type of hysteresis loop is often associated with cylindrical pores open at both ends (Mohan and Brock, 2003).

Table 1 shows the BET surface area for the Sn and Cd supported  $\text{Al}_2\text{O}_3$  catalysts. Slight reduction in surface area of supported catalysts were observed as compared to the bare  $\text{Al}_2\text{O}_3$  ( $103 \text{ m}^2 \text{ g}^{-1}$ ) which is due to incorporation of 1% metal into the pores of the  $\text{Al}_2\text{O}_3$ . BET results show that the different calcinations technique does not have a significant effect on the surface area of the catalyst, which could be due to the low metal loading (1%) used in both catalysts formulation.

Table 1: BET surface area of the 1% Sn/ $\text{Al}_2\text{O}_3$  and 1% Cd/ $\text{Al}_2\text{O}_3$  catalyst

Catalyst	BET surface area ( $\text{m}^2 \text{ g}^{-1}$ )
Sn-1	88
Sn-2	92
Sn-3	90
Cd-1	92
Cd-2	96
Cd-3	92

Table 2: Degradation of PS to gaseous and liquid products

Catalyst	Total Conversion (%)	Residue (%)	Selectivity (%)	
			Liquid	Gaseous
Without catalyst	25.25	74.75	97.0	3.0
Sn-1	46.67	53.33	91.43	8.57
Sn-2	45.33	54.67	95.59	4.41
Sn-3	47.00	53.00	89.19	10.81
Cd-1	38.92	61.08	86.07	13.93
Cd-2	36.33	63.67	91.30	8.70
Cd-3	41.80	58.20	87.73	12.27

Table 2 shows the conversion to liquid and gaseous products from the degradation of PS in the absence and presence of catalysts. In the absence of a catalyst, only 25.25% of PS undergoes thermal degradation. The conversion of PS increases in the presence of a catalyst with about 45.3-47.0% and 36.3-41.8% PS conversion were achieved when 1% Sn/ $\text{Al}_2\text{O}_3$  and 1% Cd/ $\text{Al}_2\text{O}_3$  were used respectively. The residue left after the catalytic degradation was quite high (53.00-63.67%) while the highest PS residue was observed from thermal degradation of PS. This shows that the presence of a catalyst is important to accelerate the degradation process.

However, thermal degradation of PS showed the least selectivity to gaseous product with only 3% (Table 2). The selectivity to gaseous product is the highest when 1% Cd/ $\text{Al}_2\text{O}_3$  catalyst was used as catalyst in the degradation of PS with up to 13.9% selectivity even though the PS conversions are slightly lower than that produced by 1% Sn/ $\text{Al}_2\text{O}_3$  catalysts. Williams and Bagri (2004) have reported that the presence of catalyst increases the yield of gas and decreases the yield of oil produced from recycling of PS. Similar observation has been reported by Kim *et al.* (2002) in the recycling of PP and PS mixture using silica-alumina, HZSM-5 and natural clinoptilolite zeolite where all the catalysts produced higher amount of gases and lower amount of residues than thermal degradation did. It is well known that the degraded fragments of PS have more difficulties to penetrate into the active sites of catalysts due to their structure containing aromatic group (Kim *et al.*, 2002).

For both the 1% Sn/ $\text{Al}_2\text{O}_3$  and 1% Cd/ $\text{Al}_2\text{O}_3$  catalysts, the catalyst calcined in microwave oven for duration of 5 min show the highest selectivity to liquid product even though the total conversion is the lowest.

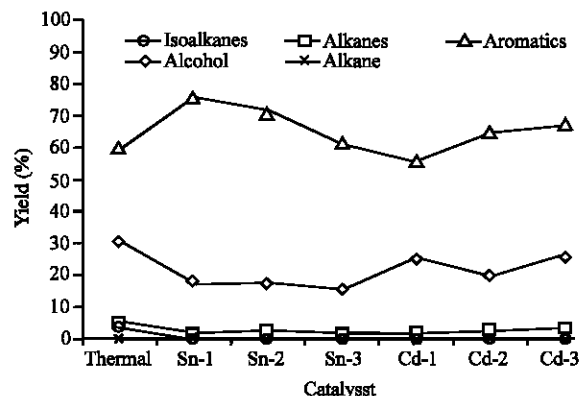


Fig. 1: Distribution of hydrocarbon components in organic liquid collected from degradation of PS

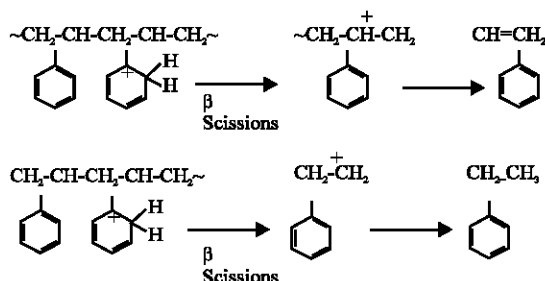


Fig. 2: C-C  $\beta$  scissions within the PS chains (Audisio *et al.*, 1990)

Both catalysts calcined in microwave oven for 5 min could due to the slightly higher surface area exhibit this. Thus, calcinations methods influence the total surface area of a catalyst, which in turn influences the total conversion influences the total conversion of PS and the selectivity to liquid and gaseous products.

