Catalytic pyrolysis of used tires on noble-metal-based catalysts to obtain high-value chemicals: Reaction pathways

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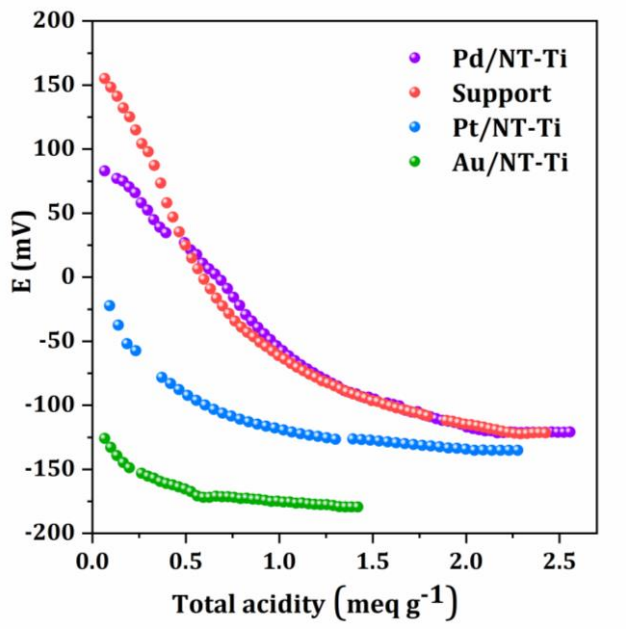

Figure S1. Potentiometric curves of acidity measurements of catalysts

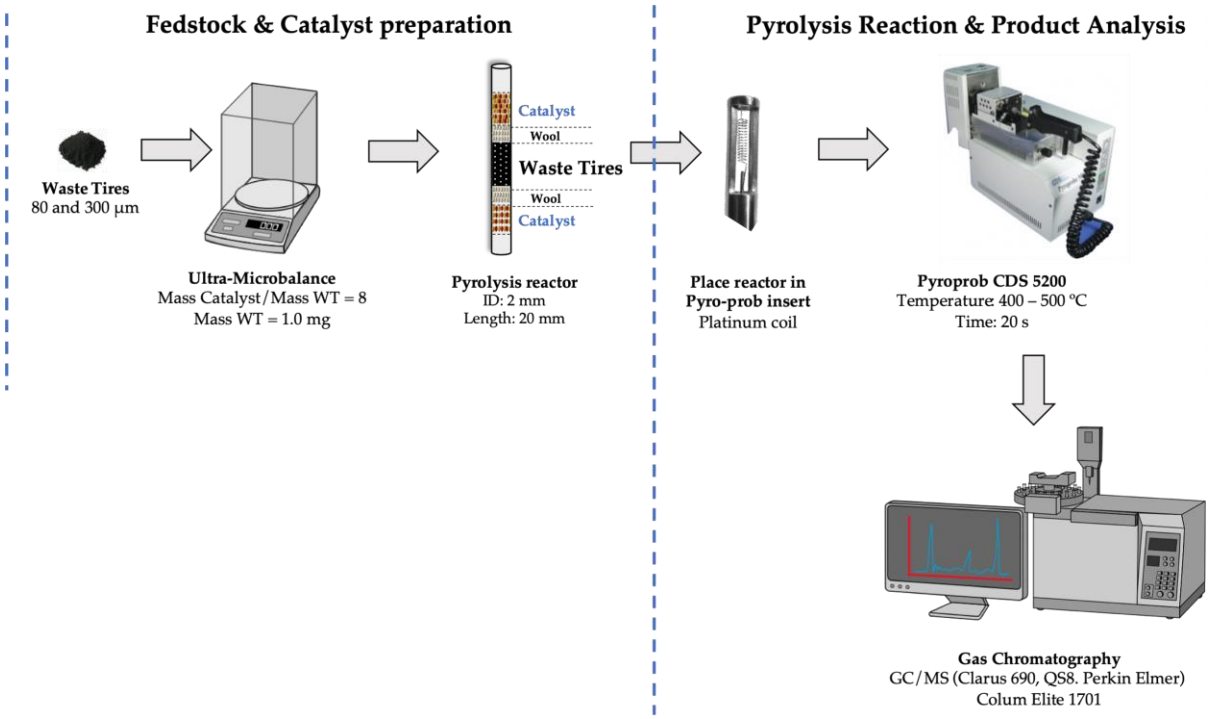

Figure S2. Schematic of a typical Py-GC/MS assay.

