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Catalytic Degradation of Acrylonitrile−Butadiene−Styrene into Fuel Oil 2. Changes in the Structure and Catalytic Activity of Iron Oxides

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The changes in the structure and catalytic activity of three iron oxides (α-FeOOH, γ-Fe$_2$O$_3$, and an Fe$_3$O$_4$−C composite) were studied by temperature-programmed desorption/degradation (TPD) and XRD analysis. Thermal desorption analysis was performed for the fresh iron oxide catalysts. Thermal degradation experiments were performed for 4-phenylbutyronitrile as nitrogen-containing model compound adsorbed over α-FeOOH, fresh or prepared by heating at 280, 350, and 400 °C. TPD was also performed for acrylonitrile−butadiene−styrene copolymer (ABS) mixed with α-FeOOH. XRD analysis was performed after each TPD experiment. Catalytic degradation of 4-phenylbutyronitrile over α-FeOOH leads to formation of light aliphatic nitriles and styrene derivatives. Increasing the temperature, α-FeOOH catalyst gradually changes its composition and crystalline structure, with decreasing the catalytic activity. The changes are accompanied by elimination of water and oxygen and can be schematically represented as follows: α-FeOOH → α-Fe$_2$O$_3$ → Fe$_3$O$_4$. Iron oxide catalysts act mainly on the primary products of ABS thermal degradation, but they can also degrade the chain end or branched styrene units in the polymer.

Introduction

Mixed plastic waste (MPW) usually contains polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET), poly(vinyl chloride) (PVC), acrylonitrile−butadiene−styrene (ABS), and others. ABS represents about 3−5 wt % of the MPW.[1] Its thermal degradation into fuel oil occurs differently with respect to other polymers due to the presence of nitrogen (N) coming from the acrylonitrile units. N remains in ABS degradation oil[2] and leads to the corrosion of engine parts and the formation of very harmful compounds when the oils are used as fuel.[3,4] Because of these problems it is very important to decrease, as low as possible, the amount of N in ABS degradation oil.

In our previous studies[5] we found that the thermal degradation of ABS by semibatch operation, at temperatures between 400 and 440 °C, gives 50−63 wt % oil. Substituted aromatics represent more than 50 wt % of the ABS degradation oil. N is present in oil mainly in compounds such as aliphatic and aromatic nitriles but also as dissolved HCN. 4-Phenylbutyronitryle is the main N-containing compound (ca. 19 wt %) obtained from ABS thermal degradation.

We also found[6] that α-FeOOH, γ-Fe$_2$O$_3$, and an Fe$_3$O$_4$−C composite iron oxide catalysts decrease the concentration of N in ABS degradation oil, from 40 to 23−30 mg/mL. At a low-temperature range of 250−300 °C α-FeOOH catalyst is selective in converting 4-phenylbutyronitrile into light aliphatic nitriles. After the catalytic degradation of ABS in a semibatch reactor all iron oxides were found to be converted into Fe$_3$O$_4$. The changes in the structure of α-FeOOH with temperature are accompanied with the formation of α-Fe$_2$O$_3$ as intermediary compound.

The discussions in this paper are focused on the changes in the structure and the activity of the iron oxides, as a second part of our study concerning the catalytic degradation of ABS into fuel oil. Temperature-programmed desorption/degradation (TPD) and XRD

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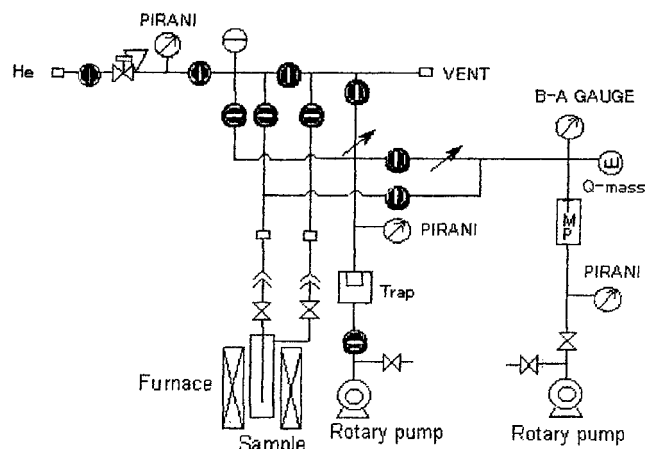
Figure 1. Schematic diagram of the temperature-programmed desorption/degradation (TPD) instrument.

analyses were performed for the catalysts and the catalyst/N-containing compound system. We used 4-phenylbutyronitrile as a model compound in reaction over α-FeOOH, to establish the active phase of the catalyst and the temperature range for its highest activity. TPD experiments with ABS polymer were also performed.

