

The Changes in the Structure and Catalytic Activity of Iron Oxides During the Degradation of ABS into Fuel Oil

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Introduction

The degradation of waste plastic into fuel is a sustainable method for saving valuable petroleum resources. ABS represents about 3-5 wt% of the municipal plastic waste. Nitrogen (N) coming from the acrylonitrile units in ABS remains in the degradation oil¹ and leads to the corrosion of engine parts and the formation of very harmful compounds when the oils are used as fuel. Because of these problems it is very important to decrease, as low as possible, the amount of N in ABS degradation oil.

Purpose of the Study

In this study the changes of the activity and the structure of Goethite (α -FeOOH), Maghemite (γ -Fe₂O₃) and a Magnetite carbon composite (Fe₃O₄-C) iron catalysts during the degradation of N-containing compounds was studied.

Experimental Methods

10g of ABS were degraded at 400°C in a glass reactor, under atmospheric pressure, by semi-batch operation. 2g catalysts were either mixed with the polymer (liquid phase contact - LPC) or laid on a stainless steel net in the middle of the reactor (vapor phase contact - VPC).

Degradation of 4-phenylbutyronitrile as model N-compound (MC) over α -FeOOH at 250, 300 and 400°C was performed in a flow-type reactor.

The degradation products were characterized by GC-TCD, GC-AED and GC-MS analysis.

Temperature programmed desorption/degradation (TPD) was performed for the catalysts and for 2 μ L of MC adsorbed on 0.05g α -FeOOH, fresh or heated in the TPD instrument up to 280, 350 and 400°C (A, B and C catalysts). XRD analysis of the catalysts was performed before and after reactions.

ABS degradation in semi-batch reactor

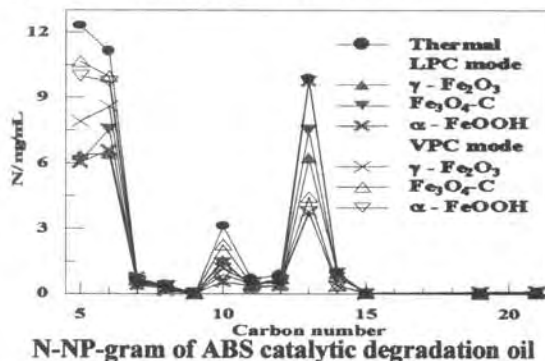
ABS thermal degradation produces mainly aliphatic and aromatic nitriles. 4-phenylbutyronitrile is the main N-containing degradation product (15-20 wt% in oil). Heterocyclic compounds such as pyridine, quinoline or pyrimidine were also observed.

Material Balance for ABS Catalytic Degradation

method	gas (%)	oil (%)	residue (%)	oil density (g/mL)	N in oil (mg/mL)
Thermal	7.2	49.5	43.3	0.868	39.9
Liquid phase contact mode (LPC)					
γ -Fe ₂ O ₃	8.6	44.3	47.1	0.872	22.7
Fe ₃ O ₄ -C	10.0	41.8	48.2	0.871	25.2
α -FeOOH	10.4	48.7	40.9	0.885	25.8
Vapor phase contact mode (VPC)					
γ -Fe ₂ O ₃	6.9	41.3	51.8	0.860	29.9
Fe ₃ O ₄ -C	6.7	39.6	53.7	0.861	26.6
α -FeOOH	9.5	40.7	49.8	0.865	23.8

The iron oxides are catalytically active for decreasing the concentration of N in ABS degradation oil from 40 to 23-30 mg/mL.

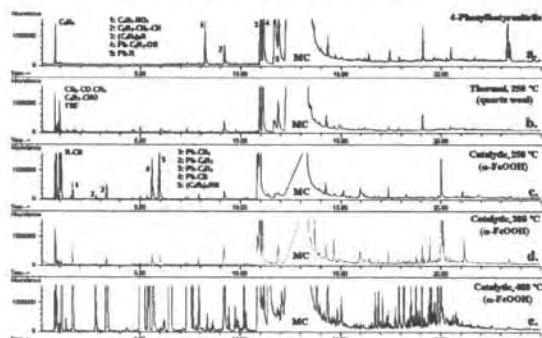
The VPC mode decreases the amount of gases and oil. The oil has lower density but the N amount increased using γ -Fe₂O₃ and Fe₃O₄-C. In VPC mode α -FeOOH decreases the amount of both 4-phenylbutyronitrile (n-C₁₃ in NP-gram) and the light aliphatic nitriles from n-C₅ - n-C₆.