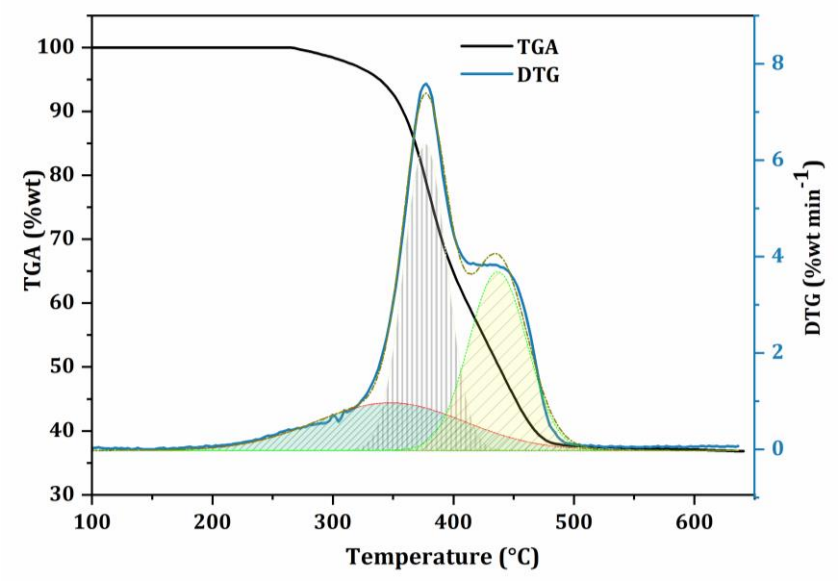

Figure S3. TGA and DTG analyses corresponding to the thermal degradation of waste tires.

