

Catalytic oxidation of alcohol moieties in lignin and lignin model compounds

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Introduction

With world demand for liquid petroleum expected to increase by more than 25% in the next 30 years¹ and reserves of readily accessible petroleum diminishing, there is a strong need to replace petro-derived fuels and chemicals with renewable and sustainable resources. Lignin (the polymer product of the three monolignols, namely, sinapyl-, coniferyl-, and p-coumaryl- alcohol) is the second most abundant biopolymer on Earth and the world's largest renewable aromatic resource. These characteristics, coupled with its present underutilization, make lignin uniquely well-suited for replacement of petroleum in chemical and fuel production.

In the present work the focus was to develop a protocol for catalytic oxidative depolymerization of lignin. An oxidative pathway to lignin depolymerization is highly desirable given that highly corrosive alkali species, high pressures of petro-derived H₂, or high temperatures (as in pyrolysis) are not required. Due to the irregular structure of lignin, its characterization remains a challenge. For this reason simple model systems were employed for the development of suitable reagents and reaction conditions. In this work, the benzylic alcohol moiety present in both the β -O-4 and β -1 linkages found in lignin was targeted for selective oxidation. In total, benzylic alcohols comprise as much as 67% of the linkages found in lignin². We show that the use of Layered Double Hydroxides (LDHs) in combination with molecular oxygen may be the key to unlocking the first step of an oxidative pathway to lignin depolymerization.

Materials and Methods

Catalysts were prepared from literature procedures via coprecipitation³. In a typical synthesis two solutions, one containing the appropriate metal nitrates and one containing a mixture of NaOH and Na₂CO₃, were simultaneously added and mixed while maintaining a constant pH (usually 8-10). The resulting slurry was aged overnight, washed to neutral pH and dried *in vacuo*.

In a typical oxidation reaction a 3-neck reaction flask was charged with catalyst (0.5 g), 1-phenyl ethanol (2 mmol) and solvent (10 mL). The mixture was stirred at the desired temperature while O₂ was continuously bubbled through it. Subsequently, the catalyst was removed by filtration and the products were analyzed using a HP6890 GC-FID equipped with a DB-Wax column (30 m x 530 μ m x 0.5 μ m).

Results and Discussion

Following the work of Choudary et al.⁴, LDHs were investigated as catalysts for the oxidation of a lignin model compound, 1-phenyl ethanol, using O₂ as the oxidant. While Choudary's Ni-Al LDH catalyst is active for benzylic alcohol oxidation in non-polar solvents

such as toluene and hexane, for this catalyst to be successful in lignin oxidation a more polar solvent is required. Consequently, solvents were screened which are compatible with organosolv lignin. During initial work it was found that the only effective solvents for conversion of 1-phenylethanol were toluene, α,α,α -trifluorotoluene, and, to a limited extent, 1,4-dioxane. Of these solvents, only 1,4-dioxane partially dissolves lignin. Thus in order to exploit the properties of both toluene (an electron rich solvent) and 1,4-dioxane (an ether), phenyl ether was chosen as solvent. Notably, phenyl ether was found to be effective as a solvent for both the dissolution of organosolv lignin and for the conversion of 1-phenyl ethanol to acetophenone in 97% yield. Other LDH catalysts, containing copper and manganese, were also found to be active for the oxidation of 1-phenyl ethanol, as shown in Table 1.

Table 1. Oxidation of 1-phenyl ethanol to acetophenone using LDH catalysts/O₂.

LDH Composition	Solvent	Time (h)	Temp. (°C)	% Yield
Ni-Al (2:1)	Phenyl ether	44	150	97.2
	α,α,α -trifluorotoluene	6	reflux	98.4
	Toluene	6	85	98.6
	Dimethyl sulfoxide	6	120	4.4
	Chloroform	6	60	1.2
	Hexachloroacetone	6	85	0.6
	1,4-Dioxane	6	85	8.2
	Benzonitrile	24	90	1.1
	1,2-Dichlorobenzene	6	85	0.5
Mn-Mg-Al (1:1:1)	Toluene	24	reflux	48.5
	1,2-Dichloroethane	24	80	4.9
Mn-Mg (1:1)	Toluene	24	reflux	68.5
	Methanol	24	80	0.7
	Phenyl ether	24	150	97.7
Ni-Fe (3:1)	Phenyl ether	20	150	51
Cu-Mg-Fe (1:1:1)	Toluene	24	reflux	47.6
Cu-Mg-Mn (1:1:1)	Toluene	24	reflux	98.8

Significance

Lignin utilization is a key component of the biorefinery concept. In this work, LDH catalysts were explored for oxidation of the benzylic alcohol moiety present in lignin in solvents suitable for lignin dissolution. This could be the first step in developing an inexpensive approach to lignin utilization.

References

1. International Energy Outlook 2013. Administration, U. S. E. I., Ed. Online, 2013.
2. Zakzeski, J.; Bruijninx, P. C. A.; Jongerius, A. L.; Wechhuysen, B. M., *Chemistry Reviews* 2010, 110, 3552.
3. Sparks, D.E.; Morgan, T.; Patterson, P.; Tackett, S.A.; Morris, E.; Crocker, M. *Applied Catalysis B* 2008, 82, 190-198.
4. Choudary, B. M.; Kantam, M. L.; Rahman, A.; Reddy, C. V.; Rao, K. K. *Angewandte Chemie International Edition* 2001, 40 (4), 763-766.