FTIR analysis was carried out to determine the functional groups present in the liquid product. All FTIR spectrum shows existence of similar peaks except the spectrum for thermal cracking of PS where the appearance of OH stretching peak was observed between  $3600-3200\text{ cm}^{-1}$  indicating the presence of molecules with hydroxyl group like alcohol.

Table 3 shows the Hydrocarbon (HC) groups detected in the liquid samples produced from the catalytic degradation of PS.

Figure 1 shows the hydrocarbon components exist in the organic liquid collected from the degradation of PS. It can be seen that degradation of PS, in all cases, gives aromatic hydrocarbons as the major hydrocarbon group with 55.53-75.85%, followed by isoalkane and alkene. Kim *et al.* (2002) reported that almost all of the liquid products in the mixture of PP and PS degradation are

Table 3: Functional group exists in the liquid product (Socrates, 2001)

Wavenumber ( $\text{cm}^{-1}$ )	Vibrating group	HC Group
2800 - 3000	C-H stretching	Alkane
1640 - 1780	C=C stretching	Alkene
1580 - 1650	C=C stretching	Aromatic
1350 - 1475	C-H bending	Alkane
650-900	C-H bending	Aromatic

aromatics since they are stable enough not to be further cracked or hydrogenated to paraffins or olefins.

As observed from the FTIR analysis, alcohol group is only present in the liquid produced from thermal cracking while n-alkane was never detected in all samples. This suggests that the PS degradation occurs very fast, thus cracking to the simple structures like n-alkane is not allowed.

The mechanisms for the catalytic degradation of PS have been proposed by Faravelli *et al.* (2001) which consist of initiation, propagation and termination steps. These steps involve radical formation from C-C  $\beta$  scissions. From the classification of liquid product into hydrocarbon groups shows that under experimental conditions used in this work, PS macromolecules undergo C-C  $\beta$  scissions in the presence of 1% Sn/ $\text{Al}_2\text{O}_3$  and 1% Cd/ $\text{Al}_2\text{O}_3$  catalysts as previously suggested by Audisio *et al.* (1990) (Fig. 2).

Thus, major product is expected to be aromatic groups followed by isoalkane and alkene. Formation of isoalkane is possible through ring-opening step. From the isoalkane produced, the main component is 2,3-dimethyl hexane, followed by 3-methyl hexane and 2,2-dimethyl pentane. The only alkene component present in the liquid product is cis-2-heptene.

Detailed analysis shows that the major component of the aromatic hydrocarbons produced from the degradation of PS whether in the absence or presence of catalyst is ethyl benzene (Fig. 3). About 80% selectivity of the aromatic hydrocarbons produced in the absence of catalyst and between 85-92% of the aromatic hydrocarbon produced in the presence of 1% Sn/ $\text{Al}_2\text{O}_3$  and 1% Cd/ $\text{Al}_2\text{O}_3$  catalysts are ethyl benzene. Other aromatic compound detected is only n-propyl benzene (7-14% selectivity).

Styrene was never detected in the organic liquid collected from the degradation of PS whether in the absence or presence of catalyst under the experimental conditions used in this work. However, the formation of styrene as a major product under thermal degradation of PS has been reported by Zhang *et al.* (1995) and later supported by Ukei *et al.* (2000). On the other hand, Lee *et al.* (2003) observed benzene as the major product in the liquid produced from catalytic cracking of PS in a fluidized-bed reactor in the presence of ZSM-5 type zeolite catalysts. Other products include ethyl