Experimental Section

1. Materials. Goethite (α-FeOOH; PDC-02), Maghemite (γ-Fe_2O_3; TR 99701) and a magnetite−carbon composite (Fe_3O_4−C; TR 990517) catalysts were cooperatively developed with Toda Kogyo Corporation, Hiroshima, Japan. Because of the three stages of FeOOH transformation during heating (see below), correspondingly, three catalysts (A, B, and C) were prepared by heating of granules of 0.05 g of α-FeOOH by 10 °C/min in TPD instrument up to 280, 350, and 400 °C, respectively, and then cooling to room temperature. 4-Phenylbutyronitrile (99% purity) and acrylonitrile−butadiene−styrene powder copolymer (ABS) containing 19−22% acrylonitrile, 37−39% butadiene, and 30−32% styrene units were obtained from Aldrich Chemical Co.

(2) Temperature-Programmed Desorption/Degradation (TPD) Method. Temperature−programmed desorption/degradation (TPD) experiments were performed on a Multitask TPD-1-ATSP (BEL Japan Co.) instrument. The schematic diagram of the TPD instrument is shown in Figure 1. The experiments were conducted at 120 Torr in a helium (He) stream of 50 mL/min, heating the samples by 10 °C/min up to 600 °C. The structure of the catalysts after each TPD experiment was analyzed using a XRD (Shimadzu XD 3A diffractometer, Cu Kα radiation) instrument. Identification of the structures was made according to a X-ray powder data file.[7]

Three groups of TPD experiments were performed, for (a) iron oxide fresh catalysts, (b) α-FeOOH/4-phenylbutyronitrile, and (c) α-FeOOH/ABS.

Granules of 0.05 g were used in the first group of experiments, for the TPD analysis of the iron oxide fresh catalysts (α-FeOOH, γ-Fe_2O_3, and Fe_3O_4−C). The MS (Q-mass) detector of the TPD instrument was set to simultaneously scan the following m/z numbers: m/z 1 (H), m/z 16 (O), m/z 17 (OH), and m/z 18 (H_2O).

In the second group of experiments the degradation of 4-phenylbutyronitrile as N-containing model compound (MC) over fresh and treated α-FeOOH (A-, B-, and C-catalyst) was performed. For TPD analysis a 2 μL amount of model compound was adsorbed on granules of 0.05 g of catalyst. A
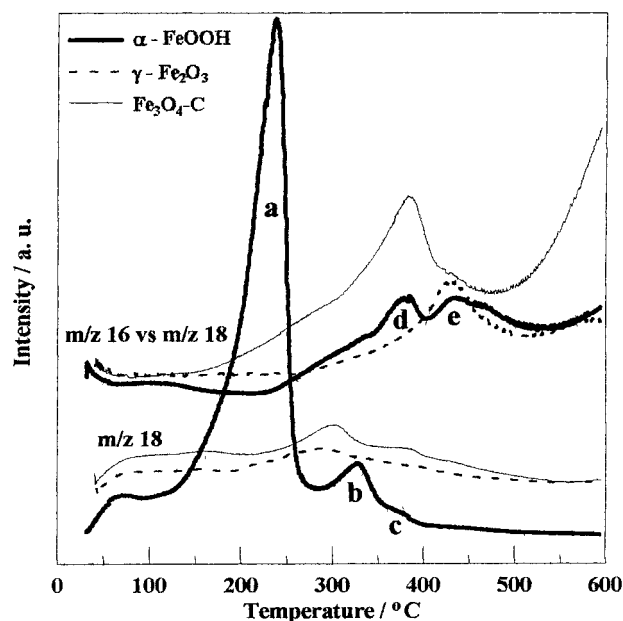
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Figure 2. TPD curves for α-FeOOH, γ-Fe_2O_3, and Fe_3O_4−C fresh catalysts.

