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Conversion of 4-Methylanisole Catalyzed by Pt/γ-Al_2O_3 and by Pt/SiO_2-Al_2O_3: Reaction Networks and Evidence of Oxygen Removal

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Abstract The conversion of 4-methylanisole, a prototypical bio-oil compound, was catalyzed by Pt/Al_2O_3, Pt/SiO_2-Al_2O_3, or HY zeolite at 573 K and atmospheric pressure. More than a dozen products were formed with each catalyst, the most abundant being 4-methylphenol, 2,4-dimethylphenol, and 2,4,6-trimethylphenol; toluene was also a major product when the catalyst was supported platinum with H_2 as a co-reactant. 4-Methylphenol was the only methylphenol isomer formed in significant yields, which indicates that migration of the methyl group on the aromatic ring is not significant under the selected reaction conditions. The data determine approximate reaction networks including reactions forming 4-methylphenol, 2,4-dimethylphenol, and toluene as primary products. The kinetically significant reaction classes were transalkylation, observed with all three catalysts, and hydrogenolysis (including hydrodeoxygenation) and hydrogenation, observed only with the platinum-containing catalysts operating in the presence of H_2. Data such as those reported here provide a starting point for predicting the conversion of whole bio-oils for removal of oxygen and upgrading of fuel properties.

Keywords Biomass conversion · Hydrodeoxygenation · 4-Methylanisole · Platinum · Reaction network

1 Introduction

Interest in the conversion of lignocellulosic biomass as a renewable feedstock for fuels and chemicals is being driven by the goal of reducing our dependence on petroleum and natural gas [1–3]. Fast-pyrolysis of lignocellulosic biomass converts much of it into liquid bio-oils [4], which might be co-fed with petroleum in refineries. But, in contrast to petroleum, bio-oils contain high concentrations of oxygen-containing compounds, which lead to immiscibility with fossil fuel feedstocks and to corrosion [5, 6], and consequently whole pyrolysis bio-oils are not appealing as petroleum refinery blending stocks or liquid transportation fuels.

Upgrading of bio-oils to make them viable alternative fuel sources requires catalytic processing to reduce the oxygen contents. Pyrolysis bio-oils are complex mixtures, typically containing several hundred compounds [7], and understanding of their catalytic conversion is therefore challenging. The data characterizing the conversion of these complex bio-oils [8–13] lack the detail to allow resolution of the reactions occurring during the catalytic upgrading—the products are not well documented, and the fundamental reaction networks are not well understood. We propose that data characterizing the conversion of individual compounds representative of bio-oils may be of value in the emergence of technology for biomass conversion, much as data characterizing the reactions of individual compounds in petroleum have been helpful in the improvement of processes for petroleum refining [14].

Thus, our goals were to investigate the catalytic conversion of a compound that is representative of bio-oils. This paper is a part of a larger investigation [15–20] of the reactions of such compounds. Our focus is on lignin-derived pyrolysis products, because they have received much less attention than those derived from cellulose

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[21–24], although lignin typically constitutes 30% of lignocellulosic biomass. The products formed in lignin pyrolysis prominently include methyl-substituted phenolics and aromatic ethers [25, 26]. 4-Methylanisole, with its methoxy and methyl group substituents, is thus a representative compound for the investigation of lignin-derived compounds and the subject of the work reported here. 4-Methylanisole is also an intermediate product in the catalytic conversion of anisole [15].

Our goal was to investigate the conversion of 4-methylanisole with a catalyst that is active for removal of oxygen, that is, one incorporating a noble metal; we chose platinum. To elucidate the roles of various catalyst functions in the conversion of this compound, we also used a solid acid, HY zeolite, and a bifunctional catalyst, platinum supported on the acidic silica-alumina. The performance of the metal-containing catalysts was assessed by determination of the reaction network for 4-methylanisole conversion in the presence of H_2.

2 Experimental

Catalytic reactions were carried out in a once-through packed-bed plug-flow reactor under the following conditions, with liquid 4-methylanisole (Sigma-Aldrich, 99%) vaporized into a flowing gas stream: catalyst mass, 10.1–402.8 mg; temperature, 573 K; pressure, 140 kPa; 4-methylanisole liquid flow rate, 0.03 mL min^{-1}; gas feed flow rate, 100 mL min^{-1} (as pure N_2 in experiments with HY zeolite and as 30% H_2/70% N_2 in experiments with Pt/Al_2O_3 or Pt/SiO_2-Al_2O_3). Each catalyst powder was diluted with particles of inert, nonporous α-Al_2O_3. The product gas stream was condensed at 285–288 K. Uncondensed gases and condensate samples collected periodically were analyzed by gas chromatography and gas chromatography/mass spectrometry.

Pt/γ-Al_2O_3 (205966-100G, Sigma-Aldrich, 1 wt% Pt) and HY zeolite (CBV 720, Zeolyst, Si:Al = 15, atomic) powders were used as received. Pt/SiO_2-Al_2O_3 (1 wt% Pt) was prepared by wet impregnation, as follows: A slurry was prepared with 1.449 g of tetraamineplatinum(II)nitrate (482293-1G, Sigma-Aldrich) and 10.2 mL of deionized water (18 MΩ, Millipore); 6.8 mL of this slurry was mixed with 5.01 g of silica-alumina (MS-25, Grace-Davison, Si:Al = 6, atomic); deionized water (18 MΩ, Millipore) was added until a paste formed. This mixture was dried in an oven at 398 K for 25 h and then calcined in a furnace by flowing zero-air at 50 mL/min as the temperature was ramped from 298 to 533 K in 180 min, followed by a 120-min period at 533 K.

