

综述与专论

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木质素的催化加氢转化

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摘要: 木质素是来源于木质纤维素的一种重要的可再生生物质资源, 可用于制备化学品和燃料。由于木质素本身结构的复杂性和稳定性使其难以有效利用。目前大量的制浆和造纸工业的木质素没有得到有效利用, 大部分用于燃烧供能, 并且造成了一定程度的环境污染。为了保护环境、实现可持续发展, 催化转化木质素制备高附加值化学品成为了研究的热点。木质素转化的研究众多, 但是进展依然相对缓慢。目前主要的转化方法包括碱催化解聚、酸催化解聚、热化学转化、加氢处理解聚、氧化解聚等。由于加氢处理解聚木质素可以获得低聚木质素、酚类等有价值的化学品和制备烃类燃料, 是目前研究的热点和最有效的方法之一。但是, 催化剂失活和解聚产物产率不高依然是需要进一步解决的问题。基于此, 梳理了近年来木质素加氢处理主要的催化体系和相关结果, 提出了尚待解决的问题, 以期今后建立有效的木质素解聚体系并实现其高值化利用的相关研究提供参考。

关键词: 生物质; 木质素; 催化剂; 加氢; 降解

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Catalytic hydroprocessing of lignin

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Abstract: Lignin derived from lignocellulose is a renewable resource for the production of chemicals and fuels. However, due to its highly irregular polymeric structure and the carbon based inactive property, lignin valorization is very difficult. Lignin is usually viewed as a waste by-product in the current biorefinery processes and most of the lignin is burned to produce heat and power for the biorefinery processes. There were a series of studies on the lignin conversion such as depolymerization over acid or base, pyrolysis, hydroprocessing and oxygenation. The degradation of lignin over hydroprocessing was the most efficient method to produce alkane fuels and high value-added chemicals such as phenols. However, there were some problems remained to be solved such as catalyst deactivation and low yield. This review focuses on the catalytic systems for lignin hydroprocessing and current challenges in order to provide a reference for efficient and large-scale application of lignin.

Key words: biomass; lignin; catalyst; hydrogenation; degradation

引 言

木质素是植物的重要组成结构之一, 在自然界

中的储量丰富^[1]。木质素是复杂的三维无定形聚合物, 主要由芥子醇、松柏醇、香豆醇 3 种结构单元 (表 1)^[2]通过碳氧键 (包括 β -O-4, 4-O-5, α -O-4

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表 1 木质素结构单元在各种植物中的含量^[2]Table 1 Abundance of primary lignin units in different types of plants^[2]

Lignin units	Grass	Softwood	Hardwood
sinapyl alcohol	20%—50%	0—1%	50%—75%
coniferyl alcohol	25%—50%	90%—95%	25%—50%
<i>p</i> -coumaryl alcohol	10%—25%	0.5%—3.4%	—

等)和碳碳键(包括 β - β , β -5, β -4, 5-5 等)(图 1)^[1,3]无规聚合形成,是自然界中非石油资源的可再生芳香化合物的主要来源^[4]。

木质素转化研究的难点在于其结构和组成的不确定性。而木质素结构的差别,是由生物质自身的种类不同,生长环境和生长季节甚至来源部位不同造成的^[5]。对木质素进行结构分析需要将木质素先分离出来,这就导致了分析出来的结构与分离过程相关,木质素的天然结构依然难以确定^[6]。木质素结构和预处理方法相关,不同的处理方法得到的木质素结构有时差异巨大^[7]。Dale 等^[8]将不同的预处理方法分为 4 类:物理处理法(例如球磨)、溶剂分离法、化学方法和生物处理方法。每种处理方法

得到的木质素都有其自身的优点和缺点,对于进一步降解木质素得到的产物和降解过程也都有一定的影响^[7]。目前,木质素的主要来源是制浆和造纸工业(如碱木素、木质素磺酸等)以及专门用于生物质生产的能源作物(如有机溶剂木质素)。根据工艺的不同,主要获得的是磺酸木质素、碱木质素、酶解木质素和有机溶剂木质素等。碱木质素和磺酸木质素是碱法和亚硫酸法造纸的副产物。

