

Synthesis of Metal Supported Catalysts for the Hydrogenolysis of Lignin

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Abstract:

Transition-metal (nickel, cobalt, copper, and iron) containing metal-oxide material (silica, alumina, and titania) were screened in an effort to develop heterogeneous catalysts for the hydrogenolysis of lignin that selectively cleave aryl ether linkages. Different combinations of active transition-metal precursors with metal-oxide supports were synthesized by sol-gel processes, and the synthetic conditions for silica-, alumina-, and titania-supported catalysts were optimized. To minimize contamination and avoid oxidation, multiple washes with deionized water followed by sonication, centrifugation, Soxhlet extraction, and calcination under flowing inert nitrogen (N) atmosphere were investigated and an optimal protocol determined. Future characterization studies and investigations on catalytic activity and selectivity for aryl ether hydrogenolysis will determine the optimal transition-metal and metal-oxide support combination for selective hydrogenolysis of lignin.

Introduction:

Plant biomass, a renewable resource rich in carbon and chemical potential energy, is a promising feedstock to displace non-renewable petroleum [1]. In particular, lignin, one of the three main components of the plant cell wall, is an under-utilized feedstock that is currently considered as waste [1].

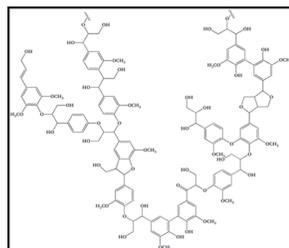


Figure 1: Representation of the molecular structure of lignin.

The highly heterogeneous structure of lignin (Figure 1) makes it difficult to deconstruct and therefore utilize; however, its rich aromatic composition is an ideal precursor for a variety of fuels and value-added reactive intermediates [1]. While many thermochemical processes can exploit lignin's potential, large energy inputs and harsh reaction conditions are required, often leading to a wide distribution of products [1].

Our research goal focused on synthesizing transition-metal containing metal-oxide catalysts that will be utilized in the production of a narrow distribution of phenolic-like products from lignin with minimal energy and material inputs. Sol-gel processes were employed due to better control on catalyst

structure and chemical properties, higher thermal stability, and its low-cost [2].

Experimental Procedure:

All catalysts were prepared by co-precipitation methods adapted from literature and had a transition-metal to metal-oxide ratio of 0.6 [2]. Active component metal precursor solutions included: either 30 mL of a 0.86 M transition-metal ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) or 53 mL of a 0.49 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution in 100% ethanol. Mesoporous variants were synthesized to control porosity using various surfactants. In each case, mesoporous variants were generated by adding hexadecyltrimethylammonium bromide (CTAB) prior to the addition of metal-oxide precursor. Figure 2 illustrates the chemistry that occurred in the synthesis of the catalysts. Figure 3 outlines the synthesis of the catalysts.

Silica-Supported Catalyst. An initial solution of tetraethyl orthosilicate and ethanol was added to 1.5 mL of 0.3 M hydrochloric acid (HCl). The solution was stirred at 50°C for 90 minutes. At 25°C, the appropriate active component metal precursor solution was added to the reaction mixture. A firm gel formed upon the slow addition of 35 mL 30% aqueous ammonium hydroxide in 65 mL ethanol.

Alumina-Supported Catalyst. A solution of 10.0 g hexylene glycol in the appropriate active component metal precursor solution was stirred at 95°C for 30 minutes. Aluminum isopropoxide (8.6 g) was then introduced to the solution and stirred at 120°C for four hours. At 95°C, a saturated solution of sodium hydroxide in ethanol (~0.5 mL) was added every 30 minutes for a span of 90 minutes. At 25°C, the pH of the solution was adjusted to 9.0 with sodium hydroxide.

Titania-Supported Catalyst: A solution containing 12.2 g titanium isopropoxide, 22 mL ethanol, and the appropriate active component metal precursor solution was mixed under inert (argon) atmosphere. A second solution consisting of 3 mL of 1.8 M nitric acid in 3 mL 100% ethanol was slowly added to the first solution, resulting in the formation of a firm gel.

For all catalysts, the gelled suspension solution was stirred at 25°C for 30 min, sonicated for 1 h, and aged at 25°C for 85 h.