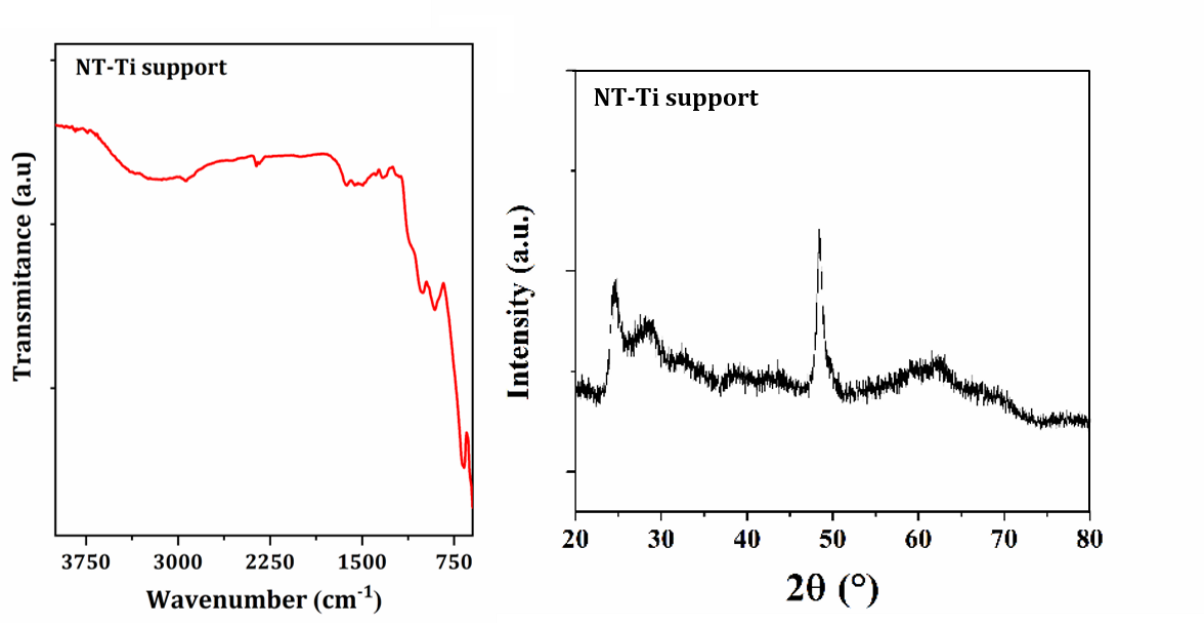

Figure S4. (a) ATR-FTIR spectra range from 500 to 4000 cm^{-1} and (b) XRD diffraction patterns for pristine-NT-Ti support.

Fourier-transform infrared (FT-IR) spectrometer (Thermo Scientific, USA) in the range of 4000–500 cm^{-1} and equipped with an attenuated total reflectance (ATR) accessory containing a germanium crystal, which has a penetration depth of approximately 0.65 μm, was used for the characterization of the synthesized catalysts. The FT-IR spectra were collected in the range of 4000 to 400 cm^{-1} with 16

cans at 4 cm^{-1} resolution. The observed area was 250 μm^2 with a pixel size of 6.25 µm × 6.25 µm. The pixel size corresponds to the size covered by each detector element of a linear array detector of pure mercury–cadmium–telluride (MCT) arranged as 16 gold-wired infrared detector elements. The background spectrum was collected before analyzing each sample. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer using a Ni filtered Cu $K_{\alpha 1}$ radiation within the range of 5–90°.

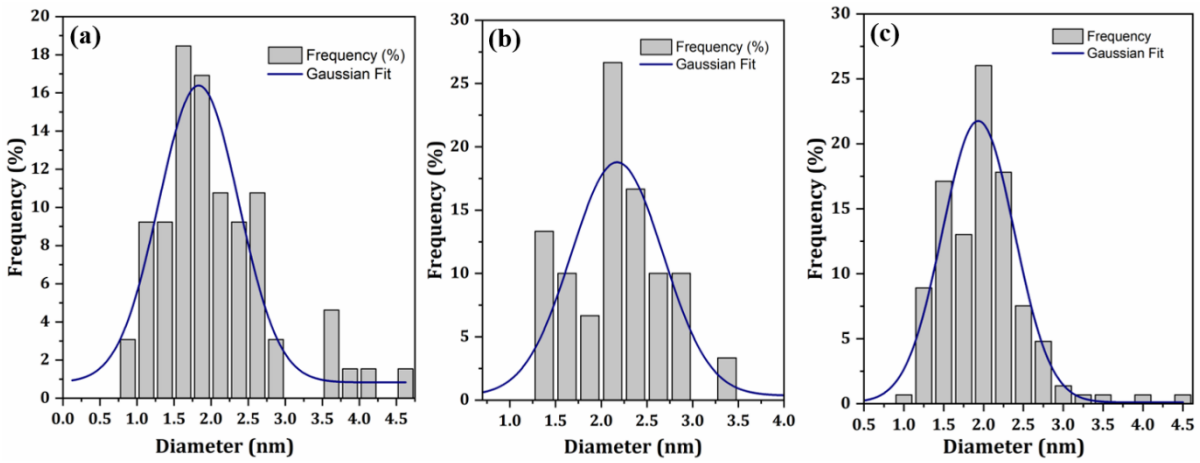

Figure S5. Histograms for the particle size distribution of (a) Pd, (b) Pt and (c) Au catalysts.