0.01 g amount of powder ABS polymer or of pellets made from ABS mixed with α-FeOOH in a 5:1 weight ratio was used for the third group of TPD experiments. The following m/z number were scanned by the MS detector: m/z 1(H), m/z 14 (N or CH_2), m/z 15 (NH or CH_3), m/z 16 (O, NH_2, or CH_4), m/z 17 (NH_3 or OH), m/z 18 (H_2O), m/z 27 (HCN or C_2H_3), m/z 28 (CO or C_2H_4), m/z 29 (C_2H_5), m/z 41 (CH_3CN), m/z 54 (C_4H_8 or C_2H_4CN), m/z 78 (C_6H_6), and m/z 91 ($C_6H_5CH_2$). The results were compared with the ones obtained in the first part of our study,[6] when the catalytic degradation of ABS and 4-phenylbutyronitrile was performed in semibatch and flow-type reactor, respectively.

Results and Discussions

1. TPD Analysis of Iron Oxide Fresh Catalysts. The results of TPD analysis of α-FeOOH, γ-Fe_2O_3, and Fe_3O_4−C fresh catalysts are presented in Figure 2. Previous results for catalytic degradation of ABS and 4-phenylbutyronitrile in semibatch and flow-type reactor showed[6] that α-FeOOH is converted into Fe_3O_4 having α-Fe_2O_3 as intermediary compound. This process occurs with elimination of water and oxygen. The intensity of m/z 16 signal scanned by the TPD instrument will include the contribution of both the oxygen that resulted from the ionization of water in the MS detector and the oxygen that was eliminated from the structure of iron oxide. To distinguish the oxygen coming from different sources, we represented in Figure 2 the m/z 16 versus m/z 18 ratio (the signal of oxygen reported to the signal of water). This ratio will give a constant value for water elimination (equivalent to the ratio of these m/z numbers in the MS spectra of water) but will vary when oxygen elimination occurs.

Water elimination from α-FeOOH occurs in a main step having the maximum at 237 °C (peak a in Figure 2). A second step for water elimination is shown by a small peak, with the maximum at 328 °C (peak b in Figure 2), followed by a long tail in the 350−400 °C temperature range (marked c in Figure 2). The m/z 1 vs m/z 18 and m/z 17 vs m/z 18 ratios (not shown in Figure 2) have constant values over the whole
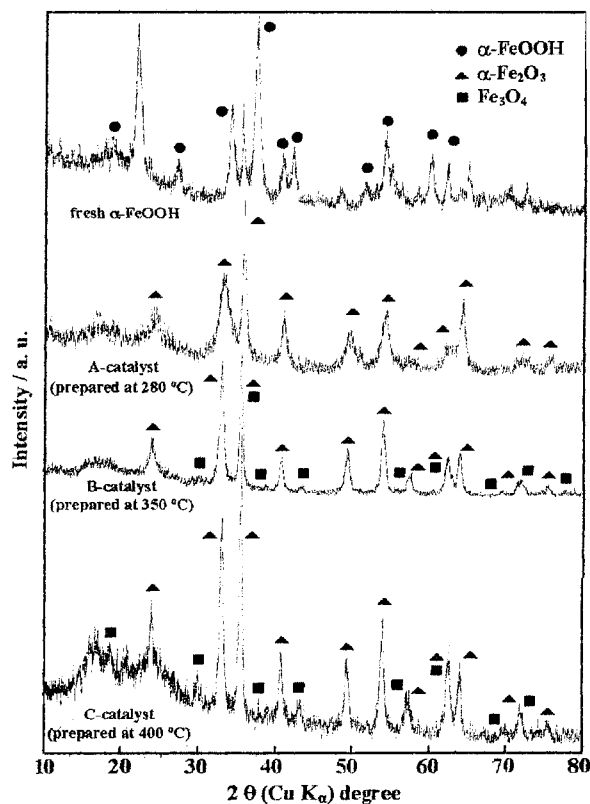
Figure 3. XRD diffractogram of α-FeOOH fresh and treated at 280, 350, and 400 °C (A-, B-, and C-catalysts).