The BET surface areas of the Pt/γ-Al_2O_3 and Pt/SiO_2-Al_2O_3 were determined with a Micromeritics ASAP 2020 instrument to be 206 ± 1 and 449 ± 1 m^2/g, respectively. The dispersions of the platinum were determined with a Micromeritics Autochem II Chemisorption Analyzer to be 0.25 and 0.26, respectively. The dispersions were calculated by assuming a stoichiometry of one H atom per exposed Pt atom.

3 Results

3.1 Major and Minor Products of 4-Methylanisole Conversion Catalyzed by Pt/Al_2O_3 and by Pt/SiO_2-Al_2O_3

More than a dozen products were observed in the conversion of 4-methylanisole with each catalyst. Catalyst deactivation, characterized by a 50% reduction in conversion within 6 h on stream, was observed with Pt/Al_2O_3 and Pt/SiO_2-Al_2O_3 catalysts working in the presence of H_2. Selectivities to major and minor products at low initial conversions (0.082 for Pt/Al_2O_3 and 0.097 for Pt/SiO_2-Al_2O_3) are summarized in Table 1; these data represent extrapolations to zero time on stream and therefore initial catalyst performance, prior to significant deactivation.

Mass balance closures were 100.0 ± 3.3% in experiments with 4-methylanisole conversions up to 8%. Details are given in Table 2. The reactant and most products have such low vapor pressures at the temperature of the condenser (which was mounted downstream of the reactor to separate the product into gas and liquid streams) that they were almost completely condensed. Consequently, mass balance closures were not significantly different from 100% even when the mass balance term accounting for the gas-phase products was neglected. But because the volume of feed liquid used in each experiment was small, the liquid hold-up in the condenser was a significant term in the overall mass balance (typically, 5% of the total). The change in the mass of the packed bed did not significantly contribute to the overall mass balance.

Data characterizing the conversion of 4-methylanisole catalyzed by Pt/Al_2O_3 as a function of time on stream at various inverse space velocities are presented in Fig. 1. Error bounds determined in replicate experiments are indicated in Fig. 1; the error bounds represent standard deviations. The data show that higher space velocities led to lower initial conversions, as expected.

The catalyst underwent deactivation during operation in the flow reactor (Fig. 1), which could be explained, in part, by accumulation of carbonaceous deposits. In a typical experiment, the deactivation led to a decline in conversion of about 50% in 6 h. Initial conversions were determined by extrapolating the data to zero time on stream.

The most abundant products in the conversions catalyzed by Pt/Al_2O_3 and Pt/SiO_2-Al_2O_3 were 4-methylphenol,

Table 1 Products of conversion of 4-methylanisole catalyzed by Pt/Al_2O_3 and by Pt/SiO_2-Al_2O_3 at 573 K

Product	Selectivity to product in reaction catalyzed by Pt/Al_2O_3	Selectivity to product in reaction catalyzed by Pt/SiO_2-Al_2O_3
4-Methylphenol	0.55	0.68
2,4-Dimethylphenol	0.26	0.17
Toluene	0.10	0.083
2,4,6-Trimethylphenol	0.096	0.030
2,4-Dimethylanisole	0.021	0.087
Tetramethylphenol	0.023	0.0083

Data were extrapolated to zero time on stream, and thus represent approximate initial selectivities determined at a weight hourly space velocity of 17 and 43 (g of reactant)/(g of catalyst × h) for Pt/γ-Al_2O_3 and Pt/SiO_2-Al_2O_3, respectively, at a pressure of 140 kPa. Conversions catalyzed by Pt/γ-Al_2O_3 and by Pt/SiO_2-Al_2O_3 were 0.082 and 0.097, respectively. Selectivity is defined as yield (mol product formed/mol of organic reactant fed)/conversion (mol of organic reactant consumed/mol of organic reactant fed). In the experiments with the Pt/Al_2O_3 catalyst, the feed molar ratio of H_2 to the organic reactant was 7

2,4-dimethylphenol, and toluene. 2,4,6-Trimethylphenol was the next most abundant product when the catalyst was Pt/γ-Al_2O_3; when the catalyst was Pt/SiO_2-Al_2O_3, 2,4-dimethylanisole was formed in yields similar to those observed for toluene. Tetramethylphenol was also formed in relatively high yields with each catalyst.

In the conversion with the supported platinum catalysts, the only methylphenol isomer formed in significant yields was 4-methylphenol, a result that indicates that migration of the methyl group on the aromatic ring (transalkylation) was not kinetically significant. In the transalkylation reactions, the observation of the methyl substituent at the position ortho to the methoxy group on the aromatic ring (the methyl group was observed in the 2-position of 2,4-dimethylanisole) is consistent with the *ortho*, *para*-directing effect expected for aromatic ethers and aromatic alcohols [27].

The formation of toluene as a product suggests the occurrence of HDO taking place via cleavage of the C–O bond in 4-methylanisole. The formation of the primary product 2,4-dimethylphenol indicates that unimolecular transalkylation (intramolecular rearrangement of 4-methylanisole) and bimolecular transalkylation (transalkylation involving 4-methylphenol and 4-methylanisole) are reactions that occur in parallel.

The occurrence of aromatic ring hydrogenation is illustrated, for example, by the appearance of methylcyclohexanone as a product in the conversion with the supported platinum catalysts in the presence of H_2.

Other products formed in the presence of these catalysts with H_2 as a co-reactant include 3,4-dimethylanisole, 3,4-dimethylphenol, and other trimethylphenols, but these were formed in low yields and not quantified. Water and methanol in the liquid samples and methane in the gas samples are other products that were observed but not quantified. Furthermore, trace products with additional methyl group substituents on the aromatic ring were observed with each catalyst.

