Research Article

Reduction of Polymer Waste Pyrolysis Fractions over Pt/Al₂O₃ with Methanol Decomposition Hydrogen to Obtain Fuel-Grade Hydrocarbons

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Received 3 February 2014; Revised 12 May 2014; Accepted 19 May 2014; Published 11 June 2014

Academic Editor: M. Fernanda Carvalho

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The hydrogenation under atmospheric pressure of waste polymer pyrolysis fractions over 5% Pt/γ-Al₂O₃ with hydrogen from the catalytic decomposition of methanol over 5% CoO/SiO₂ has been performed. A 97–100% C=C bond hydrogenation selectivity was achieved at 300°C. The obtained saturated C₆–C₂₀ and C₂₀–C₃₀ fractions can be applied as blending material for fuels and lubricants, respectively, or as hydrocarbon feed. The applied coupled catalytic system exhibited high efficiency at 300°C for at least 5 hours.

1. Introduction

The production and application of polymers is an important part of the industrial and consumer market and has been the promoter of various technological breakthroughs. The influence of polymers on consumer goods continues to rise as more functional polymers increasingly substitute other materials in various applications. Growth in production and consumption has however led to an increase in the generation of polymer waste materials, which pose a major environmental and health hazard all over the world. Outright disposal in landfills and incineration generate further pollution of the soil, groundwater, and atmosphere [1, 2]. Moreover, on the long term, they are not economically viable. Secondary recycling does not provide a viable solution either because of the additional cost of modifying agents, initiators, compatibilizers, and fillers [3] added to the polymer during the process in order to restore the original functionality. Tertiary and quaternary recycling (chemical recycling) procedures have been found to be the most viable alternatives because they provide the possibility of transformation of the waste polymers into raw materials for other processes [4]. Tertiary processes constitute mainly catalytic cracking,

low- or high-temperature pyrolysis [5], or conversion with oils [6] and coal [7] which are mainly performed today. In these processes, the hydrogenation of high molecular weight unsaturated hydrocarbons contained in the saturated oils to their saturated counterparts is of significant importance. This is due to the possibility of application of the hydrogenated products as additives to fuels [8]. Isooctane, for example, obtained in the hydrogenation of isooctenes over Co/SiO₂ has been found to be an adequate substitute to MTBE [9]. Studies, therefore, on the hydrogenation of unsaturated hydrocarbons obtained after pyrolysis of waste polymers to their saturated counterparts as potential blending material or additives to fuel are justified.

Methanol, though a C₁ compound, has generated a lot of attention over the centuries. It remains the only primary alcohol, whose decomposition has been studied with as much interest as its synthesis. The possibilities of synthesis from renewable raw materials and its application as an alternative fuel and energy are reasons for which methanol has generated much interest. The studies on the transformation of methanol have involved oxidation for the synthesis of formaldehyde [10], methyl formate [11] or as an efficient catalyst probe [12]. In these reactions, however, hydrogen is not obtained because

it is consumed by oxygen to form water. The nature and composition of methanol decomposition products depend on the acid-base character of the heterogeneous catalysts [13] over which the process is performed as well as the addition of modifying compounds such as steam [14] to improve hydrogen yield. The process, which is primarily catalytic, is performed over proven effective catalysts comprising transition metals/oxides [15–18] and noble metals [19–21] at various temperatures. Methanol decomposition has attracted the most interest because of its potential as hydrogen precursor for fuel cells [22] and constitutes a safe liquid storage medium for hydrogen. In the literature, apart from its role as fuel for fuel cells, the hydrogen produced in the catalytic decomposition of methanol has not found any applications in chemical processes.

As part of our studies on waste transformation and management, we present the hydrogenation under atmospheric pressure of unsaturated hydrocarbons contained in waste polymer pyrolysis products with H_2 and CO obtained in the decomposition of methanol to obtain high-grade saturated counterparts applicable as blending material, as additives to fuel, or as raw materials for chemical processes.

2. Materials and Methods

2.1. Catalyst Supports, Active Phase Precursors, and Polymer Pyrolysis Fractions. Cobalt(II) nitrate hexahydrate and hexachloroplatinic acid were received from Aldrich. Amorphous SiO_2 (AEROSIL 200) and Al_2O_3 (AEROXID C) powders were obtained from Evonik Industries AG (Germany).