0−600 °C temperature range as we expected from the corresponding ratios in the MS spectrum of water. The value of the m/z 16 vs m/z 18 ratio increases uniformly from 250 to 350 °C, showing the elimination of oxygen from the catalyst structure. Two peaks with maxima at 378 and 430 °C are present (Figure 2, peaks d and e), similar with the peaks for oxygen elimination from Fe_3O_4−C and γ-Fe_2O_3 fresh catalysts, respectively. Various studies[8,9] showed that water can be chemically adsorbed at the surface of the iron oxides due to either hydroxyl ions bonded to Fe^{3+} centers or to hydrogen bonds formed with the O^{2-} centers. This can explain the small peaks for water elimination (m/z 18) that appear in TPD analysis at about 280 °C for γ-Fe_2O_3 and about 300 and 375 °C for Fe_3O_4−C fresh catalysts (Figure 2).

We prepared three catalysts (A, B, and C) by stopping the heating of α-FeOOH at different temperatures for TPD: 280 °C, after the first peak of water elimination−peak a in Figure 2 (A-catalyst), 350 °C, after the second peak of water elimination−peak b in Figure 2 (B-catalyst) and 400 °C, after the first peak of oxygen elimination−peak d in Figure 2 (C-catalyst). These catalysts were analyzed by XRD and used for TPD experiments with 4-phenylbutyronitrile.

The XRD diffractograms of α-FeOOH heated at 280 °C (A-catalyst) and 350 °C (B-catalyst) (Figure 3) are similar with the diffractograms of α-FeOOH after reaction with 4-phenylbutyronitrile in flow-type reactor at 250 and 300 °C, respectively, (shown in Figure 9 of ref 6). The diffractogram of A-catalyst shows that α-FeOOH

is totally converted at 280 °C into α-Fe_2O_3, with rhombohedral symmetry and hexagonal oxygen packing. All peaks are broad, except for the one at the angle 2θ of 35.5° corresponding to the (110) plane. A similar XRD diffraction pattern was identified by Pomiès and co-workers[10] for the first stages of α-FeOOH conversion into α-Fe_2O_3. For B-catalyst all peaks of α-Fe_2O_3 are sharp, showing a high crystalline structure. Small peaks appear that corresponds to the Fe_3O_4, with a cubic symmetry and oxygen arrangement. The peaks of Fe_3O_4 increase in the diffractogram of C-catalyst. The crystalline structure of α-FeOOH, with orthorhombic symmetry and hexagonal oxygen packing, was not identified after heating at 280 °C (A-catalyst), but during TPD analysis of fresh α-FeOOH a small amount of water was still eliminated in 280−350 °C temperature range (peak b in Figure 2). Wolska and Scwertmann[11] shows that during conversion of α-FeOOH into α-Fe_2O_3 a "hydrohematite" structure is formed, with some oxygen ions replaced by hydroxyl ions. Cationic vacancies also appear causing the change in both the broadening and the intensity of the peaks in XRD diffractograms. Pomiès and co-workers[10] observed changes only in the broadening but not in the intensity of the peaks and they have attributed this effect to cationic plane stacking defects in the structure of the newly-formed α-Fe_2O_3. The authors are not in favor of the existence of "hydrohematite" and suggest that fine pores be formed in the first stages of α-FeOOH transformation into α-Fe_2O_3. The water eliminated during the reaction 2FeOOH (α) → Fe_2O_3 (α) + H_2O is trapped inside these pores, being removed at high temperatures. In our experimental conditions the second step of water elimination from α-FeOOH is accompanied by a slow elimination of oxygen and leads to the formation of Fe_3O_4, as proved by XRD analysis. This supports the idea of a "hydrohematite" structure in A-catalyst that is less stable than the normal α-Fe_2O_3 and is easily reduced to Fe_3O_4 according to the reaction $3Fe_2O_3 → 2Fe_3O_4 + O$. The elimination of oxygen above 400 °C (when the structure is equivalent to the B-catalyst) occurs in two steps with maxima at 378 and 430 °C (peaks d and e in Figure 2), similar with Fe_3O_4−C and γ-Fe_2O_3 fresh catalysts, respectively. The final form of α-FeOOH after heating at 600 °C in the TPD instrument is Fe_3O_4, as we expected from the experiments performed in a flow-type reactor.[6] The changes in the composition of α-FeOOH are accompanied by changes in the crystalline structure, as mentioned before, that also affect the activity of the catalyst.