The conversion of 4-methylanisole catalyzed by HY zeolite was similar to the conversion of anisole catalyzed by HY zeolite [15] in that transalkylation was the only kinetically significant reaction class. The results highlight the importance of the metal function in the other reactions: hydrogenolysis, hydrodeoxygenation, and hydrogenation.

In summary, an important class of reaction, observed for all three catalysts, is methyl group transfer. This was the only significant reaction class when the catalyst was HY zeolite. The occurrence of hydrogenolysis, hydrogenation, and hydrodeoxygenation in the conversions when the catalysts were supported platinum (in the presence of H_2) and not when the catalyst was the acidic zeolite demonstrates that these classes of reaction were catalyzed by the platinum.

3.2 Development of a Quantitative Reaction Network for 4-Methylanisole Conversion

Selectivity vs. conversion plots (e.g., Figs. 2, 3) were used to identify products as primary or not [15, 16]; a positive intercept on such a plot indicates that the product is primary, and a zero intercept indicates that it is non-primary. (These designations are empirical, falling short, for example, of providing information about intermediates that were too reactive to be detected.) The selectivity-conversion data observed for 4-methylanisole conversion catalyzed by Pt/γ-Al_2O_3 and by Pt/SiO_2-Al_2O_3 in the presence of H_2 (Figs. 2, 3) indicate that 4-methylphenol, 2,4-dimethylphenol, 2,4,6-trimethylphenol, and toluene were primary products. We infer, however, because the conversion involved multiple bond-breaking and bond-forming steps, that 2,4,6-trimethylphenol was produced from 4-methylanisole in a sequence of reactions; it could also have been formed in low yields from feed impurities such as methylphenols (these were <0.2 wt% of the feed liquid).

On the basis of data such as these, we infer a partial statement of the reaction network, representing just the primary products, as shown in Fig. 4. According to this representation, hydrogenolysis, methyl group transfer, hydrodeoxygenation, and hydrogenation are the kinetically significant reaction classes in the 4-methylanisole conversion catalyzed by each of the supported-platinum catalysts in the presence of H_2.

Table 2 Overall mass balance closure data; the data in each row represent results from an individual experiment characterizing 4-methylanisole conversion catalyzed by Pt/Al_2O_3, $Pt/SiO_2\text{-}Al_2O_3$, or HY zeolite

Catalyst	Experiment number	Time on stream (min)	Mass of reactant fed[a] (g)	Mass of liquid collected from condenser[a] (g)	Mass of reactant vapor leaving condenser[a] (g)	Mass of liquid remaining in condenser (g), estimated	Mass balance closure (%)
Pt/Al_2O_3	1	307	8.83	8.08	0.13	0.5	98.6
	2	229	6.61	6.25	0.10	0.5	103.5
	3	229	6.59	6.17	0.10	0.5	102.8
	4	268	7.70	7.36	0.11	0.5	103.5
	5	360	10.36	9.80	0.15	0.5	100.8
	6	355	10.20	9.03	0.15	0.5	94.8
	7	374	10.82	10.17	0.16	0.5	100.1
	8	229	6.61	6.25	0.10	0.5	103.5
	9	382	11.00	10.16	0.16	0.5	98.4
	10	299	8.15	7.97	0.12	0.5	105.4
	11	361	10.67	10.30	0.15	0.5	102.6
	12	361	10.38	9.73	0.15	0.5	100.0
	13	343	10.29	9.17	0.14	0.5	95.4
	14	362	10.42	9.97	0.15	0.5	102.0
	15	362	10.44	9.31	0.15	0.5	95.4
	16	344	9.97	8.94	0.14	0.5	96.0
	17	365	10.86	9.97	0.15	0.5	97.9
	18	358	11.46	9.29	0.15	0.5	86.7
$Pt/SiO_2\text{-}Al_2O_3$	1	268	7.80	7.13	0.11	0.5	99.1
	2	363	10.51	9.75	0.15	0.5	99.0
	3	363	10.44	9.88	0.15	0.5	100.9
	4	368	10.60	9.90	0.15	0.5	99.5
	5	357	10.29	9.67	0.15	0.5	100.2
	6	363	10.47	10.02	0.15	0.5	101.8
	7	369	10.61	9.91	0.15	0.5	99.6
	8	357	10.39	9.94	0.15	0.5	101.9
	9	357	10.29	9.91	0.15	0.5	102.6
	10	370	10.65	10.02	0.15	0.5	100.3
	11	372	10.71	9.78	0.15	0.5	97.4
	12	357	10.27	9.90	0.15	0.5	102.7
	13	365	10.50	9.36	0.15	0.5	95.3
	14	350	10.50	9.47	0.15	0.5	96.4
	15	369	10.62	10.26	0.15	0.5	102.7
	16	359	10.34	10.01	0.15	0.5	103.1
	17	359	10.35	9.93	0.15	0.5	102.2
	18	178	5.12	4.43	0.00	0.5	96.4
	19	248	7.15	6.47	0.10	0.5	98.9
HY zeolite	1	363	10.45	9.94	0.15	0.5	101.3

[a] Liquid fed, liquid collected from condenser, and reactant leaving the condenser in vapor phase are cumulative for the length of the experiment

The data characterizing the conversion of 4-methylanisole catalyzed by Pt/Al_2O_3 and by $Pt/SiO_2\text{-}Al_2O_3$ are represented satisfactorily by first-order kinetics (Fig. 5). The pseudo first-order rate constants for the overall disappearance of 4-methylanisole catalyzed by $Pt/\gamma\text{-}Al_2O_3$ and by $Pt/SiO_2\text{-}Al_2O_3$ were found to be 11 and 31 L/(g of catalyst × h), respectively, under the conditions stated in the caption of Fig. 4.