木质素的复杂酚类聚合结构具有化学稳定性,其转化所需条件非常苛刻。目前应用于木质素解聚的方法众多,主要有碱催化的解聚、酸催化的解聚、热化学催化的木质素解聚、氧化解聚、加氢处理的解聚等^[9]。其中木质素的加氢处理是木质素转化最常见和最有效的方法之一,报道的文献众多,但是所用的催化剂体系复杂,且仍有许多问题未解决。因此,本文主要介绍加氢处理木质素的解聚方法,归纳总结目前报道的催化剂及其产率,并展望未来木质素加氢处理的催化剂发展方向,以期对木质素加氢解聚工作提供理论指导。

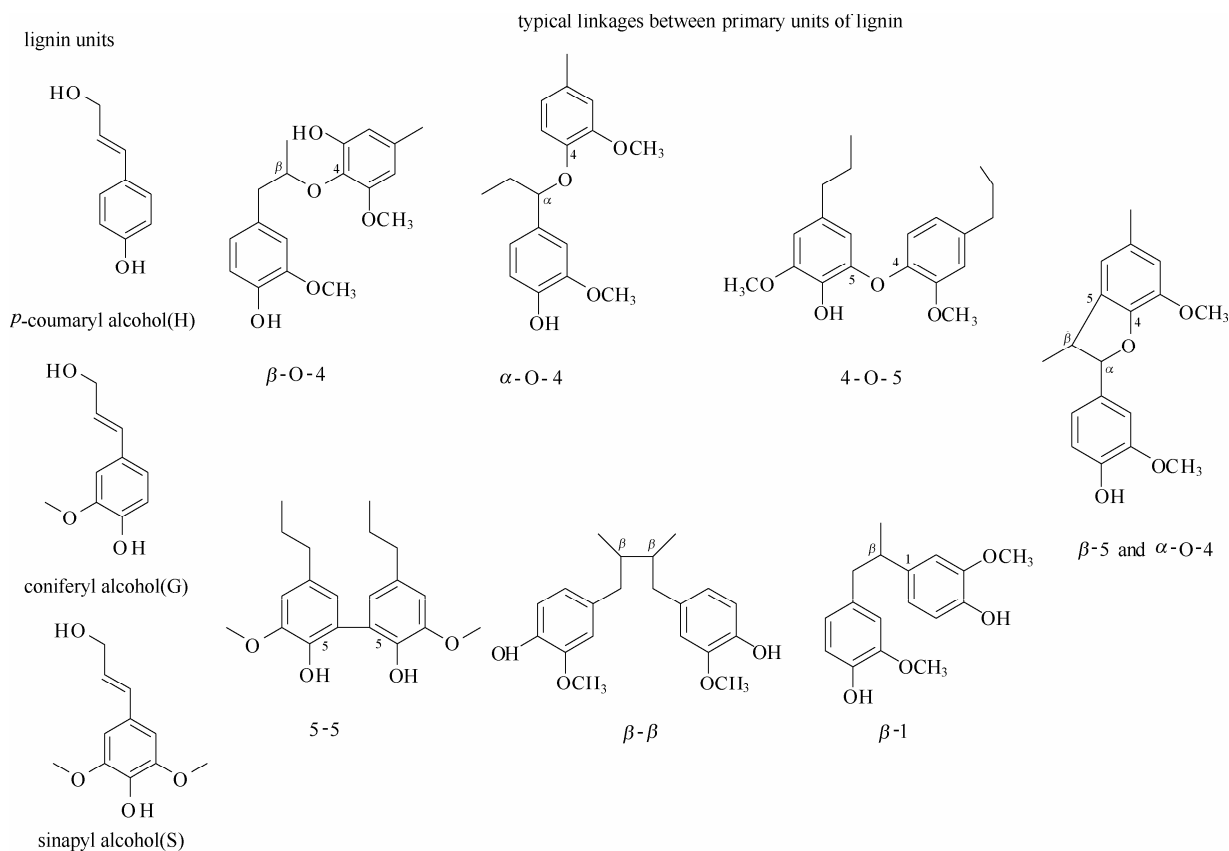


图 1 木质素结构单元及常见键接方式

Fig.1 Building blocks of lignin and typical linkages

1 木质素加氢解聚处理过程

木质素的加氢处理过程就是利用氢(氢气或其他氢源)对木质素进行热还原的过程。通过加氢处理,可以获得解聚的木质素、酚类和其他具有高附加值的化学品,以及制备小分子量的碳氢燃料。木质素的加氢处理过程涉及的主要反应类型包括氢解(hydrogenolysis)、加氢烷基化(hydroalkylation)、加氢脱氧(hydrodeoxygenation)、加氢(hydrogenation)以及综合的加氢过程(integrated hydrogen-processing)^[9]。