(2) TPD Analysis of α-FeOOH/4-Phenylbutyronitrile System. In a previous paper[6] we showed that thermal degradation of 4-phenylbutyronitrile occurs even at 250 °C when the reaction is performed in a flow-type reactor. Heating 4-phenylbutyronitrile in the TPD instrument, no distinct peak was detected up to 600 °C (Figure 4). Only the signals for m/z 27, 28, and 91 start to increase at temperatures higher than 250 °C and continue up to the end of the experiment. This is explained by the fact that MC leaves the reactor as soon as the temperature reaches its boiling point but con-

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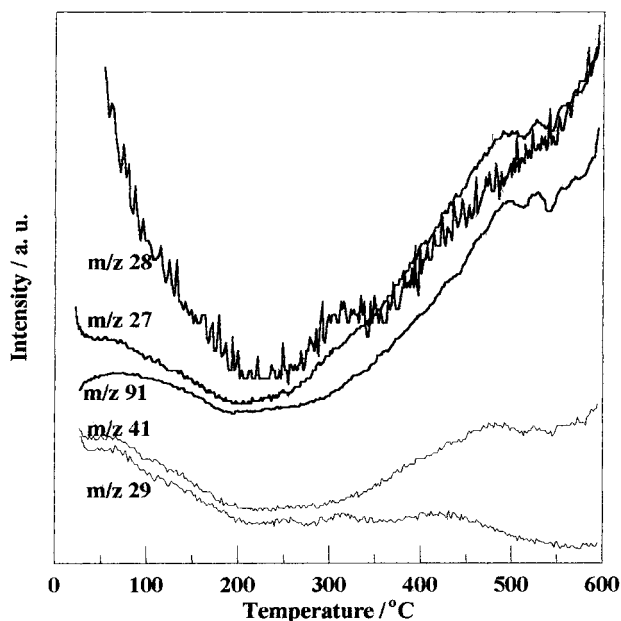
Figure 4. TPD curves for 4-phenylbutyronitrile.

denses on the cold wall of the glass line that connects the reactor with the MS detector, that are at the room temperature. Due to the very short residence time in the reactor, no degradation product is formed.

For TPD experiment with MC we used granules of 0.05 g of α-FeOOH catalyst, fresh or heated at 280 °C (A-catalyst), 350 °C (B-catalyst), and 400 °C (C-catalyst). A 2 μL volume of MC as N-containing model compound was adsorbed on the surface of the catalysts. Although 13 different m/z numbers were simultaneously scanned by the MS detector, only the most important 7 ones are presented in Figure 5.

2.1. TPD Experiments on Fresh α-FeOOH. The curve in Figure 5 corresponding to m/z 18 (H_2O) shows that when MC was adsorbed on α-FeOOH, the water is eliminated from the catalyst in a main step (peak a′ in Figure 5) with maximum at 245 °C (237 °C for the fresh α-FeOOH, peak a in Figure 2). The second step that appears at 328 °C for the fresh catalyst (peak b in Figure 2) is shifted now to a lower temperature of 297 °C (peak b′ in Figure 5). A third step of water elimination appears, that has the maximum at 358 °C (peak c′ in Figure 5). In TPD analysis of the fresh α-FeOOH only a long tail for water elimination appeared in this temperature range (marked c in Figure 2). The difference for α-FeOOH/MC system could be due to reduction of iron oxides by the organic compounds, and explains why no peak for m/z 16 attributed to oxygen elimination was detected at 430 °C as in the case of fresh α-FeOOH (peak e in Figure 2). These results show that during the reaction with MC the conversion of α-FeOOH into Fe_3O_4 occurs at lower temperature compared with the fresh catalyst in an inert atmosphere.