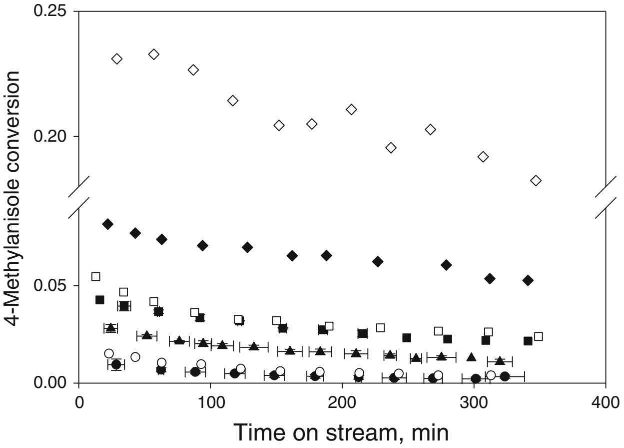


Fig. 1 Change in 4-methylanisole conversion catalyzed by Pt/Al_2O_3 as a function of time on stream at 573 K and 140 kPa at various values of WHSV, in units of (g of reactant)/(g of catalyst × h): 4.3 (*open diamond*), 17.0 (*filled diamond*), 30.7 (*open square*), 34.6 (*filled square*), 57.4 (*filled triangle*), 139 (*open circle*) and 166 (*filled circle*). The *error bars* show the standard deviations determined in replicate experiments

Data characterizing the formation of some individual products were also obtained in sufficient detail to allow the preparation of first-order kinetics plots (Fig. 6), and it is evident that these reactions are also satisfactorily represented by such kinetics. The rate constants are summarized in Table 3. The results allow the partially quantified statement of the reaction network shown in Fig. 4.

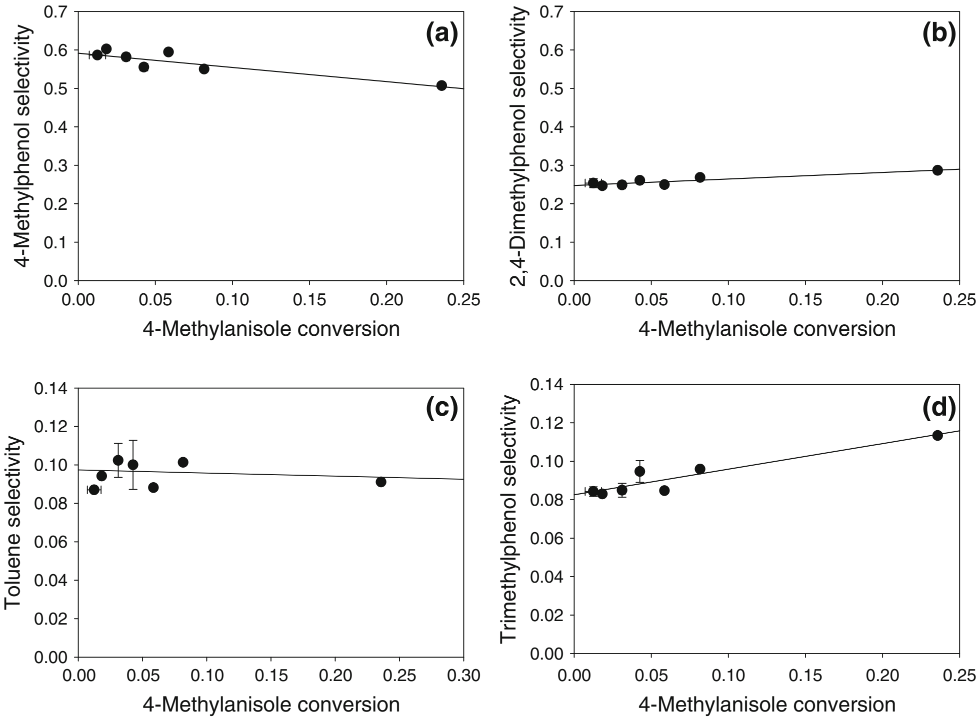
The product formed fastest from 4-methylanisole was 4-methylphenol; it was formed more than five times faster than 2,4-dimethylphenol when the catalyst was Pt/SiO_2-Al_2O_3 but only twice as fast when the catalyst was Pt/γ-Al_2O_3 (the other products were formed even more slowly). The formation of 4-methylphenol was more than five times faster than the formation of toluene with each of these catalysts. 2-Methylphenol was formed nearly twice as fast as 2,4-dimethylanisole when the catalyst was Pt/SiO_2-Al_2O_3 and an order of magnitude faster when the catalyst was Pt/γ-Al_2O_3. Each of the products was possibly formed in a primary reaction, although these products could also have been formed in sequential reactions.

In contrast, we infer that 2,4,6-trimethylphenol was formed only in a sequence of reactions, methyl-group transfers. The primary product, for example, can be inferred to be 2,4-dimethylphenol or 2,4-dimethylanisole.

Working from the result that methyl group transfer, HDO, hydrogenolysis, and hydrogenation are the important reaction classes, and by recognizing which compounds were primary products, we inferred the reaction network of Fig. 7 for 4-methylanisole conversion catalyzed by the supported platinum catalysts in the presence of H_2. The network is based not just on the identification of these kinetically significant reaction classes, but also on our judgment of the most likely pathways for formation of the minor and trace compounds—via these classes of reactions.