氢解是氢断裂碳碳键或碳杂原子(O、N、S等)键的化学反应^[10]。氢解是木质素中加氢处理断裂碳氧键的主要方式。加氢脱氧(HDO)可以去除酚类分子中的氧,用于制备碳氢化合物。加氢脱氧是生物油转化的重要方法,属于氢解的一种反应。加氢反应是利用一对氢原子饱和或者还原有机化合物的化学反应。碳碳双键、碳碳叁键、碳氧双键在加氢过程中饱和,增加了产物中氢原子的含量。通过选择合适的催化剂^[11-12]和反应条件可以选择性控制芳香基团中的碳碳双键和非芳香环中的碳碳双键、碳碳叁键、碳氧双键的饱和。通常加氢反应和氢解反应是同时发生的。由于木质素的复杂结构,难以获得单一的产物。其加氢过程也不是单一的一种反应,在氢解或加氢过程中,实际上还包含其他的反应过程。综合的加氢过程既包括木质素的解聚也包括解聚产物的转化。

加氢处理过程对反应条件的要求较高,因此催化剂对于加氢处理就显得非常重要。其中用于木质素加氢处理研究较多且效果较好的金属主要是镍、钼、钨、铈、铈、铈、铈和铂等。单金属催化剂、双金属催化剂和双功能催化剂用于加氢处理木质素及其模型物的工作也有报道。

2 镍催化木质素加氢处理

早在20世纪40年代,镍基催化剂就已经应用于木质素的加氢、氢解反应^[13]。Wenkert等^[14]报道了镍化合物和格氏试剂高效催化氢解芳基碳氧键的研究结果。

Sergeev等^[15]报道了可溶性镍化合物用于催化氢解二芳醚的研究。该催化剂对于底物有较宽的适用范围,不论是富电子基团取代还是缺电子基团取代的二芳基醚都能有效氢解。其对于碳氧键的断裂活性为 $\text{Ar}-\text{O}-\text{Ar} \gg \text{Ar}-\text{OMe} > \text{ArCH}_2-\text{OMe}$ 。随

后,非均相的镍基催化剂^[16]也相继出现,并且在负载量低至0.25%(mol)时,催化效果依然明显。在这些镍催化的反应中,添加碱很重要,但是具体的碱在反应中的作用依然不是很清楚。同时,均相和非均相的镍催化剂对于产物的选择性有很大的影响,这些结果都列在表2中。

Zhao等^[24]报道的Ni/SiO₂催化剂,能在水相中催化断裂芳香基的碳氧键。与之前报道的均相催化体系不同,该催化剂可以在水相中使用。通过催化氢解可以解开 β -O-4和 α -O-4键中碳氧键连接。由于水的存在,4-O-5键的断裂是氢解和水解共同作用的结果。但是,在断裂碳氧键的同时,不可避免地发生了苯环的加氢,在产物中能检测到环己醇的存在。

镍负载在碳和氧化镁上制成的催化剂不但能催化氢解模型物中的碳氧键,也能断裂磺酸木质素中的 β -O-4键,并使苯环不加氢^[19,25]。Wang等^[20]利用Ni/AC催化剂在醇溶剂中直接氢解真实木质素。在该反应中,醇溶剂亦可以作为氢源。Rinaldi等^[26]也发现了相似的氢转移解聚木质素的反应,并用镍基催化剂直接解聚白杨木质素。