The signal for m/z 16 (O, NH_2, or CH_4) shows four peaks in the 100–450 °C temperature range. The first peak of m/z 16, with the maximum at 181 °C, is also the biggest one and is accompanied by peaks for m/z 14 (N or CH_2) and m/z 15 (NH or CH_3). The m/z 17 (OH or NH_3) vs m/z 18 (H_2O) ratio shows a peak only in 105–235 °C temperature range (not shown in Figure 5), proving the formation of ammonia, and remains con-
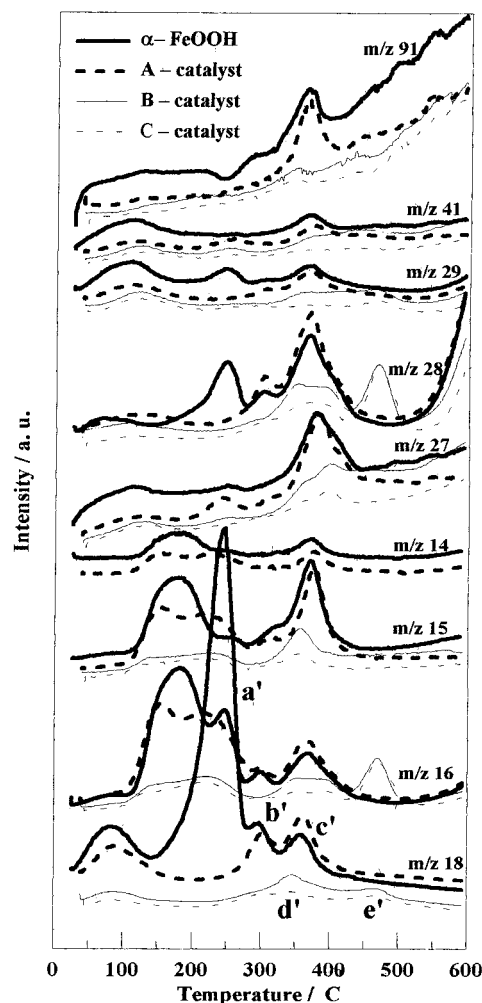

Figure 5. TPD curves for α-FeOOH/4-phenylbutyronitrile system.

stant with increasing the temperature up to 600 °C. The other three peaks of the m/z 16 signal except for the first one, having the maxima at 181 °C, overlap with the peaks of water elimination (a′, b′, and c′ for m/z 18 in Figure 5) and are related with oxygen from water ionization or with CH_4 from organic compounds.

All the m/z numbers of different organic fragments show peaks overlapped with the peaks of water elimination. These results suggest that the catalytic activity of α-FeOOH be due to the changes that appear in the composition and crystalline structure.

The water elimination at 245 °C (peak a′ in Figure 5) is accompanied by peaks for m/z 27 (C_2H_3), 28 (C_2H_4), and 29 (C_2H_5) and shoulders for m/z 14 and 15 (as shown in Figure 5). This suggests the formation of gaseous hydrocarbons such as CH_4 and C_2H_6 during this step.

Peaks for all scanned m/z numbers overlap in the 325–450 °C temperature range. Some of them have a maximum at the same temperature making it possible to distinguish the formation of different classes of hydrocarbons. The maximum at 363 °C for m/z 91 (C_6H_5-CH_2) shows the formation of toluene and ethylbenzene. The signals for m/z 14, 15, 16, 28, 29, and 41 have a maximum at 368 °C showing the formation of aliphatic nitriles (CH_3CN: m/z 14 and 41; C_2H_5CN: m/z 15 and 28; C_3H_7CN: m/z 29 and 41; C_4H_4CN: m/z 15, 28, and 41). The peak corresponding to m/z 27 (HCN or C_2H_3)

is very broad, overlapping the narrow peaks of the other m/z numbers, but is the only peak having the maximum at 378 °C. We can attribute this temperature to the maximum for the evolution of HCN. The maximum at 396 °C for m/z 78 (C_6H_6) shows the formation of styrene monomer. The signals for m/z 28 and 91 show a strong increase at high temperatures, similar to the case of the TPD experiment for only 4-phenylbutyronitrile (shown in Figure 4) so we can assign them to the model compound.

2.2. TPD Experiments on Treated α-FeOOH (A-, B-, and C-Catalysts). Differences appear in the evolution of organic and inorganic compounds when MC was adsorbed on α-FeOOH heated at 280 °C (A-catalyst), 350 °C (B-catalyst), and 400 °C (C-catalyst), as shown in Figure 5.

The main peak for m/z 18 that appears for α-FeOOH (a′ in Figure 5) is not present in A-, B-, and C-catalysts because the main part of water was eliminated during the treatment procedure. B- and C-catalysts show a broad peak for water elimination in the 300−400 °C temperature range (d′ in Figure 5). A supplementary peak appears at 465 °C (e′ in Figure 5), accompanied by peaks for m/z 16 (O) and 28 (CO). This suggests an advanced reduction of iron oxide that occurs at this temperature, under the influence of organic compounds, and leading to the formation of water and CO.