N-NP-gram of ABS catalytic degradation oil

Degradation of 4-phenylbutyronitrile as model compound over α -FeOOH in flow-type reactor

The activity of α -FeOOH is the highest among the studied iron oxides and strongly depends on the contact mode. We used this catalyst for degradation of 4-phenylbutyronitrile at 250, 300 and 400 °C



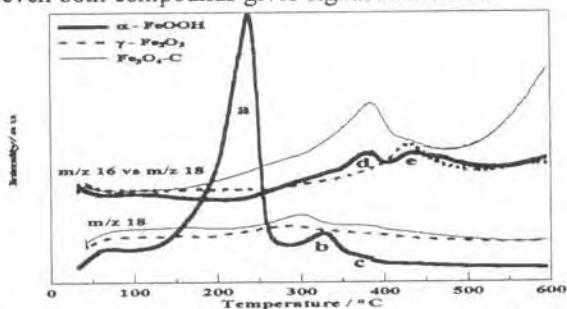
GC-MS chromatograms of model compound and its thermal and catalytic degradation products

The peak at 12.2 to 14 min. retention time corresponds to the model compound (MC). The other peaks in row a shows the presence of small amount of impurities. Thermal degradation of MC at 250°C gives mainly degradation products of the impurities (row b). α -FeOOH causes the degradation of MC even at 250°C (row c), producing light aliphatic nitriles (acetonitrile, propanenitrile, butane- and isobutane-nitrile, pentenenitrile) and aromatics (toluene, ethylbenzene, styrene). New compounds appear at 300°C, both lighter and especially heavier than MC (row d). The number and amount of heavy hydrocarbons increase for the degradation at 400°C. Compounds with condensed rings were identified so the degradation products have low quality.

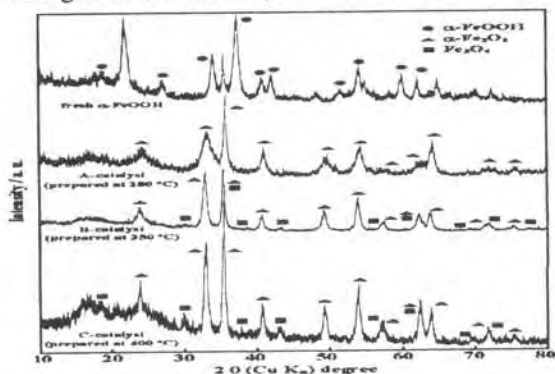
The XRD analysis shows changes in the composition and crystalline structure of the catalyst as following: α -FeOOH \rightarrow α -Fe₂O₃ \rightarrow Fe₃O₄.

TPD analysis of iron oxide catalysts

The m/z 16 vs m/z 18 ratio help to distinguish the water and oxygen elimination from the catalysts even both compounds gives signal for m/z 16.



TPD curves for α -FeOOH, γ -Fe₂O₃ and Fe₃O₄-C
 α -FeOOH loose water in a main peak at 273°C (peak a) and a small one at 328°C (peak b) followed by a long tail (marked c). The beginning of oxygen elimination overlap the peak b for water loose and shows two maxima at 378 and 430°C (peaks d and e), similar with Fe₃O₄-C and γ -Fe₂O₃ fresh catalysts. Three catalysts (A, B and C) were prepared by heating α -FeOOH at 280, 350 and 400°C.

