

Electronic Supporting Information

Catalytic Conversion of Compounds Representative of Lignin-derived Bio-oils: A Reaction Network for Conversion of Guaiacol, Anisole, 4-Methylanisole, and Cyclohexanone Catalyzed by Pt/ γ -Al₂O₃

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General Procedure

- Materials

Chemicals and catalyst were obtained from commercial suppliers and used as provided: guaiacol (Sigma), anisole (Sigma-Aldrich, 99.8%), 4-methylanisole (Sigma-Aldrich, 99%), cyclohexanone (Acros, 99.5%), Pt/ γ -Al₂O₃ powder (Sigma-Aldrich, 1 wt% Pt, < 100 mesh, Pt dispersion: 0.25, BET surface area: 206 ± 1 m²g⁻¹), and HY zeolite (Zeolyst, CBV 720, Si/Al = 30.0, atomic).

N₂ (Praxair, 99.997%), was purified with a hydrocarbon trap (Agilent Technologies, BHT-4) and was used as an inert carrier gas in test reactions and in the gas chromatographs (GCs). H₂ (99.999%), generated by water electrolysis (Domnick Hunter, model 40H) was used as a reactant in some test reactions and in the GCs. Helium (Praxair, 99.995%) was purified with a hydrocarbon trap (Agilent Technologies, BHT-4), a moisture trap (Agilent Technologies, BMT-4), and an oxygen trap (Agilent Technologies, a BOT-4) prior to use in the GCs. Zero-air (<0.1 ppm hydrocarbon (as methane)), was generated from house air in an air generator (Domnick Hunter, model UHP-10ZAW) and was used in the GC flame ionization detectors (FIDs).

A Micromeritics ASAP 2020 instrument was used to measure the BET surface area of the catalyst. A Micromeritics Autochem II instrument was used to measure the dispersion of the platinum in the catalyst.

- Methods

The catalytic conversions were carried out in a continuous down-flow tubular reactor, mounted in a well-insulated three-zone furnace (Applied Test Systems Series 3210). The catalyst bed consisted of fresh powder catalyst (4–400 mg) mixed with particles of inert, nonporous α -Al₂O₃ (Fisher A634-3, 90 mesh). The vaporized reactant at the inlet of the reactor was mixed with flowing N₂. H₂ was co-fed in some experiments. Gas flow rates were measured and controlled by using Brooks mass flow controllers. A water-cooled condenser downstream of the reactor was used to separate condensable

from volatile products at approximately 285 K. The gas product stream flowed to an online GC-refinery gas analyzer (Agilent 7890A) equipped with three sample loops, five columns, and three detectors (one FID and two thermal conductivity detectors (TCDs)), the flow rate of this stream was monitored with a mass flow meter (Brooks, model SLA7860S). Peak identification for fixed gases was made by comparison with a Praxair RGA gas calibration standard. The liquid samples were collected periodically for analysis with an off-line GC equipped with a mass selective detector (MSD, Agilent 5975C). Peaks were identified on the basis of the mass spectra by matching to a library of NIST spectra. GC/FID was used to determine the concentrations of products in the liquid samples. Typical times on stream were between 3–6 h.

Table ESI-1: Most abundant and trace^a products formed in the conversion^b of guaiacol catalyzed by Pt/ γ -Al₂O₃ (liquid sample). Compounds were identified by using the NIST EI mass spectral database; some were confirmed by using authentic standards.

| Product | Classification based on abundance in product stream ^c |
|--|--|
| benzene | minor |
| anisole | minor |
| cyclohexanone | minor |
| toluene | minor |
| phenol | major |
| 2-methylphenol (<i>o</i> -cresol) | minor |
| 1,2-benzenediol (catechol) | major |
| 1,2-benzenediol-3-methyl (3-methylcatechol) | major |
| 2-methoxy-3-methylphenol (3-methylguaiacol) | minor |
| 2-methoxy-6-methylphenol (6-methylguaiacol) | minor |
| 1,2-dimethoxybenzene (veratrole) | minor |
| cyclohexene | trace |
| cyclohexane | trace |
| 1-methoxycyclohexane | trace |
| <i>p</i> -xylene | trace |
| cyclohexanol | trace |
| 2-methylcyclohexanone | trace |
| 3-methylcyclohexanone | trace |
| 2-methylanisole | trace |
| 4-methylanisole | trace |
| 2-methoxy-4-methylphenol (4-methylguaiacol) | trace |
| 2-methoxy-5-methylphenol (5-methylguaiacol) | trace |
| 2,3-dimethylphenol | trace |
| 2,5-dimethylphenol | trace |
| 2,6-dimethylphenol | trace |
| 3,4-dimethylphenol | trace |
| 2,3,5-trimethylphenol | trace |
| 2,3,6-trimethylphenol | trace |
| 2,4,6-trimethylphenol | trace |
| 3,4,5-trimethylphenol | trace |
| water | trace |
| methanol ^d | minor |

^aIdentifications of some trace products were not confirmed with standard samples; therefore, for example, substituted benzenes and substituted phenols other than those listed are possible products.

^bConversion conditions: temperature, 573 K; WHSV, 19.8 ± 0.1 (g of guaiacol)/(g of catalyst × h); initial conversion of guaiacol, approximately 0.075.

^cA product was classified as “major” when its response in a chromatogram was greater than 1.2 × 10⁷ pico-Amps (pA); as “minor” when its response was between 1.0 × 10⁶ and 1.2 × 10⁷ pA; and as “trace” when its response was less than 1.0 × 10⁶ pA.