Ammonia formation on A-catalyst occurs in one wide step that consists of two not separated stages, the first one at 156 °C and the second one, wider, at 214 °C. This is proved by peaks for the m/z 17 vs m/z 18 ratio that appear in the same temperature range (not shown in Figure 5). When α-FeOOH was preheated at 350 °C (B-catalyst) and 400 °C (C-catalyst) the amount of NH_3 significantly decreases and also the peak of m/z 16 corresponding to organic hydrocarbons that becomes a flat plateau in the 350−390 °C temperature range. The formation of NH_3 from 4-phenylbutyronitrile seems to be generated mainly by α-FeOOH but also by the α-Fe_2O_3 structure that is present when the catalyst was preheated at 280 °C (A-catalyst). Fe_3O_4 is less active in formation of ammonia. This is proved by the decrease in NH_3 amount, observed for B- and C-catalysts, when the α-Fe_2O_3 structure starts to be converted into Fe_3O_4. These results explain the decreasing order α-FeOOH > γ-Fe_2O_3 > Fe_3O_4−C for the amount of NH_3 obtained during catalytic degradation of ABS in a semibatch reactor (shown in Table 2 of ref 6).

The peak of water elimination at 245 °C from fresh α-FeOOH (peak a in Figure 2) is not present for treated α-FeOOH, due to the preparation procedure. This leads to the disappearance of the peak for m/z 28 and 29 corresponding to gaseous hydrocarbons, that appear in the same temperature range for the degradation of the model compound over fresh α-FeOOH. These results explain the higher amount of gases obtained when α-FeOOH was used for catalytic degradation of ABS compared to γ-Fe_2O_3 and Fe_3O_4−C catalysts (shown in Table 1 of ref 6). Treated catalysts show new peaks at 250 °C for m/z 27 and 41 suggesting the formation of HCN and CH_3CN. The intensity of these peaks decreases in the following order: A- → B- > C-catalyst.

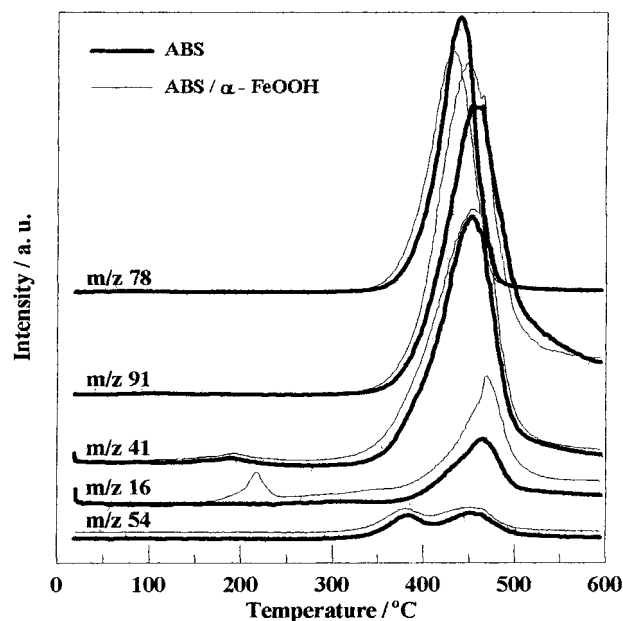When α-FeOOH catalyst was preheated at 350 °C (B-catalyst) and especially at 400 °C (C-catalyst), the peaks

Figure 6. TPD curves for α-FeOOH/ABS system.

for light organic compounds become broad, suggesting a low degree of degradation for 4-phenylbutyronitrile.

TPD analysis of 4-phenylbutyronitrile as a N-containing model compound over fresh and treated α-FeOOH proved that the active phases of the catalyst are the α-FeOOH and "hydrohematite" centers. This can be explained by the fact that these centers loose the water with formation of hydrogen and hydroxyl groups that can initiate the radicalic−ionic degradation of 4-phenylbutyronitrile, with formation of mainly ammonia and gases at temperatures lower than 275 °C. Fe_3O_4 oxide centers are less active. In this case, due to the strong adsorption on the catalyst, 4-phenylbutyronitrile remains inside the pores even at high temperatures, when thermal degradation occurs. The organic radicals that are formed can extract the oxygen from the structure of Fe_3O_4 leading to the elimination of water and carbon monoxide.