Table S1. Compounds identified as WTs pyrolysis products.

t_R (min)	Compound	t_R (min)	Compound
	Alkenes		
1.8	Butadiene	22.6	1,5-Cycloundecadiene, 8,8-dimethyl-9-methylene-
2.1	Isoprene	22.7	1,5-Cycloundecadiene, 9-(1-methylethylidene)-
7.6	2,6-Dimethyl-1,6-heptadiene	23.4	1,5-Cyclodecadiene, 1,5-dimethyl-8-(1-methylethylidene)-, (E,E)-
8.4	(E,E,E)-2,4,6-Octatriene	23.7	1-Cycloheptene, 1,4-dimethyl-3-(2-methyl-1-propene-1-yl)-4-vinyl-
13.0	2,5,5-trimethyl-1,6-Heptadiene	23.8	Bicyclo[5.2.0]nonane, 4-methylene-2,8,8-trimethyl-2-vinyl-
14.0	2,5,6-trimethyl-1,3,6-Heptatriene	24.0	Cyclohexane, 1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-, [1S-(1α,2β,4β)]-
14.5	2,6-dimethyl-2,6-Octadiene	24.2	Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-
		30.7	1,5,5-Trimethyl-6-(3-methyl-buta-1,3-dienyl)-cyclohexene
15.5	2,6-Dimethyl1,3,5,7octatetriene	31.0	Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-
15.6	1,6-Dimethyl-hepta-1,3,5-triene		**Alkanes**
16.0	DL-Limonene	19.5	Dodecane
12.2	1,5,5,6-tetramethyl-1,3-cyclohexadiene	20.9	Dodecane, 2,6,11-trimethyl-
14.0	4-ethenyl-1,4-dimethyl cyclohexene	21.1	Dodecane, 2,6,10-trimethyl-
15.0	5-ethyl-1,5-dimethyl-1,3-cyclohexadiene	23.1	Tetradecane
15.2	3,7-dimethyl 2,4,6-octatriene	26.2	Hexadecane
15.4	2,6-dimethyl-1,6-octadiene	28.9	Octadecane
15.6	3,7-dimethyl-2,6-octadiene	30.5	(E,E,E)-3,7,11,15-Tetramethylhexadeca-1,3,6,10,14-pentaene
15.8	3,7-dimethyl-1,3,6-octatriene		**Aromatic compounds**
16.5	D,L-limonene	3.14	Benzene
	Cycloalkenes	5.38	Toluene
2.97	Cyclohexene	10.2	Ethylbenzene
4.05	3,5-Dimethylcyclopentene	10.7	Xylenes
4.79	1-Methyl-1,4-cyclohexadiene	12.9	Styrene
6.98	4-Ethenyl- cyclohexene	14.5	Benzene, 1-ethyl-3-methyl-
13.4	4-ethenyl-1,4-dimethyl- cyclohexene	16.5	p-Cymene
15.2	4-methyl-1-(1-methylethenyl)- cyclohexene	17.8	Toluene, p-ethynyl-
17.6	γ-Terpinene	18.5	p-Cymenene
17.9	α-Terpinene	21.3	Benzene, 1,4-bis(1,1-dimethylethyl)-