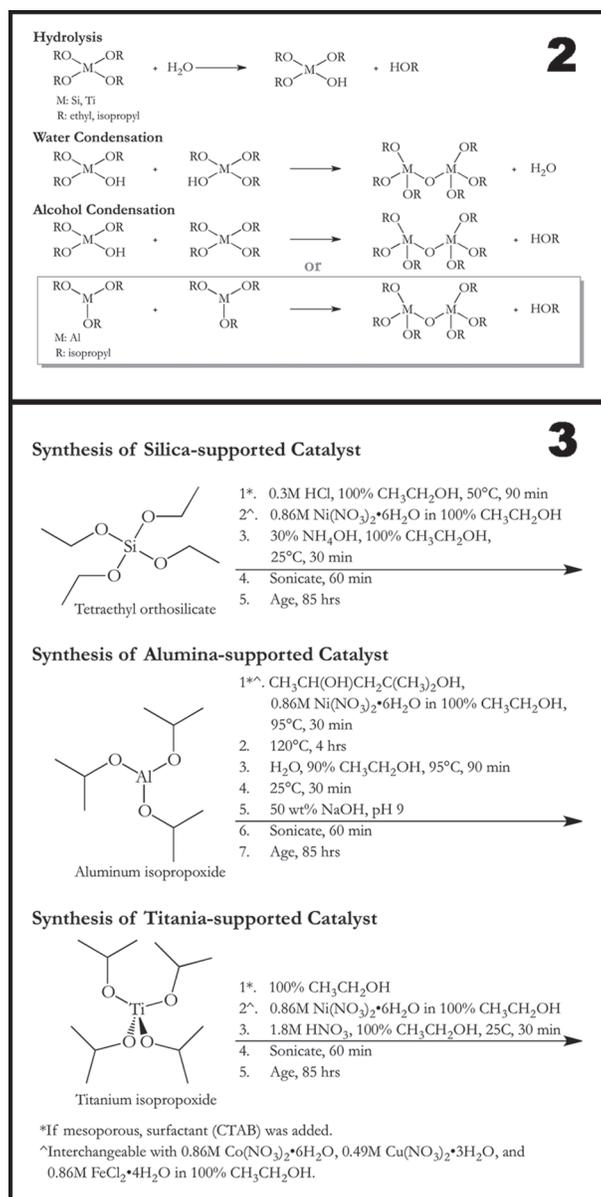


Figure 2, top: Three primary reactions in silica, titania, and alumina gel formation.

Figure 3, bottom: Adapted synthesis protocol for metal supported catalysts.

Purification of Catalysts. Catalysts were washed with deionized water, collected by centrifugation, and underwent Soxhlet extraction with deionized water overnight and then with ethanol overnight or 48 hours for mesoporous variants. Catalysts were dried overnight at 105°C under vacuum and calcinated under flowing inert N atmosphere at 550°C for 5 h.

Conclusions and Future Work:

Metal supported catalysts were successfully synthesized after modifications to the synthesis and purification protocols. Sol-gel condensation reactions in alumina-supported catalysts were optimized at 25°C at a pH of 9.0. To prevent premature

gelling and the formation of heterogeneous products, titania-supported catalysts required lower reaction concentrations. Furthermore, the incorporation of the transition-metals in the titania-supported catalysts appeared to be low due to their appearance. Ultimately, future work with titania will use an alternative procedure.

To minimize contamination by unincorporated metal precursors, multiple washes with deionized water followed by sonication, centrifugation, and Soxhlet extraction were determined to be optimal. In addition, calcination can cause significant oxidation and charring, and therefore must be performed under flowing inert nitrogen atmosphere rather than in air.

Future work includes characterizing the chemical and physical properties of the catalysts by several methods (Table 1). To determine the effect catalyst structure has on the activity and selectivity for aryether hydrogenolysis, catalysts will be screened against model compounds and lignin. Various preparation methods will be explored to investigate the effect preparation method has on catalyst structure. Ultimately, the goal is to determine the optimal transition-metal and metal-oxide support combination for aryl ether hydrogenolysis.

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References:

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 [2] Goncalves, G., et al.; Journal of Non-Crystalline Solids, 352(32), 3697-3704 (2006).

Method or Instrument	Purpose
Brunauer-Emmett-Teller (BET) method	Specific surface area
Barrett-Joyner-Halenda (BJH) method	Pore diameter
Fourier transform infrared spectroscopy (FTIR)	Carbon contamination
Inductively coupled plasma mass spectrometry (ICP-MS)	Metal composition
Hammett acidity function	Acidity of catalyst
Esterification	Acidity of catalyst
Transmission electron microscopy (TEM)	Particle size and shape

Table 1: Characterization methods for determining the chemical and physical properties of the catalysts.