Two in-house obtained polymer waste pyrolysis fractions were taken for reduction reactions:

- (i) low-temperature ($<360^\circ C$) pyrolysis fraction of a wide range of polymers (F1) of average molecular weight 201.1 g/mol with an unsaturated hydrocarbon content of 56.6%;
- (ii) high-temperature ($>360^\circ C$) pyrolysis fraction of polymers (F2) of average molecular weight 313 g/mol with an unsaturated hydrocarbon content of 18.1%.

2.2. Catalyst Preparation

2.2.1. Supports. In the preparation of the silica support for the CoO active phase in the methanol decomposition catalyst—CoO/ SiO_2 , amorphous silica powder was mixed with an appropriate amount of twice-distilled deionized water, kneaded to a thick consistency, and then placed in a temperature-controlled chamber to be dried at 40, 80, and finally $120^\circ C$ for 24 h at each temperature. The oxide obtained in this process was then fractionalized on a sieve to obtain a grain fraction of 0.6–1.2 mm in diameter and then calcined at 250 and $600^\circ C$ for 4 h at each temperature.

The same drying and fractionation process was applied for alumina used as support for Pt in the hydrogenation catalyst—Pt/ $\gamma-Al_2O_3$. In this case, however, calcination was performed initially at $250^\circ C$ for 4 h and then at $550^\circ C$ for 4 h in order to ensure the formation of the γ phase.

2.2.2. Catalysts. The methanol decomposition catalyst CoO/ SiO_2 was prepared by the incipient wetness of an aqueous solution of cobalt(II) nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$] on the silica fraction obtained as described above. The amount of aqueous precursor was calculated as to obtain a 5% deposition of the active phase (CoO) on the support after calcination.

The hydrogenation catalyst Pt/ $\gamma-Al_2O_3$ was prepared according to the same procedure, whereby an aqueous solution of hexachloroplatinic acid [$H_2PtCl_6 \cdot x(H_2O)_6$] was used as active phase precursor. The reduction of the deposited $PtCl_2$ to the Pt phase was performed with the gaseous products from methanol decomposition.

2.3. Catalyst Characterization

2.3.1. Specific Surface Area. The specific surface area and porosity of the catalysts were measured in a Tristar II apparatus from Micromeritics. The samples were initially degassed under vacuum (16.0 Pa) at $300^\circ C$ for 3 h before analysis. Analysis was performed using the static method at 77 K with nitrogen as the adsorbent.

2.3.2. Surface Morphology. SEM-EDS analysis was performed using a JOEL JSM 6490LV apparatus equipped with an energy dispersive X-ray microanalyzer (EDS) with an acceleration voltage of 20 kV.

2.4. Reactions. The reaction system was comprised of an integrated catalytic system in which methanol decomposition was performed in Stage I and the gaseous products were directed to Stage II as reducing stream. A schematic representation is presented in Figure 1.

Stage I. 0.5 g of CoO/ SiO_2 was placed in a vertical tubular glass reactor with a fixed bed and calcined in a stream of air for 1 h at $450^\circ C$. The reactor was cooled to $100^\circ C$, the carrier gas changed to argon (1 L/h), and then methanol fed into it with an infusion pump at $0.9\text{ cm}^3/\text{h}$. The decomposition of methanol resumed at $100^\circ C$, but $350^\circ C$ was chosen as reaction temperature to ensure catalyst longevity. H_2 and CO mixture obtained in this reaction was then fed to Stage II (hydrogenation) reaction system.

Stage II. 0.5 g of $PtCl_2/\gamma-Al_2O_3$ was placed in a vertical tubular glass reactor and then calcined in a stream of air and then in nitrogen at $450^\circ C$ for 1 h at each temperature. The reactor was cooled to $100^\circ C$ and then methanol decomposition gaseous mixture ($2H_2 + CO$) fed into it and the temperature ramped at $10^\circ C/\text{min}$ to $450^\circ C$ and maintained for 1 h (Figure 3). The catalytic system was cooled to $100^\circ C$ and then waste polymer pyrolysis fractions were fed into it by an infusion pump at $3\text{ cm}^3/\text{h}$. The raw material stream was heated with a heating belt to $110^\circ C$ to ensure homogeneity and low viscosity. The reactions were carried out in a $100\text{--}400^\circ C$ temperature range and samples were collected at $100^\circ C$ intervals. The first sample was taken after the reaction had stabilized for 90 min at $100^\circ C$, after which the temperature was ramped to $200^\circ C$ at $5^\circ C/\text{min}$.

FIGURE 1: Schematic representation of the hydrogenation of polymer waste fractions with the hydrogen obtained in the catalytic decomposition of methanol.