对于许多反应,在催化剂中引入第2种金属可以有效地提升催化效果^[27]。Zhang等发现Ni-W₂C负载在碳上制备的催化剂,不但可以催化纤维素转化到乙二醇^[28-30],还可以催化木质素得到单酚类,产率可以达到46.5%^[21]。有趣的是,不论单独使用Ni/AC还是单独使用W₂C/AC进行反应,单酚的产率都不超过20%,Ni和W₂C的协同作用影响了木质素的转化反应。相似的Ni-TiN^[18]、NiAu^[23]和NiM(M=Rh, Ru, Pd)^[22]也都被制备并用于催化有机溶剂木质素氢解。协同作用的机理研究^[17,22]显示主要有3个方面的影响因素:①增加了表面金属活性位点;②提高了H₂和底物的反应活性;③阻碍了苯环的进一步加氢。

3 钼催化木质素加氢处理

20世纪80年代钼氧化物、钼硫化物、钼氮化物和钼碳化物已用于催化木质素及其模型物的加氢脱氧反应^[31]。在氧化钼催化的木质素模型物加氢脱氧的反应中,氧化钼优先断裂Ph—O—Me键中酚氧键^[32]。在碳化钼催化的苯甲醚加氢脱氧^[33]的反应中也有相同的结果。在载体和氮化方法的研究中发现,载体通过对活性位点的修饰可以改变产物的选择性,同时,分散度和氮化程度对于钼的催化活性

表 2 镍催化的木质素加氢处理

Table 2 Nickel catalytic lignin hydroprocessing

Catalyst	Reaction condition			Lignin(model) compound	Major products	Conversion	Ref.
	$T/^{\circ}\text{C}$	p/MPa	Solvent				
Ni(COD) ₂ , SiPr-HCl	120	0.1	<i>m</i> -xylene			>85%	[15]
heterogeneous Ni	120	0.1	<i>m</i> -xylene			72%	[16]
heterogeneous Ni, BuONa	120	0.1	<i>m</i> -xylene			19%	[16]
heterogeneous Ni, BuONa	120	0.1	<i>m</i> -xylene			>90%	[16]
Ni/SiO ₂	120	0.6	H ₂ O			6%—21%	[16]
Raney Ni	90	5	EtOH			33%	[17]
Raney Ni	90	5	decalin or methylcyclohexane			99%—100%	[17]
Ni-TiN	150	1.2	EtOH			99%	[27]
Ni/AC	200	5	EG	lignosulfonate	monophenols	68%	[19]
Ni/C	200	0.1(Ar)	MeOH, EtOH, EG	birch sawdust	monophenols	48%—54%	[20]
Ni-W ₂ C	235	6	H ₂ O	raw woody biomass	monophenols	46.5%	[21]
Ni ₈₅ Ru ₁₅	130	1	H ₂ O	organosolv lignin	monophenols	42%	[22]
Ni ₈₅ Rh ₁₅	130	1	H ₂ O	organosolv lignin	monophenols	50%	[22]
Ni ₈₅ Pd ₁₅	130	1	H ₂ O	organosolv lignin	monophenols	56%	[22]
Ni ₇ Au ₃	170	1	H ₂ O	organosolv lignin	monophenols	14%	[23]

表 3 钼催化的木质素加氢处理

Table 3 Molybdenum catalytic lignin hydroprocessing

Catalyst	Reaction conditions			Lignin(model) compound	Major products	Conversion	Ref.
	$T/^{\circ}\text{C}$	p/MPa	Solvent				
MoS ₂ / Al ₂ O ₃	250—450	3.4	1-methylnaphthalene	4-propylguaiacol	propylphenols, propylbenzenes	38%—99%	[37]
MoS ₂	350	4	decalin	4-methylphenol	toluene	60%	[36]
MoS ₂ / AC	300	5	decalin	guaiacol	phenol	30%	[35]
Mo ₂ C	150	0.1		anisole	benzene	100%	[33]
Mo ₂ N	300	5	decalin	guaiacol	phenol	10%	[38]
Mo ₂ N/ Al ₂ O ₃	300	5	decalin	guaiacol	catechol	66%	[10]
Mo ₂ N/ SAB-15	300	5	decalin	guaiacol	phenol	44%	[10]
MoN/ AC	300	5	decalin	guaiacol	phenol	$9.6 \times 10^{-6} \text{ mol} \cdot (\text{g cat})^{-1} \cdot \text{s}^{-1}$	[34]
MoP/ SiO ₂	300	0.1		guaiacol	benzene, phenol	54%	[39]
MoP	350	4	decalin	4-methylphenol	toluene	90%	[36]
MoO ₂	350	4	decalin	4-methylphenol	toluene	55%	[36]
MoO ₃	350	4	decalin	4-methylphenol	toluene	100%	[36]
MoO ₃	320	0.1		<i>m</i> -cresol	toluene	48.9%	[32]
MoO ₃	320	0.1		anisole	benzene	78.7%	[32]
MoO ₃	320	0.1		guaiacol	phenol, benzene	74.2%	[32]
MoO ₃	320	0.1		diphenyl ether	phenol, benzene	82.6%	[32]