Table S2. Identified compounds during BR pyrolysis reaction

Identified Compounds	t_R	Selectivity (%)	
		BR	BR-catalyzed
Alkenes			
1,3-Butadiene	1.718	4.4	11.9
Isoprene	1.928	1.2	7.8
1,6-Heptadiene, 2,5,5-trimethyl-	13.009	1.0	0.6
2,6-Octadiene, 2,6-dimethyl-	14.497	0.3	0.7
Cycloalkenes			
Cyclohexene	2.486	0.6	1.1
1,3-Cyclopentadiene, 1-methyl-	2.977	1.8	0.0
Cyclohexene, 4-ethenyl-	6.961	65.2	4.9
Cyclohexene, 4-ethenyl-1,4-dimethyl	13.414	0.7	0.1
Limonene	15.977	1.4	7.7
γ-Terpinene	17.616	0.0	0.7
Cyclohexene, 3-ethenyl-4-(1-methylethenyl)-	18.067	3.8	0.5
Bi-2,4-cyclopentadien-1-yl, 1,1',2,2',3,3',4,4',5,5'-decamethyl-	19.343	0.7	1.0
Cyclohexene, 1-ethyl-4,5-divinyl-	20.687	3.2	1.1
Cyclooctene, 5,6-diethenyl-	21.183	5.4	0.8
Ciclohexene, 1,5,5-Trimethyl-6-(3-methyl-buta-1,3-dienyl)-	30.645	0.5	0.6
Aromatic compounds			
Benzene	3.136	0.0	14.0
Toluene	5.378	0.0	18.5
Ethylbenzene	10.148	0.0	8.2
p-Xylene	10.726	0.0	0.7
p-Cymene	16.53	0.0	0.0
Benzene, 1,4-bis(1,1-dimethylethyl)-	21.308	2.0	2.0
Alkanes			
Dodecane, 2,6,11-trimethyl-	20.911	0.5	2.5
Tetradecane	23.074	0.1	1.3
Dodecane, 2,6,10-trimethyl-	27.58	0.8	1.7
Octadecane	28.91	0.2	0.6
Cycloalkanes			
Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-	31.008	1.5	2.4
Cyclohexane, 1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-, [1S-(1α,2β,4β)]-	31.904	0.5	0.7
Others			
Benzothiazole	22.507	0.5	0.5

Table S3. Identified compounds during SBR pyrolysis reaction

Identified Compounds	t_R	Selectivity (%)	
		SBR	SBR-catalyzed
Alkenes			
1,3-Butadiene	1.721	3.59	8.29
Isoprene	1.922	1.16	5.44
2,6-Octadiene, 2,6-dimethyl-	14.497	0.22	0.54
2,6-Dimethyl1,3,5,7-octatetraene	15.501	0.00	0.35
1,3,6-Heptatriene,2,5,6-trimethyl	15.895	2.05	0.08
Cycloalkenes			
Cyclohexene, 4-ethenyl-	6.932	43.73	7.43
Cyclohexene4-ethenyl-1,4-dimethyl	13.414	0.53	0.08
Limonene	15.963	2.05	4.88
Cyclohexene, 3-ethenyl-4-(1-methylethenyl)-	18.506	2.29	0.31
Cyclohexane, 1,2,4-triethenyl-	19.204	3.62	0.70
Cyclooctene, 5,6-diethenyl-, cis-	19.714	4.09	0.98
1,5-Cyclooctadiene, 3-(1-methyl-2-propenyl)-	20.446	1.23	0.42
Cyclooctene, 5,6-diethenyl-, cis-	21.177	3.89	0.97
1,5,9-Cyclododecatriene, (E,E,Z)-	21.271	2.08	1.90
γ-Terpinen	17.616	0.00	0.49
Bi-2,4-cyclopentadien-1-yl, 1,1',2,2',3,3',4,4',5,5'-decamethyl-	19.343	2.10	1.15
Cyclohexene, 1,5,5-Trimethyl-6-(3-methyl-buta-1,3-dienyl)	30.645	0.11	0.40
Aromatic compounds			
Styrene	12.578	15.71	12.83
Benzene	3.136	0.00	9.81
Toluene	5.378	0.00	13.49
Ethylbenzene	10.148	0.04	9.67
p-Xylene	10.726	0.30	0.50
Benzene, 1-ethyl-3-methyl-	14.747	0.00	3.38
p-Cymene	16.53	0.00	0.00
Benzene, 1,4-bis(1,1-dimethylethyl)-	21.308	2.08	1.90
Alkanes			
Dodecane, 2,6,11-trimethyl-	20.911	0.57	0.47
Dodecane, 2,6,10-trimethyl-	21.761	0.12	0.68
Tetradecane	23.074	0.00	0.93
Dodecane, 2,6,10-trimethyl-	27.58	0.80	1.14
Octadecane	28.91	0.14	0.33
Cycloalkanes			
Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-	31.008	0.79	1.04
Cyclohexane, 1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-, [1S-(1α,2β,4β)]-	31.904	0.38	0.36
Others			
Benzothiazole	22.493	0.51	0.36
β-D-Glucopyranose, 1,6-anhydro-	30.239	0.22	0.20
Quinoline, 1,2-dihydro-2,2,4-trimethyl-	26.346	0.77	0.14