For example, we infer that xylenes (trace products) were formed from 4-methylanisole via sequential HDO and

Fig. 2 Selectivity for the formation of 4-methylphenol, 2,4-dimethylphenol, 2,4,6-trimethylphenol, and toluene in the conversion of anisole catalyzed by Pt/γ-Al_2O_3 at 573 K. Data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts of regression lines significantly different from zero selectivity at zero conversion (analyzed with 95% confidence limits) indicate primary products, in this case 4-methylphenol, 2,4-dimethylphenol, 2,4,6-trimethylphenol, and toluene



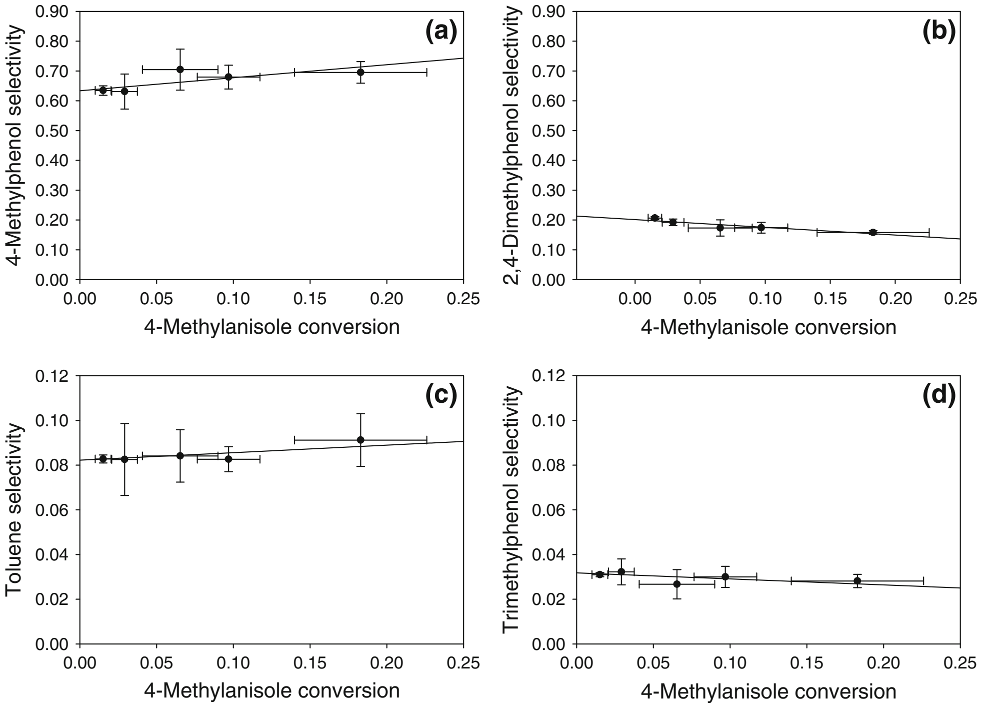


Fig. 3 Selectivity for the formation of 4-methylphenol, 2,4-dimethylphenol, toluene, and 2,4,6-trimethylphenol in the conversion of anisole catalyzed by Pt/SiO_2-Al_2O_3; conditions are stated in the text. Data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts significantly different from zero at zero conversion (analyzed with 95% confidence limits) indicate primary products, in this case 4-methylphenol, 2,4-dimethylphenol, 2,4,6-trimethylphenol, and toluene

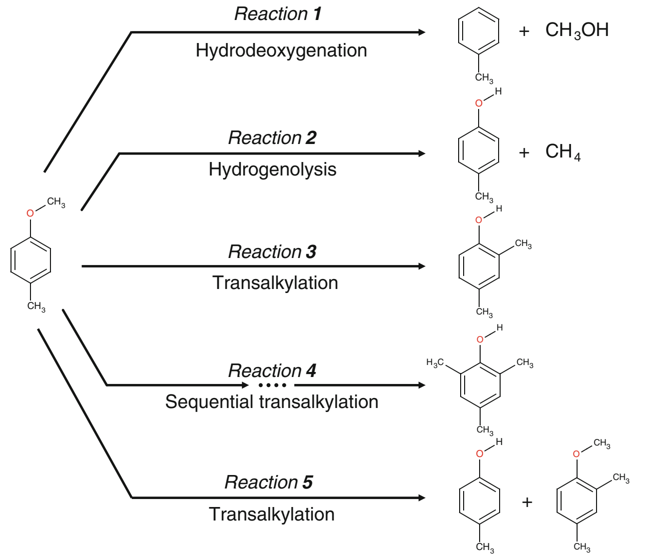


Fig. 4 Reaction network for formation of primary products based on analysis of selectivity-conversion plots for the conversion of 4-methylanisole catalyzed by Pt/Al_2O_3 or Pt/SiO_2-Al_2O_3 in the presence of H_2 at 573 K. H_2 as a reactant is omitted for simplicity. 2,4,6-Trimethylphenol appears on the basis of the selectivity-conversion plot to be a primary product, but we infer that it must instead have been formed by a sequence of reactions

transalkylation reactions, and that trimethylanisoles (which were identified as trace products) were formed from the primary product 2,4-dimethylanisole by sequential transalkylation reactions. But we caution that more detailed investigations could lead to modifications of the suggested reaction network.