FIGURE 2: SEM image and EDS analysis of methanol decomposition catalyst 5% CoO/SiO₂.

The second sample was taken after 30 min at this temperature. The samples at 300 and 400°C were taken after the reaction had stabilized at these temperatures for 30 minutes after being ramped at 5°C/min from the previous temperature. The liquid reaction products were passed through a condenser and analyzed while the gaseous products were passed through an alkaline and then an acidic absorber.

2.5. Substrate and Product Analysis. The composition of the substrate and the reaction products was analyzed by GC/MS instrument (HP 5890 II PLUS GC/5989 MS Engine) using a Carbowax capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness).

Methanol decomposition products were analyzed in BET/TPR/TPD/TPO ChemBet 3000 apparatus from Quantachrome coupled with a PrismaPlus 220 mass spectrometer from Pfeiffer. 2 mL of the gaseous mixture was taken from the outlet of the methanol decomposition reactor and injected into the apparatus. Argon (mass = 40) was used as carrier gas instead of N₂ (mass = 28) to avoid misinterpretation of the CO (mass = 28) signal.

3. Results and Discussion

3.1. Specific Surface Area. The specific surface area using the Brunner Emmett Teller method (S_{BET}) and pore volume

(Barrett-Joyner-Halenda (BJH) method) of the supports and the influence of the deposition of active phases on it are presented in Table 1.

A decrease in the surface area of the supports as well as an increase in the particle size was observed as a result of active phase deposition. Thus, for the silica support, 6.5% and 12.3% decrease were observed after the preparation of 5% CoO/SiO₂. 5% CoO/SiO₂ is a sample of the catalyst regenerated after a 24 h process. The higher decrease in its specific surface area (S_{BET}) can be attributed to carbonaceous deposits during methanol decomposition. For the modified alumina catalysts for alumina a 4.5% and 3.0% decrease in specific surface area. The higher decrease in S_{BET} of the hydrogen-reduced PtCl₂/Al₂O₃ can be attributed to a deeper reduction of the active phase. The higher pore volume (BJH adsorption) observed for the alumina-based catalysts could be as a result of the influence of the acidic platinum precursor—hexachloroplatinic acid.

3.2. CoO/SiO₂ Catalyst

3.2.1. SEM-EDS Analysis. The results of SEM-EDS analysis of the methanol decomposition catalyst performed after thermal treatment are presented in Figure 2. The magnification image of the CoO/SiO₂ particles shows a uniform deposition on the support without phase boundaries. EDS analysis confirms the presence of Co, O, and Si on the surface of

FIGURE 3: SEM image and EDS spectrum of $\text{PtCl}_2/\gamma\text{-Al}_2\text{O}_3$ prior to reduction with methanol decomposition gases.

TABLE 1: Specific surface areas of the supports and catalyst systems.

Catalyst	Specific surface area (S_{BET}) [m^2/g]	Pore volume [cm^3/g] (BJH adsorption)	Average particle size [nm]
SiO_2	198.8	0.7	30.2
5% CoO/SiO_2	185.9	0.7	32.3
*5% CoO/SiO_2	174.3	0.7	34.4
$\gamma\text{-Al}_2\text{O}_3$	92.7	0.3	64.7
5% $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ (H_2)	88.5	0.6	67.7
**5% $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ met	89.9	0.5	66.8

*5% CoO/SiO_2 : catalyst after methanol decomposition.

**5% $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ met: catalyst prepared with methanol decomposition gases.

the sample. N species from the active phase precursor (cobalt(II) nitrate hexahydrate) were not observed.

3.3. $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ Catalyst

3.3.1. SEM-EDS Analysis. The preparation, thermal treatment, and reduction of PtCl_2 have an influence on the activity of the platinum catalyst in the reduction of waste polymers. Reduction with hydrogen is deep and causes a partial separation of the round metal particles of platinum from alumina. Hydrogenation reactions therefore proceed by the initial adsorption of hydrogen on the surface of the metal and the desorbed proton further reacts with the substrate adsorbed on the oxide surface in what is referred to as spillover [23]. This would not be expected to take place in the case of reduction with a mixture of H_2 and CO from methanol decomposition. The platinum phase was expected to remain “chemically glued” [24] to the surface in a complex structure in a milder process due to the CO content in the reducing mixture. In the adopted prereaction PtCl_2 reduction procedure, calcination in air at 450°C followed by reduction for 1 h, no significant differences were observed between both samples reduced either by hydrogen or by the methanol decomposition mixture (Figures 4 and 5). Traces of chlorine were observed to be present on the catalyst surface in both samples as shown in Figure 4 as well as the peak to the left of the O peak in Figure 5. A reduction duration of a few hours would be appropriate in order to entirely eliminate chlorine from the samples. The results indicate, however, that

the $\text{H}_2 + \text{CO}$ mixture is as effective a medium in reducing the $\text{PtCl}_2/\gamma\text{-Al}_2\text{O}_3$ to the $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst as hydrogen gas.