也有很大的影响^[10, 34]。碳负载的硫化钼作为催化剂用于木质素加氢脱氧反应, 硫化钼的活性与所用的碳的结构和化学性质并没有太大关系^[35]。Smith 等^[36]比较了没有负载的低表面积的钼基催化剂 (MoS_2 、 MoO_2 、 MoO_3 和 MoP) 在 4-甲苯酚加氢脱氧反应中的活性。基于 CO 脱附的催化 TOF 值为 $\text{MoP} > \text{MoS}_2 > \text{MoO}_2 > \text{MoO}_3$, 活化能递增顺序为 $\text{MoP} < \text{MoS}_2 < \text{MoO}_2 < \text{MoO}_3$ 。催化剂的活性与钼的电子密度有关。有关钼催化剂的反应结果在表 3 中列出。

4 铂族金属催化木质素加氢处理

在涉及氢的反应中, 铂族金属 (铂、钯、钌、铑、铱) 拥有优异的催化性能^[9]。与镍基催化剂不同, 铂族金属拥有更高的加氢活性, 常常用于原始木质素或预处理的木质素直接加氢。不过, 铂族催化剂更倾向于使用温和的催化条件, 铂族催化剂催化氢解得到的氢解产物在较高的条件下不稳定。在温和条件下, Al-SBA-15 负载的 Ni、Pd、Pt、Ru^[39] 和 Pd/C^[40] 催化降解木质素得到单酚, 二聚体和低聚物, 选择性地断裂 $\text{Ar}-\text{O}-\text{R}$ 和 $\text{Ar}-\text{O}-\text{Ar}$ 链接。单体单元 (芥子醇、松柏醇、香豆醇) 组成比例不同的稻壳木质素可以通过钌碳^[41] 选择性地催化转化得到 4-乙基苯酚。来自不同原料的木质素和不同方法提取的木质素有明显的区别, Bouxin 等^[42] 研究了 Pt/ Al_2O_3 催化的不同木质素氢解产物的区别。他们发现木质素中 $\beta\text{-O-4}$ 键的含量越高, 单体的产率也就越高。高度缩合的木质素产生的主要是无烷基的酚类产物, 而没有缩合的木质素主要产生的是保留了侧链碳的酚类。

木质素二聚体模型物氢解^[19]的反应中, 钌碳催化解聚的产物主要是二聚体、环己烷和 Ni/C 的产物。钌碳不仅催化 $\beta\text{-O-4}$ 键的断裂还会使得芳环加氢。Abu-Omar 等^[43] 证明在钌催化剂中加入锌可以有效增加催化剂的活性, 相较于钌碳催化剂更加有

效地断裂了 $\beta\text{-O-4}$ 键。氢解之后芳香醇的加氢脱氧反应没有对芳环进行加氢, 保留了产物的芳香性减少了氢气的消耗。当对真实的木质素原料进行氢解时, 加入一定量的无机酸^[44] 或者固体酸^[45] 可以有效降低氢解的条件并提升解聚效率。通常, 铂族催化^[46] 的氢解反应都伴随有加氢反应。根据反应条件的不同, 两步反应相继或同时发生。

除了芳香醚结构, 木质素中还存在许多脂肪族醚和呋喃结构, 然而这些碳氧键因为缺少烯丙基和苄基连接, 反应活性较低。Marks 等^[47] 利用均相三氟磺酸过渡金属盐和负载型钼纳米粒子催化剂在离子液中催化醚键氢解。形成饱和醇并且不会有芳香基团的损失。如果反应是在 $\text{Hf}(\text{OTf})_4$ 和 Pd/AC 催化下的无溶剂体系中反应, 底物范围可以拓宽到脂肪醚和呋喃。