3. TPD Analysis of α-FeOOH/ABS System. Pellets were made from ABS polymer mixed with powder α-FeOOH in a 5:1 ratio (similar to catalytic degradation in semibatch operation).[6] TPD experiments were performed for 0.01 g of pellet and also for 0.01 g of powder of pure ABS. The signals for the most important 5 m/z numbers from the 13 simultaneously recorded ones, are presented in Figure 6.

For TPD analysis of ABS the signal for m/z 54 has a peak with the onset temperature at about 285 °C and the maximum at 384 °C. This peak is accompanied by shoulders for the signals of m/z 27 (C_2H_3) and 28 (C_2H_4) (not shown in Figure 6) and corresponds to $CH_2{=}CH{-}CH{=}CH_2$. Peaks corresponding to other organic fragments start to appear at about 340 °C and overlap having maxima in 440−466 °C temperature range. These results prove that the first product obtained during heating of ABS is the 2-butylene monomer coming from butadiene units in ABS, in good agreement with the results reported by Suzuki and co-workers[12] for ABS degradation studied by TGA-FTIR. For the

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400−500 °C temperature range we can distinguish the formation of various degradation products. At 440 °C the maximum for the signal of m/z 78 (C_6H_6) corresponds to formation of styrene. The maxima at 444 °C for m/z 14 (N or CH_2) and 27 (HCN or C_2H_3) (not shown in Figure 6) suggest the formation of HCN. Nitrile derivatives are indicated by the maxima at 451 °C for m/z 15 (CH_3) (not shown in Figure 6), 41 (CH_3CN), and 54 (here corresponding to CH_2CH_2CN). The maximum for m/z 91 at 460 °C corresponds to a $C_6H_5CH_2$ fragment coming from toluene and benzene derivatives. The maxima at 465 °C for m/z 16 (NH_2 or CH_4), 28 (C_2H_4), and 29 (C_2H_5) (the last two not shown in Figure 6) show the formation of NH_3 and gaseous products such as methane and ethane. The peak of m/z 16 has the highest onset temperature (about 365 °C), suggesting that NH_3 is produced at high temperatures only after the cyclization of acrylonitryle units in ABS, similar with the degradation of polyacrylonitrile,[13] while the other compounds come mainly from degradation of butadiene and styrene units.

The influence of α-FeOOH in ABS degradation in this experimental condition manifests by shifting to lower temperatures the maxima for the peak of m/z 78 (C_6H_6) and 91 ($C_6H_5CH_2$) with 7 and 14 °C, respectively. This very small effect was expected for the physical mixture of catalyst and ABS and the fast removal of the degradation products by the He flow. A stronger effect was recorded for the catalyst/MC system because the liquid MC protrudes from even the smallest pores of the catalyst increasing the contact time. However the differences suggest that the ABS macromolecule contains chain end or branched styrene units that can protrude from the pore of the catalyst, being degraded to styrene or benzene derivatives. The degradation of the polymeric chain starts from butadiene units and continues in styrene−acrylonitrile regions. This can be explained by the heterogeneous nature of ABS, the butadiene units having higher mobility compared with styrene−acrylonitrile units, as proved by Steeman and co-workers[14] using 2D-IR spectroscopy. Piton and Rivaton[15] showed that butadiene units are also the initiation sites for the photodegradation of ABS. The iron oxide catalysts act mainly on the primary degradation products of ABS, even in the case of liquid-phase contact mode.

Conclusions

The α-FeOOH catalyst gradually changes its composition and crystalline structure with increasing the temperature. The changes can be schematically represented as following: α-FeOOH → α-Fe_2O_3 → Fe_3O_4. The process is accompanied by two steps of water elimination (at 125−275 and 275−350 °C) and two steps of oxygen elimination (at 350−400 and 400−500 °C) from the structure of the catalyst. Catalytic degradation of 4-phenylbutyronitrile as a N-containing model compound over α-FeOOH is strongly related with the process of the elimination of the water from the structure of the catalyst. The catalytic activity of the species involved in the transformation of α-FeOOH decreases in the following order: α-FeOOH > hydrated α-Fe_2O_3 > α-Fe_2O_3 > Fe_3O_4. Iron oxide catalysts can degrade the chain end or branched styrene units in the ABS macromolecule, but they act mainly on the primary degradation products of the polymer.

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