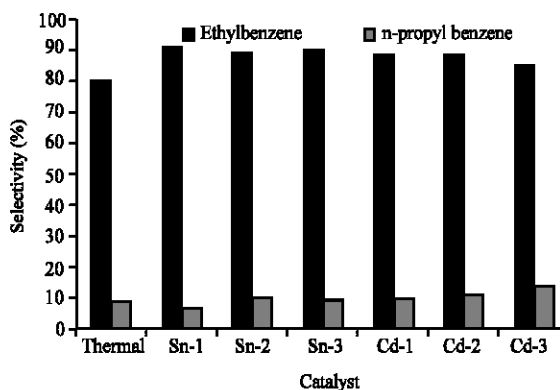


Fig. 3: Selectivity of aromatic hydrocarbons produced from the degradation of PS

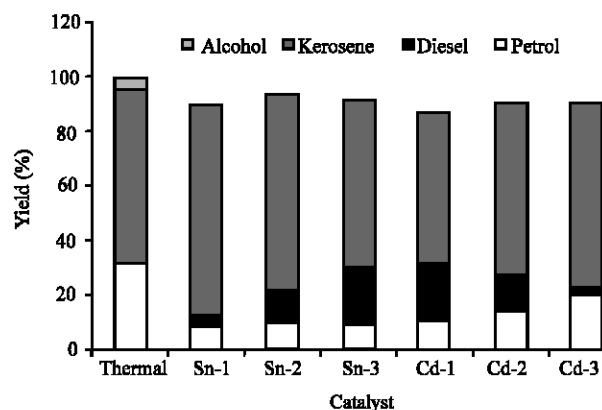


Fig. 4: Selectivity of OLP suitable for use as fuels

benzene,  $\alpha$ -methyl styrene, styrene monomer and toluene (Lee *et al.*, 2003).

Kim *et al.* (2002) found that the yield to styrene decreases as the yield to ethyl benzene increases when protonated catalysts were used. They suggested that the hydrogenation of degraded styrene can occur more easily in the protonated catalysts and that it leads to the increased production of ethyl benzene. Ogawa *et al.* (1982) reported the hydrogenation of styrene monomer to ethylbenzene with silica-alumina catalyst at 300°C. The most likely reaction pathway of the acid catalyzed cracking of PS involves the attack of proton associated with a Bronsted acid site to the aromatic rings of PS, due to the reactivity of its side phenyl groups towards electrophilic reagents. The resulting carbenium ion may then undergo  $\beta$ -scission followed by a hydrogen transfer.

However, Nanbu *et al.* (1987) reported that the protonated polymer backbone could also proceed through cross-linking reactions among adjacent polymeric chains or even inside the same polymer. Serrano *et al.* (2000) reported that the cross-linking reactions were favoured by

strong Bronsted acidic sites, especially at low temperatures. When the cross-linking reactions are accelerated, the competing catalytic cracking may occur to a smaller extent. Silica-alumina (SA), having medium strength Lewis acidic sites with relatively small amount of Bronsted acid sites, does not seem to promote these cross-linking reactions very significantly, but accelerate hydrogenation reactions. This may be the reason why styrene was never detected in the liquid produced and a high amount of ethyl benzene was detected in the degradation of PS (Lee *et al.*, 2001).

Commercial fuels of petrol, diesel, kerosene and alcohol were used in determination of hydrocarbon components exist in the organic liquid collected from the degradation of PS for its suitability for use as fuels. The distribution of these fuel components in the organic liquid is shown in Fig. 4 where at least 96.43% (v/v) of hydrocarbon components derived from the degradation of PS under experimental conditions used are suitable for blending into various fuels. Results show that the thermal degradation of PS yielded kerosene as a major fuel (64.0%) and petrol as secondary fuel components (31.99%) while alcohol is produced in trace amount (4%).

Kerosene is still the major product yielded in the degradation of PS in the presence of  $\text{Al}_2\text{O}_3$  supported Sn and Cd catalysts. However, the volume of kerosene reduces as diesel concentration increases when the calcinations method of the Sn catalyst is changed from conventional to microwave irradiation. On the other hand, when Cd catalyst was calcined by microwave irradiation, the concentration of both kerosene and petrol increase as the concentration of diesel decreases.

The differences in product distribution is suggested to be due to the calcinations method used where conventional calcinations method normally gives  $\text{Al}_2\text{O}_3$  supported catalysts a mesoporous structure while the microwave irradiated catalysts normally have nano crystalline structures. Similar observation was reported by Chen and co-workers in the microwave-assisted synthesis of Pt/C catalysts for fuel cell applications (Chen *et al.*, 2002).

## CONCLUSION

PS has been successfully pyrolysed via thermal and catalytic cracking in the presence of 1% Sn/ $\text{Al}_2\text{O}_3$  and 1% Cd/ $\text{Al}_2\text{O}_3$  as catalyst. Major component in liquid product is aromatic hydrocarbon with at least 80% selectivity to ethylbenzene in all cases. Alcohol in small yield is only detected from thermal cracking of PS. Liquid product is suitable to be used as fuel with kerosene as the main component in all cases. In the presence of 1% Sn/ $\text{Al}_2\text{O}_3$

catalyst, the yield to diesel increases as the yield to kerosene decreases when the calcinations of catalyst were changed from conventional method to microwave calcinations. However, the reversed is observed when 1% Cd/Al<sub>2</sub>O<sub>3</sub> was used as catalyst.

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