均相钌催化剂在催化 $\beta\text{-O-4}$ 键断裂中也表现出很高的催化活性, 并且能保留芳香环^[46, 48-49]。均相钌催化剂, 如 $\text{Ru}(\text{Cl})_2(\text{PPh}_3)_3$ 、 $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ 、Ru-xantphos, 通过氧化还原过程同时发生脱氢和 C—O 键断裂过程。

5 金属磷化物催化的木质素加氢处理

Ni_2P 、 Fe_2P 、 Co_2P 和 WP 都被应用于木质素衍生物的加氢脱氧反应 (表 4)。与贵金属催化剂相比, 这些金属磷化物催化剂在转化率没有降低的情况下可以提高产物的选择性; 与商业的 CoMoS 催化剂相比, 在气相加氢脱氧反应中有更好的稳定性^[52-55]。

6 双金属催化剂催化木质素加氢处理

与单金属催化剂相比较, 双金属催化剂能调节催化性能和产物的选择性。Co、Ni、Mo 和 W 的混合硫化物催化剂以及 PtSn ^[56]、 PtRh ^[57]、 NiRe ^[58]、 PtRe ^[59] 和 ZnPd ^[49] 等双金属催化剂常用于木质素的加氢脱氧反应。这些双金属催化剂相较于单金属催

表 4 金属磷化物催化的木质素加氢处理

Table 4 Metal phosphide catalytic lignin hydroprocessing

Catalyst	Support	Reaction condition			Model compound	Products	Conversion(yield)	Ref.
		$T/^\circ\text{C}$	p/MPa	Gas				
Co_2P	SiO_2	300	0.1	80% H_2/N_2	guaiacol	benzene	70%(52)	[50]
Ni_2P	SiO_2	300	0.1	80% H_2/N_2	guaiacol	benzene	80%(60)	[50]
WP	SiO_2	300	0.1	80% H_2/N_2	guaiacol	benzene	60% (100)	[50]
Fe_2P	SiO_2	300	0.1	80% H_2/N_2	guaiacol	phenol	64%(94)	[50]
FeS_2	AC	250	10	H_2	dibenzyl ether	toluene	98%(100)	[51]

化剂在加氢脱氧反应中表现出了更好的选择性。早在约 130 年前就有工作报道了 CoMo 催化剂在苯酚加氢脱氧反应中表现出了较高的反应活性^[60]。与单独的 MoS₂ 催化剂相比, Co 或 Ni 提高了 Mo 催化芳香化合加氢脱氧反应的速率^[61-63]。

木质素的加氢脱氧主要包括两条路径: 加氢然后脱氧或者直接的脱氧^[62, 64]。一些报道指出, Co 或者 Ni 添加到 Mo 催化剂中可以显著增强直接脱氧的能力^[62], 但是也有报道认为是脱甲氧基能力增强的结果^[61, 63]。硫化 CoMo 催化剂在愈创木酚加氢脱氧反应中受载体效应影响。与 γ -氧化铝和二氧化钛相比, 二氧化钛载体的催化剂在 HDO 反应中表现出更好的催化活性^[61]。

在木质素加氢脱氧反应中, CoMo 催化剂要优于 Ni 化合物, 因为 CoMo 较低的加氢活性可以很好地保留原料中的芳环^[63, 65-66]。在不同底物的反应中, Weckhuysen 等^[60]发现 CoMo 硫化催化剂加氢脱氧反应中 β -O-4 和 β -5 比 5-5 连接更易解开, 并且主要的产物是不完全脱氧的酚或者儿茶酚。

引入第 2 种金属的优点主要可以归结为: ① 增加催化活性; ② 增加催化剂稳定性; ③ 改变选择性。而这又主要由 4 种效应控制, 分别是: 几何效应、电子效应、协同效应和双功能效应^[67]。一般来说, 催化活性和选择性主要受几何效应和电子效应影响, 而反应速率受到协同效应和双功能效应的影响。值得注意的是, 后两种效应的影响往往会产生新的反应路径。

双金属催化的优点显而易见, 但是仍然有许多问题需要克服。首先, 碳在 (Ni, Co) 和 (Mo, W) 催化剂^[68]表面的沉积就是一个大问题, 结焦随催化剂酸性的增加而增加, 但是加氢脱氧反应又需要酸性位点^[69]。其次, 催化剂容易发生氧化失活现象, 但是生物油中氧和硫的含量是比较高的^[70]。氧化物(底物)的性质和载体的表面性质对催化剂中毒都