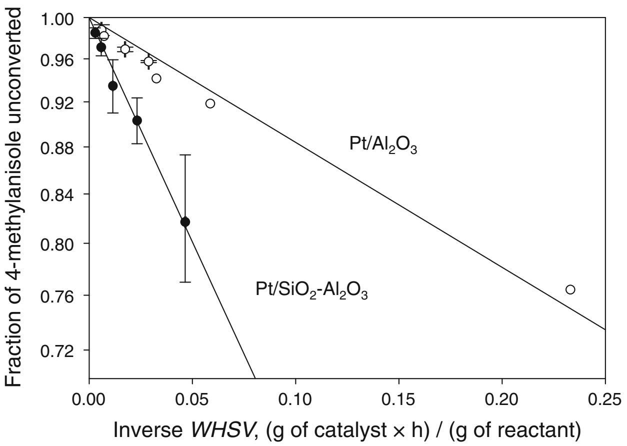


Fig. 5 Demonstration of first-order kinetics of overall conversion of anisole catalyzed by Pt/Al_2O_3 and by Pt/SiO_2-Al_2O_3 at 573 K; other conditions stated in the text

4 Discussion

4.1 Products Formed in the Conversion of 4-Methylanisole: Roles of Catalyst Functions

An important result is that transalkylation involving methyl in methoxy groups is the only kinetically significant reaction class observed with the acid catalyst (the zeolite). Thus, the major products formed from 4-methylanisole in the presence of this catalyst were 4-methylphenol, 2,4-dimethylanisole, 2,4-dimethylphenol, and 2,4,6-trimethylphenol, and the minor and trace products included phenols and anisoles with increased numbers of methyl substituents on their aromatic

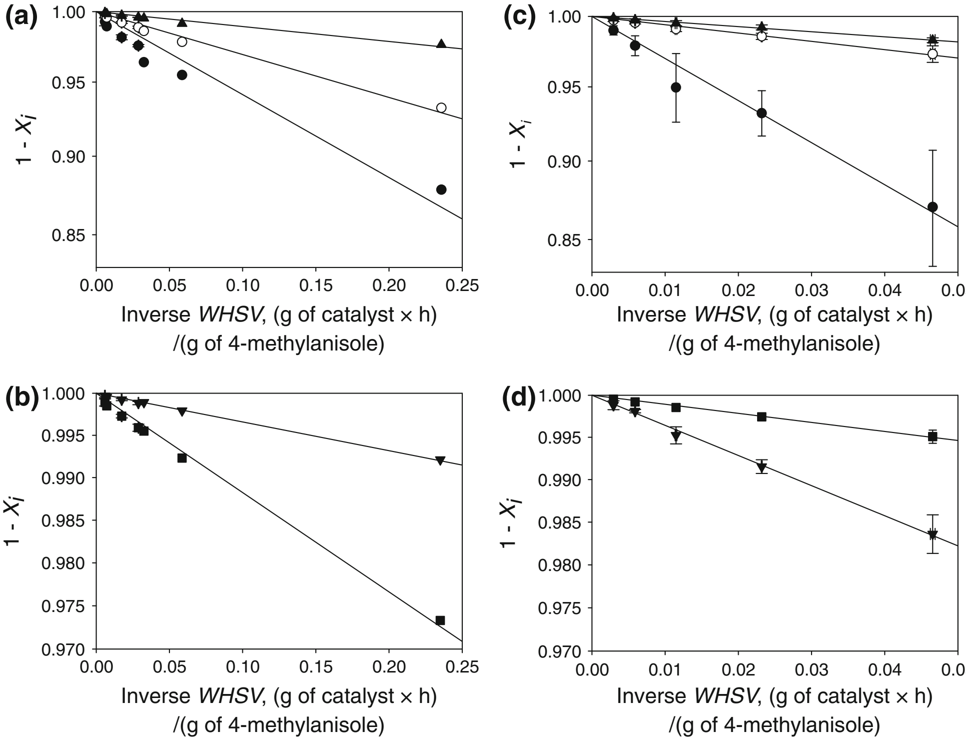


Fig. 6 Semi-logarithmic plots of the conversion of 4-methylanisole catalyzed by Pt/γ-Al_2O_3 (**a, b**) or by Pt/SiO_2-Al_2O_3 (**c, d**) in the presence of H_2 at 573 K to give 4-methylphenol (*filled circle*), 2,4-dimethylphenol (*open circle*), toluene (*filled triangle*) 2,4,6-trimethylphenol (*filled square*), and 2,4-dimethylanisole (*filled inverted triangle*). The term $(1-X_i)$ represents the conversion to product i. Conversion was varied by changing the catalyst mass in the packed bed reactor

Table 3 Pseudo-first-order rate constants characterizing of conversion of 4-methylanisole catalyzed by Pt/Al_2O_3 and by Pt/SiO_2-Al_2O_3 and of anisole catalyzed by Pt/Al_2O_3 at 573 K

Reaction number (keyed to Fig. 4)	Product	Pseudo-first-order rate constant for reaction of 4-methylanisole catalyzed by Pt/Al_2O_3	Pseudo-first-order rate constant for reaction of 4-methylanisole catalyzed by Pt/SiO_2-Al_2O_3	Pseudo-first-order rate constant for reaction of anisole catalyzed by Pt/Al_2O_3
1	Toluene	0.76	2.6	–
2	4-Methylphenol	4.2	21	–
3	2,4-Dimethylphenol	2.2	4.2	–
4	2,4,6-Trimethylphenol	0.82	0.75	–
5	2,4-Dimethylanisole	0.24	2.5	–
–	Benzene	–	–	0.86
–	Phenol	–	–	12
–	2-Methylphenol	–	–	2.8
–	2,6-Dimethylphenol	–	–	0.49
–	2-Dimethylanisole	–	–	0.14

Pseudo-first-order rate constants for the formation of individual primary products are stated in units of L/(g of catalyst × h). These rate constants were determined from the conversions to the individual products

rings. Transalklyation involving the methyl group substituted on the aromatic ring, as indicted by the lack of 2-methylanisole or 2-methylphenol formed in the conversion of 4-methylanisole, was not kinetically significant.