Table S4. Identified compounds during IR pyrolysis reaction

Identified Compounds	t_R	Selectivity (%)	
		IR	IR-catalyzed
Alkenes			
1,3-Butadiene	1.718	0.00	0.00
Isoprene	1.922	19.49	13.79
1,6-Heptadiene, 2,5,5-trimethyl-	13.009	0.37	0.15
1,3,6-Heptatriene2,5,6-trimethyl	14.024	0.24	0.35
2,6-Octadiene, 2,6-dimethyl-	14.497	0.46	0.13
2,6-Dimethyl1,3,5,7-octatetraene	15.501	0.98	0.43
(E,E,E)-3,7,11,15-Tetramethylhexadeca-1,3,6,10,14-pentaene	30.534	0.11	0.62
Cycloalkenes			
Cyclohexene	2.486	0.00	0.00
1,3-Cyclopentadiene, 1-methyl-	2.977	0.00	0.00
1,4-Cyclohexadiene, 1-methyl-	4.789	0.92	0.14
Cyclohexene, 4-ethenyl-	6.961	0.00	0.00
Cyclohexene4-ethenyl-1,4-dimethyl	13.414	5.08	0.73
.p-Mentha-3,8-diene	15.192	0.32	0.06
Limonene	16.042	56.03	28.62
γ-Terpinen	17.616	0.30	0.32
1,5-Cycloundecadiene, 8,8-dimethyl-9-methylene-	22.615	0.38	0.28
1,5-Cycloundecadiene, 9-(1-methylethylidene)-	22.694	0.61	0.22
1,5-Cyclodecadiene, 1,5-dimethyl-8-(1-methylethylidene)-, (E,E)-	23.443	0.72	0.11
1-Cycloheptene, 1,4-dimethyl-3-(2-methyl-1-propene-1-yl)-4-vinyl-	23.687	1.23	0.27
Aromatic compounds			
Benzene	3.136	0.00	0.00
Toluene	5.378	0.35	6.31
o-Xylene	10.726	0.55	2.67
p/m/xylenes	12.33	0.14	3.94
Styrene	12.912	0.39	0.04
Benzene, 1-ethyl-3-methyl-	14.747	0.77	0.66
p-Cymene	16.53	0.27	24.20
p-Cymenene	18.515	0.38	3.12
Benzene, 1,4-bis(1,1-dimethylethyl)-	21.308	0.13	0.56
Alkanes			
Dodecane, 2,6,11-trimethyl-	20.911	1.07	0.64
Dodecane, 2,6,10-trimethyl-	21.761	0.10	0.32
Tetradecane	23.074	0.31	0.75
Dodecane, 2,6,10-trimethyl-	27.58	0.11	0.60
Octadecane	28.91	0.04	2.20
Cycloalkanes			
Bicyclo[5.2.0]nonane, 4-methylene-2,8,8-trimethyl-2-vinyl-	23.84	0.72	0.23
Cyclohexane, 1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-, [1S-(1α,2β,4β)]-	24.015	0.45	0.39
Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-	24.183	1.27	0.62
Cyclohexene, 1,5,5-Trimethyl-6-(3-methyl-buta-1,3-dienyl)	30.645	0.13	0.55
Others			
Benzothiazole	22.507	0.40	0.37
Quinoline, 1,2-dihydro-2,2,4-trimethyl-	26.346	0.60	0.43