有重要的影响^[71]。为了解决这些问题, Yang 等^[70, 72]发展了一系列无定形的 (Co, Ni)-(Mo, W) 基催化剂。其中, Mo 和 W 氧化物主要作为布朗斯特酸位点起到脱水的作用, 而 Ni 和 Co 起到催化加氢的作用。再之, 催化剂和杂质间的相互作用也尚未明确。这个问题在真实木质素作为原料时尤为突出。对于结构和催化效果之间的关系仍需要大量的研究。有关双金属催化剂的反应结果列于表 5。

7 双功能催化体系催化木质素加氢处理

为了克服传统含硫催化剂的失活问题, 科学家构建了包括金属和酸性化合物的双功能催化剂。Kou 等^[74]报道了 Pd/C、Pt/C、Ru/C 或 Rh/C 和磷酸组成的催化体系, 可以选择性地催化酚类化合物加氢脱氧得到环烷烃和甲醇。与含硫催化剂不同^[75-76], 在该反应中, 金属催化加氢, 酸催化水解或脱水, 两者耦合在一起。系统的动力学研究^[77]表明两种催化能力是相互独立的, 但是酸催化的步骤决定了加氢脱氧反应速率。因此, 高效的加氢脱氧催化剂中需要高浓度的酸性位点。此外, Kou 等^[78]将 Pd/C 替换为金属纳米粒子和布朗斯特酸离子液, 可以更加有效地催化反应进行。

固体布朗斯特酸组成的双功能催化剂在加氢脱氧反应中同样有效^[79-83]。与其他固体酸(硫酸氧化锆、大孔树脂 15、全氟磺酸/SiO₂、Cs_{2.5}H_{0.5}OW₁₂O₄₀)相比, HZSM-5 表现出较高的反应速率和较低的表面活化能, 因为沸石孔道较高的酸密度^[79]。此外, Pd/C 和 HZSM-5 组成的催化剂体系不仅能催化酚类单体加氢还可以催化酚类二聚体加氢^[79]。镍基的加氢催化剂, 如 Raney Ni 与全氟磺酸(或二氧化硅)^[80], Ni/HZSM-5^[84-85], Ni/Al₂O₃-HZSM-5^[82]也能有效催化加氢脱氧反应。

表 5 双金属催化剂催化的木质素加氢处理

Table 5 Bimetallic catalyst catalytic lignin hydroprocessing

Catalyst	Support	Reaction condition			Lignin(model) compound	Major products	Conversion (yield)	Ref.
		T/°C	p/MPa	Solvent				
Ni _{57.9} Cu _{7.0}	SiO ₂	320	17		guaiacol	aliphatics C ₅ —C ₇ + benzene	87.1%(72.7)	[73]
Ni _{55.4}	SiO ₂	320	17		guaiacol	aliphatics C ₅ —C ₇ + benzene	97.7%(90.9)	[73]
Zn/Pd	AC	150	2	MeOH	β -O-4 synthetic lignin polymer	guaiacol and 4-propyl- guaiacol	90%(85)	[49]
Zn/Pd	AC	150	2	MeOH	vanillin	creosol	>99%(81)	[49]
Zn/Pd	AC	150	2	MeOH	4-(methoxymethyl)- guaiacol	creosol	>99%(81)	[49]
Zn/Pd	AC	150	2	MeOH	vanillyl	creosol	>99%(80)	[49]
Zn/Pd	AC	150	2	MeOH	β -O-4 synthetic lignin polymer	4-propyl-guaiacol; dihydroconiferyl alcohol	100%(80)	[49]