3.4. Methanol Decomposition and the Determination of Optimal Reaction Conditions. The decomposition activity of CoO/SiO_2 was initially studied. This reaction has been carried out over a number of heterogeneous catalysts [25], but CoO/SiO_2 was chosen for the inert nature of SiO_2 allowing for the activity of only the deposited phase [13] and simplicity in preparation. Methanol was fed at $0.9 \text{ cm}^3/\text{h}$ into the reactor containing 5% CoO/SiO_2 . Argon at $1 \text{ dm}^3/\text{h}$ was applied as carrier gas. The gaseous mixture from methanol decomposition was passed through 0.5 g copper oxide placed in a tubular flow system vertical reactor in a furnace at 375°C . Reduction of the oxide to metallic copper was observed after about 5 min. The methanol decomposition reaction can thus be presented as follows according to the reaction

HCHO , H_2O , CO_2 , and methanol were found in the product mixture at temperatures below 350°C (in Figure 6(a)), so this temperature was chosen as optimal for the decomposition reaction and catalyst longevity (in Figure 6(b)).

The importance of catalytic decomposition of methanol lies in its potential significance as a safe carrier for hydrogen for fuel cells, chemical processes, and transportation. Depending on the feed and conditions (methanol-steam

FIGURE 4: SEM image and EDS spectrum of Pt/γ-Al₂O₃ after reduction with hydrogen. FIGURE 5: SEM image and EDS spectrum of Pt/γ-Al₂O₃ after reduction with methanol decomposition gases.

reforming and water-gas shift reaction), the reaction can also proceed in two different pathways [14]:

Hydrogen production can thus be improved by adding steam to the methanol feed in what is referred to as steam reforming. This would probably be necessary in the case reaction for higher hydrogen and substrate volumetric flow, but not in this reaction, in which the substrate flow was 3 cm³/h. Moreover, the disadvantage of steam reforming is in the production of carbon dioxide in the process. Steam reforming is environmentally justified when performed on materials which have their original source in plants (such as biooils from cellulosic materials), so the carbon dioxide equation is balanced [26, 27]. This is not the case in our reaction of obtaining high-value hydrocarbons from waste polymers of fossil fuel origin.

3.5. Hydrogenation of the Waste Polymer Pyrolysis Fractions

3.5.1. Fraction F1. For comparison purposes the reduction of F1 was initially performed over Pt/Al₂O₃ using hydrogen as reducing gas. Hydrogenation of unsaturated hydrocarbons is

generally performed over catalyst made up of noble metals (palladium, platinum, rhodium, or ruthenium) deposited on aluminum oxide species (γ or α). Rhodium and ruthenium active phases were not considered due to their high price and low activity, respectively. Platinum and palladium deposited on alumina are catalysts for the reduction of unsaturated C=O and C=C bonds, respectively, but platinum was considered for these reactions because of the carbon monoxide in the reducing stream. The results of hydrogenation reaction of F1 as well as conversion and catalyst selectivity are presented in Tables 2 and 3, respectively. The saturated substrate and product components are presented in bold letters while unsaturated contents are in italics.

The percentage substrate conversion was calculated according to the formula

$$\left[\frac{S_{\text{UH}} - S_{\text{UH}'}}{S_{\text{UH}}} \right] \cdot 100, \quad (4)$$

where S_{UH} are unsaturated substrate hydrocarbons before hydrogenation and $S_{\text{UH}'}$ are unsaturated substrate hydrocarbons after hydrogenation, while percentage selectivity was derived according to

$$\left[\frac{P_{\text{SH}'} - S_{\text{SH}}}{S_{\text{UH}} - S_{\text{UH}'}} \right] \cdot 100, \quad (5)$$

FIGURE 6: MS spectra of methanol decomposition gases at 200°C (a) and 350°C (b).