^dMethanol was observed in liquid samples; however, its concentration in the gas phase was not quantified.

Table ESI–2: Most abundant products and trace^a products formed in the conversion^b of anisole catalyzed by Pt/ γ -Al₂O₃ (liquid sample). Compounds were identified by using the NIST EI mass spectral database; some were confirmed by using authentic standards.

| Product | Classification based on abundance in product stream |
|-------------------------|--|
| benzene | major |
| cyclohexanone | major |
| 2-methylanisole | major |
| phenol | major |
| 2-methylphenol | major |
| 2,6-dimethylphenol | major |
| methoxycyclohexane | minor |
| 4-methylanisole | minor |
| 4-methylphenol | minor |
| cyclohexane | trace |
| methylcyclohexane | trace |
| 1,1 dimethylcyclohexane | trace |
| <i>p</i> -xylene | trace |
| <i>o</i> -xylene | trace |
| 2-methylcyclohexanone | trace |
| 2,6-dimethylanisole | trace |
| 2,4-dimethylphenol | trace |
| trimethylphenol | trace |
| water | n/a |
| Methanol ^c | n/a |

^aIdentifications of trace products were not confirmed with standard samples; therefore, for example, substituted benzenes and substituted phenols other than those listed are possible products.

^bConversion conditions: temperature, 573 K; WHSV, 4.46 (g of anisole)/(g of catalyst × h); initial conversion of anisole was approximately 0.2.

^cMethanol was observed in liquid samples; its concentration in the gas phase was not quantified.

Table ESI-3: Most abundant products and trace^a products formed in the conversion^b of 4-methylanisole catalyzed by Pt/ γ -Al₂O₃ (liquid sample). Compounds were identified by using the NIST EI mass spectral database; some were confirmed by using authentic standards.

| Product | Classification based on abundance in product stream |
|---------------------------|--|
| toluene | Major |
| 2,4-dimethylanisole | Major |
| 4-methylphenol | Major |
| 2,4-dimethylphenol | Major |
| 2,4,6-trimethylphenol | Major |
| anisole | Minor |
| 4-methylcyclohexanone | Minor |
| 3,4-dimethylanisole | Minor |
| 3,4-dimethylphenol | Minor |
| 2,4,5-trimethylphenol | Minor |
| 3,4,5-trimethylphenol | Minor |
| 2,3,5,6-tetramethylphenol | Minor |
| methylcyclohexane | Trace |
| <i>p</i> -xylene | Trace |
| 2-methylanisole | Trace |
| pentamethylbenzene | Trace |
| 2,3,4,5-tetramethylphenol | Trace |
| water | n/a |
| Methanol ^c | n/a |

^aIdentifications of some trace products were not confirmed with standard samples; therefore, for example, substituted benzenes and substituted phenols other than those listed are possible products.

^bConversion conditions: temperature, 573 K; WHSV, 30.7 (g of 4-methylanisole)/(g of catalyst × h); initial conversion of 4-methylanisole, approximately 0.06.

^cMethanol was observed in liquid samples; however, its concentration in the gas phase was not quantified.

Table ESI-4: Most abundant and trace products formed in the conversion^a of cyclohexanone catalyzed by Pt/ γ -Al₂O₃ (liquid sample). Compounds were identified by using the NIST EI mass spectral database; some were confirmed by using authentic standards.

| Product | Classification based on abundance in product stream^b |
|------------------|--|
| benzene | minor |
| cyclohexane | major |
| cyclohexanol | major |
| cyclohexen-1-one | major |
| phenol | major |
| cyclohexene | trace |
| water | n/a |

^aConversion conditions: temperature, 573 K; WHSV, 56.0 ± 1.3 (g of cyclohexanone)/(g of catalyst \times h); initial conversion of cyclohexanone, approximately 0.22.

^bA product was classified as “major” when its response in a chromatogram was greater than 1.2×10^7 pico-Amps (pA); as “minor” when its response was between 1.0×10^6 and 1.2×10^7 pA; and as “trace” when its response was less than 1.0×10^6 pA.

Table ESI-5: Products of conversion of guaiacol catalyzed by Pt/ γ -Al₂O₃ at various H₂ partial pressures (liquid samples).^a

| Product | Selectivity to product in reaction catalyzed by Pt/Al ₂ O ₃ at various H ₂ partial pressures (P_{H_2} , kPa) | |
|------------------|---|--------------------------|
| | $P_{\text{H}_2} = 41^b$ | $P_{\text{H}_2} = 127^c$ |
| toluene | 0.0004 | 0.001 |
| anisole | 0.009 | 0.04 |
| cyclohexanone | 0.03 | 0.2 |
| phenol | 0.3 | 0.5 |
| catechol | 0.4 | 0.07 |
| 3-methylcatechol | 0.1 | 0.002 |

^aData were extrapolated to zero time on stream, and thus represent initial selectivities. Reaction conditions were: WHSV = 20 (g of guaiacol)/(g of catalyst × h); pressure = 140 kPa; and temperature = 573 K. Selectivity is defined as yield [mol product formed/mol of organic reactant fed]/conversion [mol of organic reactant consumed/mol of organic reactant fed].

^bFeed molar ratio of H₂ to guaiacol was 10.

^cFeed molar ratio of H₂ to guaiacol was 33.