表6 双功能催化剂催化的木质素加氢处理

Table 6 Bifunctional catalyst catalytic lignin hydroprocessing

Catalyst	Reaction condition			Lignin (model) compound	Products	Conversion (yield)	Ref.
	<i>T</i> /°C	<i>p</i> /MPa	Solvent				
Pd/C+H ₃ PO ₄	250	5	H ₂ O	cerulignol	propylcyclohexane	100%(66)	[74]
Pd/C+H ₃ PO ₄	250	5	H ₂ O	methoxyeugenol	propylcyclohexane	92%(58)	[74]
Pd/C+H ₃ PO ₄	250	5	H ₂ O	4-ethylguaiacol	ethylcyclohexane	100%(80)	[77]
Pd/C+ H ₃ PO ₄	200	2	MeOH	birch sawdust	monophenols	42%	[87]
Rh NPs	130	4	[Bmim][NTF ₂]	4-ethylguaiacol	ethylcyclohexane	84%(99)	[78]
Rh/Ru NPs	130	4	[Bmim][NTF ₂]	4-ethylguaiacol	ethylcyclohexane	99%(99)	[78]
Pd/C +HZSM-5	200	5	H ₂ O	4-methylguaiacol	methylcyclohexane	88%(100)	[79]
Ru+HZSM-5	200	5	H ₂ O	eugenol	propylcyclohexane	85%(100)	[88]
Ni+ SiO ₂ -ZrO ₂	300	5	dodecane	guaiacol	cyclohexane	97%(100)	[89]
Raney Ni + Nafion/ SiO ₂	300	4	H ₂ O	4-ethylguaiacol	ethylcyclohexane	71%(100)	[80]
Ru,Rh,Pt/Al ₂ O ₃ + acidic zeolite	250	4—5	H ₂ O	steam explosion lignin	toluene and alkylbenzenes	65%—70%(35—60)	[90]
Ni+ HZSM-5	220	0.1(Ar)	MeOH-H ₂ O	kraft lignin	alkyl substituted phenols	55%(97)	[84]
Pt/NbOPO ₄	190	5	cyclohexane	birch sawdust	liquid hydrocarbon	28.1%	[91]

Ni 和酸性沸石分子筛双组分催化剂^[86]用于纤维素水解酶木质素解聚。当使用 Raney Ni 作为催化剂时单酚产率只有 12.9% (质量), 只有分子筛时产率不到 5%, 但是 Ni 和分子筛的双功能催化剂可以使单酚的产率增加到 21%~27.9% (质量)。有关双功能催化体系的反应结果列于表 6。

8 总结展望

木质素作为生物质的的重要组成部分, 其催化转化制备高附加值的化学品的研究一直是学术界和工业界的关注重点。木质素转化是现代生物精炼中的重要部分, 并且木质素的结构和组成决定木质素制备精细化学品的路径是独一无二的。加氢处理作为木质素解聚的一种手段已经取得了一定的成果, 但是仍然无法满足木质素的工业转化的要求。

目前, 含有 β -O-4、 α -O-4、4-O-5 连接键的木质素模型物的加氢解聚催化体系有大量报道并获得了较好的结果。但是, 针对模型物的催化体系在真实木质素的解聚过程中并不是都能起到很好的作用。这主要是因为真实木质素结构的稳定性和复杂性以及解聚过程中的高活性中间产物易重新聚合形成更加稳定的聚合物。虽然 Ni、Pd、Ru 和 Pt 的单金属催化剂在真实木质素解聚中的应用较多, 但是双金属和双功能催化剂在真实木质素解聚中表现出更加优异的效果。与单金属催化剂相比较, 双金属催化剂可以通过调节金属间的几何效应和电子效应从而实现协同调节催化剂的催化性能和产物的选择性并且具有更高的反应活性。Ni、Ru、Rh、Pd 的

双金属催化剂可以催化有机溶剂木质素解聚得到单酚。由金属和酸性化合物组成的双功能催化剂, 可以解决传统催化剂失活的问题, 同时也提高了木质素的解聚效率。从现有报道的结果来看, 双金属和双功能催化剂更具潜力。

总之, 真实木质素催化加氢处理难点主要是两方面: 其一, 木质素的三维结构的复杂性, 使得其在溶剂中的溶解性以及金属活性中心的接触都受到阻碍, 因而难以有效解聚; 另外, 真实木质素加氢解聚需要较高的反应温度、催化剂酸性中心易结焦、解聚产物易重聚合、含有大量杂质等^[92]都是需要进一步解决的问题。针对上述问题, 要实现木质素的有效加氢解聚, 需要进一步设计和筛选合适的溶剂体系和具有较高活性和稳定性的催化剂。

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