The fact that these acid-catalyzed reactions were also observed with the supported platinum catalysts leads to the inference that the supports (γ-Al_2O_3 and SiO_2-Al_2O_3) were responsible for these reactions in the presence of the supported metal catalysts. This inference is consistent with results characterizing the conversion of anisole [15, 17] and guaiacol [16, 18] catalyzed by Pt/γ-Al_2O_3.

Other products observed only when the catalyst was a supported metal, either Pt/γ-Al_2O_3 or Pt/SiO_2-Al_2O_3, include toluene. This result indicates the need for a metal function and H_2 to remove oxygen bonded to the aromatic ring.

4.2 Comparison of Reaction Networks of 4-Methyanisole and Anisole

The reaction network of Fig. 7 accounts for the major products, as well as minor and trace products, in the

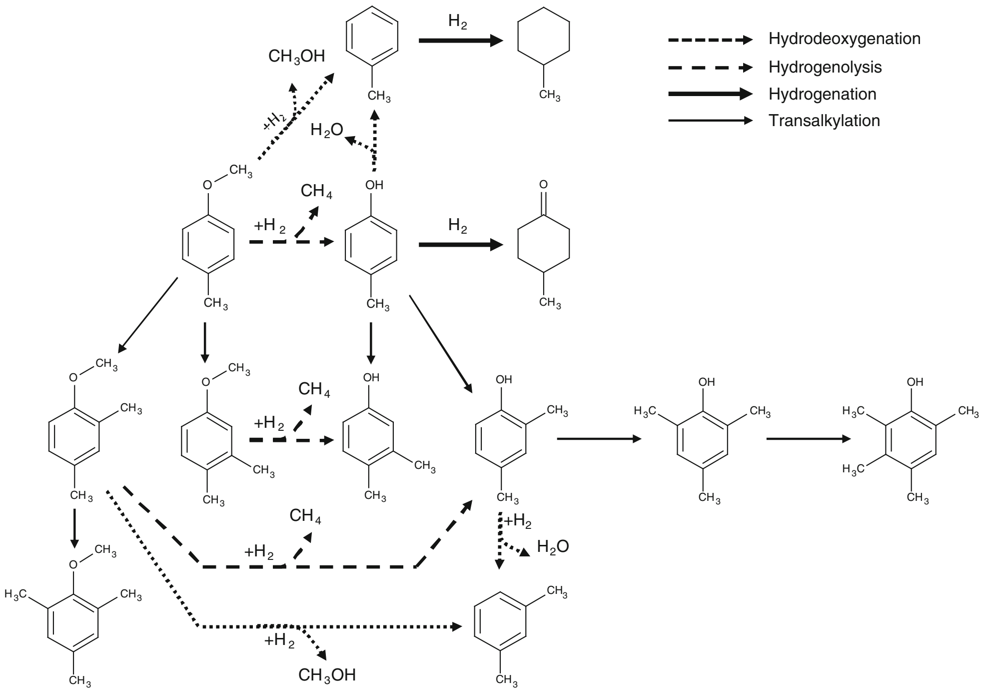


Fig. 7 Reaction network for the conversion of 4-methylanisole and H_2 catalyzed by supported platinum catalysts at 573 K. Hydrodeoxygenation, hydrogenolysis, hydrogenation, and transalkylation reactions are represented by *different styles of arrows* shown in the legend. H_2, as a reactant, is omitted for simplicity. The representation in this network is simplified: for example, in transalkylation reactions in which two 4-methylanisole molecules are involved (e.g., 2,4-methylanisole→4-methylphenol + 2,4-dimethylanisole), the stoichiometry is not represented here

conversion of 4-methylanisole catalyzed by supported platinum. The data presented here characterizing the conversion of 4-methylanisole and a comparison with the data obtained under the same conditions for the conversion of anisole [15] show that the patterns of reactivity are essentially the same for the two reactants. The reaction classes are the same: transalkylation, HDO, hydrogenolysis, and hydrogenation. The data indicate the effect of the methyl substituent on the aromatic ring.

For example, 4-methylanisole conversion leads to products that are homologues of those formed in the conversion of anisole; specifically, toluene is formed in the conversion of 4-methylanisole, and benzene is formed in the conversion of anisole. The formation of 4-methylphenol, 2,4-dimethylphenol, 2,4-dimethylanisole, and 4-methylcyclohexanone in the conversion of 4-methylanisole parallels the formation of phenol, 2-methylphenol, 2-methylanisole, and cyclohexanone in the conversion of anisole.

The data allow a comparison of the rate constants of these reactions. The rate constants characterizing the hydrogenolysis and HDO reactions catalyzed by Pt/γ-Al_2O_3 in the conversion of anisole are greater than those characterizing the analogous reactions in the conversion of 4-methylanisole (Table 3). For example, the rate constants for conversion of 4-methylanisole to toluene and of anisole to benzene are, respectively, 0.76 and 0.86 L/(g of catalyst × h); and the rate constants for conversion of 4-methylanisole to 4-methylphenol and of anisole to phenol are, respectively, 4.2 and 12 L/(g of catalyst × h). Intramolecular transalkylation leading to the formation of 2-methylphenol from anisole is faster than transalkylation leading to the formation of 2,4-dimethylphenol from 4-methylanisole, as indicated by the respective rate constants of 2.8 and 2.2 L/(g of catalyst × h). Intermolecular transalklyation is faster in the conversion of 4-methylanisole than in the conversion of anisole; for example, the rate constants for conversion of 4-methylanisole to 2,4-dimethylanisole and of anisole to 2-methylanisole are 0.24 and 0.14 L/(g of catalyst × h), respectively.