TABLE 2: Results of the reduction of fraction F1 over 5% Pt/ γ -Al₂O₃ with gaseous hydrogen and hydrogen from methanol decomposition.

(a)				
Fraction composition		Before hydrogenation reactions		
		Contents [%]		Total [%]
Saturated hydrocarbons	C ₈ –C ₁₉	31.2		43.4
	C ₂₀ –C ₂₅	12.2		
Unsaturated hydrocarbons	C ₈ –C ₁₉	56.6		56.6
	C ₂₀ –C ₂₅	0.0		
(b)				
Temp.	Hydrogenation with hydrogen		Hydrogenation with hydrogen from methanol decomposition	
	Contents [%]	Total [%]	Contents [%]	Total [%]
100	35.2	60.6	38.7	58.3
	25.4		19.6	
	39.4	39.4	34.5	41.7
	0.0		7.2	
200	53.4	74.1	48.6	78.4
	20.7		29.8	
	25.9	25.9	18.1	21.6
	0.0		3.5	
300	78.8	94.1	59.7	95.7
	15.3		36.0	
	5.9	5.9	4.3	4.3
	0.0		0.0	
400	37.2	80.5	56.4	91.2
	43.3		34.8	
	12.8	12.8	5.1	5.1
	0.0		0.0	

where $P_{SH'}$ are saturated product hydrocarbons (C₈-C₁₉ for F1 and C₂₀-C₂₅ for F2), S_{SH} are saturated substrate hydrocarbons (C₈-C₁₉ for F1 and C₂₀-C₂₅ for F2), S_{UH} are unsaturated substrate hydrocarbons before hydrogenation, and $S_{UH'}$ are unsaturated substrate hydrocarbons after hydrogenation.

The fractions have been grouped according to the length of the hydrocarbon chain. Prior to hydrogenation the fraction

possessed already 31.2 and 12.2% of C₈-C₁₉ and C₂₀-C₂₅ saturated, respectively, making a total of 43.4% content. The object of hydrogenation which was the (C₈-C₁₉) unsaturated hydrocarbons consisted of 56.6% of the composition. No higher carbon-chain alkene content was observed. The hydrogenation with hydrogen led to a steady increase from 35.2% at 100°C to 78.8% in the C₈-C₁₉ content in the products

TABLE 3: Fraction 1 conversion and selectivity versus temperature in reduction reactions with hydrogen and methanol decomposition mixture.

Temperature [°C]	Fraction conversion [%]		Selectivity [%]	
	H ₂	H ₂ + CO	H ₂	H ₂ + CO
100	30.4	39.1	7.1	13.3
200	54.2	68.0	39.2	30.7
300	89.6	92.4	84.1	50.4
400	77.4	91.0	21.4	44.5

at 300°C. An initial increase in the saturated C₂₀–C₂₅ content was also observed at 100°C, but at 300°C this had decreased to about the same amount as in the substrate (15.3%). The C₈–C₁₉ content decreased above this temperature to 37.2% at 400°C and an increase in the C₂₀–C₂₅ content was observed once more. The highest conversion (with the lowest unsaturated carbon content) was observed at 300°C, but this decreased at 400°C. The appearance of a higher amount of C₂₀–C₂₅ fraction and the lowered conversion at 400°C could be ascribed to condensation reactions and coking, respectively. Byproducts such as cyclic compounds and C₃₀ and above were also observed at this temperature.

In the hydrogenation reactions carried out with methanol decomposition products, a 38.7% (an increase from 31.2% of the C₈–C₁₉ content) was observed at 100°C. Conversion to the saturated C₁₉–C₂₀ fraction was lower at this temperature than that with hydrogen as reducing agent (19.6% as against 25.4%). Methyl and dimethyl substituted unsaturated hydrocarbons accounted for the increase in the length of the unsaturated hydrocarbon chain in the products collected at 100°C. A simultaneous increase with temperature of both saturated product fractions was observed up to 300°C, after which substrate conversion decreased. A high conversion was however maintained at 400°C as compared with the process with hydrogen. It is expected that coking will be less because of the consumption of oxygen in the transformation of the carbon monoxide to the dioxide species.

An unexpected appearance of C₆ and C₃₀ hydrogenated compounds, which were not present in the feed, was observed. This is most probably a result of condensation/rearrangement reactions occurring during the reduction process with the hydrogen and carbon oxide mixture. An increase in the percentage part of the C₂₀–C₂₅ saturated hydrocarbons was observed in relation to hydrogenation with hydrogen. This can be credited to condensation reactions resulting in an almost threefold increase (from 12.2% to 36%) in the amount of C₂₀–C₂₅ saturated compounds in the product at the expense of shorter chains. This is most probably due to the concerted adsorption mechanism (on the support and active phase) as proposed by [23]. The mechanism is not fully known, but the adopted reactions conditions in a thermodynamic rather than kinetic character, favor, however, condensation route to higher alkyl chains.