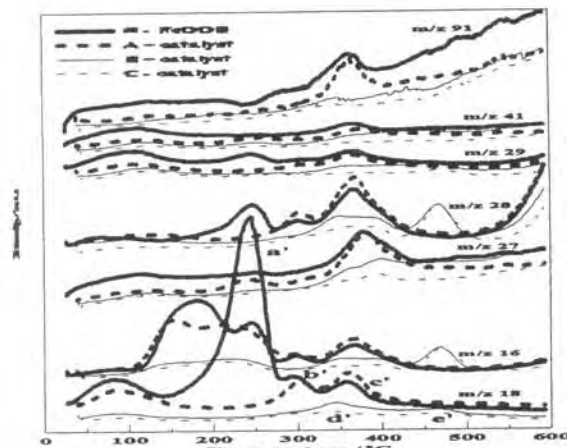


XRD analysis of α -FeOOH, A, B and C catalysts

The XRD diffractograms of A and B catalysts are similar with those of α -FeOOH after reaction with MC at 250 and 350°C. At 280°C (A catalyst) α -FeOOH is totally converted into α -Fe₂O₃ ($2\text{FeOOH}(\alpha) \rightarrow \text{Fe}_2\text{O}_3(\alpha) + \text{H}_2\text{O}$) but the peaks in the diffractogram are broad. The B-catalyst shows a high crystalline structure of α -Fe₂O₃ and the apparition of Fe₃O₄. The conversion of A-catalyst into B-catalyst is accompanied by water and oxygen elimination in 280-350°C range. This suggest the presence of a "hydrohematite" structure in A-catalyst, that is less stable than the normal α -Fe₂O₃ and is easy reduced to Fe₃O₄ ($3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{O}$). The formation of a "hydrohematite" structure, with some oxygen ions replaced by hydroxyl ions and apparition of cationic vacancies that causes the broadening of the XRD peaks was also suggested by Wolska and Scwertman² for the conversion of α -FeOOH into α -Fe₂O₃. The final form of α -FeOOH after heating at 600°C is Fe₃O₄.

TPD analysis of model compound over α -FeOOH

In reaction with MC, the water elimination (m/z 18) from α -FeOOH occurs in three steps with maxima at 245, 297 and 358°C (a', b' and c'), with no peak for oxygen at 430°C like in pure α -FeOOH (peak e). The difference is due to the reduction of iron oxide by the organic compounds.



TPD curves for α -FeOOH/4-phenylbutyronitrile

The m/z 16 signal shows four peaks in 100-450°C range. The first one (181°C) corresponds to NH₃ (proved by peak for m/z 17 vs m/z 18, not shown). The other three peaks for m/z 16 overlap with peaks for water elimination and are related with oxygen from water or with CH₄.

All peaks for various organic fragments overlap with water elimination. Therefore the catalytic activity of α -FeOOH is due to the changes in the composition and crystalline structure. The peak at 245°C for m/z 27, 28 and 29 correspond to gases such as CH₄ and C₂H₆. m/z 91 (363°C) corresponds to toluene and ethylbenzene. m/z 16, 28, 29, 41 (368°C) correspond to aliphatic nitriles. m/z 27 (378°C) shows the evolution of HCN. m/z 78 at 396°C correspond to styrene monomer.

The evolution of organic and inorganic compounds changes for MC adsorbed on A, B and C catalysts.

A supplementary peak for water elimination appears at 465°C (peak e') in B and C catalysts, accompanied by peaks for m/z 16 (O) and 28 (CO). This shows an advanced reduction of iron oxide under the influence of organic compounds, with formation of water and CO. m/z 16 shows two flat plateaus at 120-230 and 350-390°C showing the decrease of NH₃ and light organic hydrocarbons. NH₃ is formed mainly on α -FeOOH but also on α -Fe₂O₃; Fe₃O₄ is less active. Treated catalysts show new peaks at 250°C for m/z 27 and 41 (HCN and CH₃CN). The intensity of these peaks decreases from A to C catalyst. The peaks of light organic compounds become broad in B and C catalysts so the MC degradation is less effective.

Conclusions

The efficiency of iron oxides in reducing nitrogen concentration in ABS degradation oil decreases as following: α -FeOOH(VPC) > α -FeOOH(LPC) > γ -Fe₂O₃ ~ Fe₃O₄-C. α -FeOOH is selective in converting 4-phenylbutyronitrile into light aliphatic nitriles only at low temperatures (250-300°C). During degradation α -FeOOH changes its composition and crystalline structure (α -FeOOH \rightarrow α -Fe₂O₃ \rightarrow Fe₃O₄) with water and oxygen elimination and losing its activity.

References

1. Brebu, M.; Uddin, M. A.; Muto, A.; Sakata, Y.; Vasile, C. *Energy and Fuels* **2000**, *14*, 920-928.
2. Wolska, E.; Schwertmann U. *Physica Status Solidi A* **1989**, *114*, K11.