Extension of this type of analysis as further data are accumulated is expected to be of value for prediction of reactivities of mixtures of compounds characteristic of bio-oils.

4.3 Role of the Support: Quantitative Comparison of Conversions Catalyzed by Supported Platinum Catalysts

The data show how the rates of conversion differed from one catalyst to the other, with the conversion catalyzed by Pt/SiO_2-Al_2O_3 being three times faster than the conversion catalyzed by Pt/Al_2O_3. These two supported platinum samples catalyzed similar reactions as they both contained platinum with essentially the same loadings and dispersions, but the supports have different acidities. The initial conversions were higher when the catalyst was Pt/SiO_2-Al_2O_3 than when it was Pt/γ-Al_2O_3 at the same inverse space velocity (Fig. 5). The higher activity of the Pt/SiO_2-Al_2O_3 is inferred to be an indication of its greater support acidity.

The selectivity also differed from one catalyst to the other (Table 3). For example, transalklyation reactions leading to the formation of 2,4-dimethylphenol and 2,4-dimethylanisole were faster when the supported platinum catalyst incorporated the more acidic support, SiO_2-Al_2O_3. The rate constant for HDO was also greater for the more acidic support; this result was unexpected because the metal loading and dispersion of the two catalysts were similar. The selectivity of HDO conversion to toluene, however, was similar for the two supported metal catalysts.

The effect of the acidity of the support on HDO indicates an opportunity to tune the acid and metal functions to optimize the activity and selectivity in HDO, but we emphasize that the H_2 partial pressure is another significant variable.

5 Conclusions

In the conversion of 4-methylanisole catalyzed by Pt/Al_2O_3, Pt/SiO_2-Al_2O_3, or HY zeolite, methyl group transfers were found to be kinetically significant reactions that were catalyzed by the acidic catalyst functions and did not involve the platinum. Transalkylation reactions involving the methyl group bonded to the aromatic ring were not found to be significant. When the catalyst included platinum and the conversion took place in the presence of H_2, the reactions included C–O bond-breaking and hydrogenation. The Pt/SiO_2-Al_2O_3 catalyst, with its higher surface area and more acidic support, was more active than Pt/γ-Al_2O_3 for the formation of 4-methylphenol, 2,4-dimethylphenol, 2,4-dimethylanisole, and toluene. The increase in the rate of HDO resulting from the replacement of the γ-Al_2O_3 support with SiO_2-Al_2O_3 is a surprising result; the selectivity for oxygen removal, however, was reduced slightly by this replacement. The data suggest opportunities for using higher H_2 partial pressures and for tuning the catalyst functions to increase both the activity and selectivity for oxygen removal.

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References

1. Huber GW, Iborra S, Corma A (2006) Chem Rev 106:4044
2. Zakzeski J, Bruijnincx PCA, Jongerius AL, Weckhuysen BM (2010) Chem Rev 110:3552
3. Corma A, Iborra S, Velty A (2007) Chem Rev 107:2411
4. Bridgwater AV (2007) Biomass Bioenergy 31:VI
5. Czernik S, Bridgwater AV (2004) Energy Fuels 18:590
6. Oasmaa A, Czernik S (1999) Energy Fuels 13:914
7. Branca C, Giudicianni P, DiBlasi C (2003) Ind Eng Chem Res 42:3190
8. Sharma RK, Bakhshi NN (1993) Energy Fuels 7:306
9. Sharma RK, Bakhshi NN (1993) Biomass Bioenergy 5:445
10. Adjaye JD, Katikaneni SPR, Bakhshi NN (1996) Fuel Process Technol 48:115
11. Elliott DC, Hart TR, Neuenschwander GG, Rotness LJ, Zacher AH (2009) Environ Prog Sustain Energy 28:441
12. Elliott DC, Neuenschwander GG (1997) In: Bridgwater A, Boocock DGB (eds) Developments in thermochemical biomass conversion. London, Blackie, p 611
13. Samolada MC, Baldauf W, Vasalos IA (1998) Fuel 77:1667
14. Girgis MJ, Gates BC (1991) Ind Eng Chem Res 30:2021
15. Runnebaum RC, Nimmanwudipong T, Block DE, Gates BC (2011) Catal Lett 141:817
16. Nimmanwudipong T, Runnebaum RC, Block DE, Gates BC (2011) Catal Lett 141:779
17. Runnebaum RC, Nimmanwudipong T, Block DE, Gates BC (2011) Energy Fuels 25:4776
18. Nimmanwudipong T, Runnebaum RC, Block DE, Gates BC (2011) Energy Fuels 25:3417
19. Nimmanwudipong T, Runnebaum RC, Tay K, Block DE, Gates BC (2011) Catal Lett 141:1072
20. Runnebaum RC, Nimmanwudipong T, Block DE, Gates BC (2011) Catal Sci Technol doi:10.1039/C1CY00169H
21. Huber GW, Chheda JN, Barrett CJ, Dumesic JA (2005) Science 308:1446
22. Román-Leshkov Y, Barrett CJ, Liu ZY, Dumesic JA (2007) Nature 447:982
23. Kunkes EL, Simonetti DA, West RM, Serrano-Ruiz JC, Gartner CA, Dumesic JA (2008) Science 322:417
24. Bond JQ, Alonso DM, Wang D, West RM, Dumesic JA (2010) Science 327:1110
25. Jiang G, Nowakowski DJ, Bridgwater AV (2010) Energy Fuels 24:4470
26. Ben H, Ragauskas AJ (2011) Energy Fuels 25:2322
27. Streitwieser A Jr, Heathcock CH (1985) Introduction to organic chemistry. Macmillan, New York