In relation to substrate conversion and selectivity, the following relation with temperature can be proposed: 300 > 400 > 200 > 100°C.

TABLE 4: Results of the reduction of F2 over 5% Pt/γ-Al₂O₃ with the methanol decomposition gases.

(a)			
Fraction composition		Before hydrogenation reactions	
		Contents [%]	Total [%]
Saturated hydrocarbons	C ₈ –C ₁₉	1.0	81.9
	C ₂₀ –C ₂₅	80.9	
Unsaturated hydrocarbons	C ₈ –C ₁₉	<i>0.0</i>	<i>18.1</i>
	C ₂₀ –C ₂₅	<i>18.1</i>	
(b)			
Temp.	Hydrogenation with hydrogen from methanol decomposition		
	Contents [%]		Total [%]
100	1.0		91.9
	90.9		
	<i>0.0</i>		
	<i>9.1</i>		
200	2.7		95.1
	92.4		
	<i>0.0</i>		
	<i>4.9</i>		
300	0.0		100.0
	100.0		
	<i>0.0</i>		
	<i>0.0</i>		
400	2.7		100.0
	97.3		
	<i>0.0</i>		
	<i>0.0</i>		

TABLE 5: F2 conversion and selectivity versus temperature in reduction reactions with methanol decomposition mixture.

Temperature [°C]	Fraction conversion [%]	Selectivity [%]
100	50.3	55.3
200	72.9	63.5
300	100.0	100.0
400	100.0	90.6

3.5.2. *Fraction F2.* The catalyst was used for the hydrogenation of the second substrate fraction which contained long-chain unsaturated hydrocarbons exclusively. This fraction contained 81.9% of hydrogenated hydrocarbons and a small fraction (only 18.1%) of C₂₀–C₂₅ unsaturated hydrocarbons. The C=C hydrogenation results are presented in Table 4.

A 55.3% conversion of the unsaturated hydrocarbon content was observed at 100°C (Table 5). This conversion value increased with an increase in temperature attaining 69.1% at 200°C and 100% at 300 and 400°C. Selectivity at 200 and 400°C was lower than conversion because of the appearance of C₈–C₁₉ saturated hydrocarbons in the products. Branched hydrocarbons were not observed in

the products. This particular hydrocarbon fraction can be applied exclusively as blend for lubricants or for chemical or cosmetic processes as required.

3.6. Hydrogenation Catalyst Longevity. The catalyst was subjected to a durability test in its hydrogenation activity of F2 at 300°C, at which 100% conversion and selectivity were observed. In a reaction carried out at a constant temperature of 300°C optimum catalyst activity was observed to be maintained for 5 h in the hydrogenation of unsaturated hydrocarbons. This is a unique phenomenon as it can be proposed that both decomposition gases (2H_2 and CO) are active in sustaining catalyst activity in a similar way as they inhibited the complete detachment of the platinum particles during catalyst preparation.

4. Conclusions

The performed studies confirm the possibility of hydrogenation of waste polymer pyrolysis fractions over noble metal/ Al_2O_3 systems with hydrogen obtained in the catalytic decomposition of methanol. The saturated hydrocarbon products obtained can be used as blending material for fuels and lubricants. Both catalysts—for methanol decomposition and hydrogenation—were found to maintain high catalyst activity for hours. The thermodynamic conditions are much milder than in the case of the application of pure hydrogen and are not in any way inferior in activity. The applied two-step catalytic flow system was found to be effective at atmospheric pressure. In situ studies are however still needed to be performed in order to elucidate the nature of the activity of $2\text{H}_2 + \text{CO}$ on the surface of $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ and its influence on activity (e.g., the role of CO and CO_2 in coking prevention). The studies are one of the applications of methanol as a safe and cheap hydrogen carrier and justify the research being made on the synthesis and applications of methanol as an alternative source of energy and raw materials for the chemical industry.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors wish to express appreciation to the Polish Ministry of Science and Higher Education for financial support as Grant no. PBZ-MNiSW-5/3/2006 and to Dr. Aneta Łukomska for SEM-EDS analysis.

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