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Two-step Process for Etherification of Phenolic-oil with Methanol under Catalysis of Alumina-Supported Metal Salts

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1. Mass balance

After reaction, the liquid, gas and solid products are simultaneously generated. The mass of liquid can be directly obtained from the weight of product liquid. The mass of gas product is obtained by internal standard method with the instrument of GC (gas chromatography), and the carrier gas of N_2 is used as the internal standard substance. The mass of solid is calculated according to the mass difference between the fresh catalyst and the used catalyst after reaction.

Because the mass of solid deposited on the internal wall of reaction pipe is hard to be obtained, and some liquid components in low boiling point like methanol can hardly be completely recovered, the summary mass of all products must be less than the initial mass of reactants. It determines that the mass balance is less than 100%, while a higher mass balance indicates a higher level of data reliability. The mass balance may vary with catalytic conditions. So, herein the mass balances of 6 representative experiments (the conversion of phenolic-oil with addition of guaiacol over Na_2SO_3/AA, and the conversion of phenolic-oil free of alkoxyphenol over KH_2PO_4/AA) under different conditions are illustrated, as showed in Table S1.

Table S1: Product distribution and level of mass balance

Catalyst	Temperature/°C	GHSV/h^{-1}	Liquid recovery/wt%	Gas yield/wt%	Solid proportion/wt%	Summary/wt%
Na_2SO_3/AA	450	1818	73.22	11.08	11.77	96.07
	500	1944	70.38	15.15	13.31	98.84
	550	2070	66.35	16.08	15.92	98.35
KH_2PO_4/AA	450	1416	71.56	8.08	18.92	98.56
		1818	72.47	7.23	17.08	96.78
		2221	73.00	6.38	16.46	95.85

The results show that the maximum error of mass balance is no higher than 5wt%, indicating a qualified reliability of the experimental system. Additionally, it can be seen that the liquid recovery decreases with the increase of reaction temperature, and meanwhile the formations of solid and gas products are promoted at higher temperatures. Compared between the two catalysts at the same temperature of 450°C, the liquid recoveries are in similar level, but more gases are generated over Na_2SO_3/AA, whereas the catalyst KH_2PO_4/AA favors the formation of solid. The gas hourly space velocity (GHSV) is also influential to the mass distribution of products in a slight degree. A higher GHSV favors the increase of liquid recovery and meanwhile hinders the formation of solids and gases over KH_2PO_4/AA at 450°C.

2. **The distribution of methanol**

To evaluation the utilization efficiency of methanol, herein the distribution of methanol in different outputs is roughly estimated. A known mass of methanol (m_0) is added into the raw material as a methylation reagent. After reaction, a part of methanol is consumed for alkylation of phenols (m_a), a part of methanol is converted to gas product (m_g), and a part of unreacted methanol is remained in the liquid product (m_u). Assuming that there is no mass loss of methanol before and after reaction, the summary mass of the three parts is equal to the original mass of methanol added to the system, which can be expressed by the equation of $m_0=m_a+m_u+m_g$.

The mass of methanol remained in liquid product (m_u) can be obtained by internal standard method with the instrument of GC/MS (gas chromatography combined with mass spectrometry). Assuming that the gas products of CO, CO_2 and CH_4 are merely produced from methanol, the mass of methanol converted to gas product (m_g) can be roughly obtained according to the mass balance of C element. The mass of methanol consumed for alkylation of phenols (m_a) can thereby be obtained from the subtraction: $m_a=m_0-m_u-m_g$.

The ratios of m_a, m_u, and m_g to the original mass of methanol m_0 is respectively defined as the mass distribution of methanol in alkylated product (R_a), in gas product (R_g), and in unreacted methanol (R_u). To be mentioned, considering that the volatilization of methanol is unavoidable and the gas products of CO, CO_2 and CH_4 may also be generated from a fraction of phenols, although the decomposition of aromatic ring is more difficult than that of methanol, the distributions of methanol in different outputs are merely roughly estimated data.

The distribution of methanol in different outputs may vary with reaction conditions, because of the different conversion of phenols and different product selectivity under different conditions. So, herein 6 representative data are listed in Table S2 (the reaction systems and corresponding conditions are same to those mentioned in Table S1).

Table S2: Mass distribution of methanol in different outputs

Catalyst	Temp. / °C	GHSV/ h^{-1}	m_0 / g	m_u / g	m_g / g	m_a / g	R_u / wt%	R_g / wt%	R_a / wt%
Na_2SO_3/AA	450	1818	6.21	1.24	1.21	3.76	19.96	19.55	60.49
	500	1944	6.24	0.58	1.73	3.93	9.23	27.78	62.99
	550	2070	6.20	0.20	2.03	3.96	3.27	32.79	63.94
KH_2PO_4/AA	450	1416	7.55	2.07	0.80	4.68	27.46	10.53	62.01
		1818	7.51	2.50	0.70	4.31	33.32	9.33	57.35
		2221	7.52	3.36	0.62	3.54	44.68	8.27	47.05

The results show that the distribution of methanol to alkylated products (R_a)

slightly increases in the range of 60.49%-63.94% with the increase of temperature over Na_2SO_3/AA, while remarkably decreases from 62.01% to 47.05% with the increase of GHSV over KH_2PO_4/AA. A higher temperature or a lower GHSV favors the distribution of methanol in gas product (R_g), and meanwhile decreases the fraction of unreacted methanol (R_u). Compared between the two catalysts at the same temperature of 450°C, more unreacted methanol is left over KH_2PO_4/AA while gases are more generated under catalysis of Na_2SO_3/AA.

3. Performance of Al_2O_3 without modification of metal salt

To make a verification on the role of metal salts, the effects of mere Al_2O_3 are tested on the conversions of the phenolic-oils with and without addition of guaiacol, respectively on the conditions optimized for the first step and the second step. However, the experiments have never been completed normally when Al_2O_3 is used, because too much solid is generated, leading to a severe blockage. It determines that the liquid recovery is lower and hard to be strictly quantified. To make a qualitative discussion, the solid deposition is dissolved with chloroform first and then mixed with the obtained liquid product. The chloroform in the liquid mixture is evaporated away through a rotary evaporator, and then the liquid residue is analysed by GC/MS. The corresponding TICs (total ion chromatograms) of the two products respectively obtained from the conversion of the phenolic-oil with addition of guaiacol and the alkoxyphenol-free phenolic-oil are showed in Fig. S1, and the major products are listed in Table S3 (the areas of chloroform and methanol have been excluded).

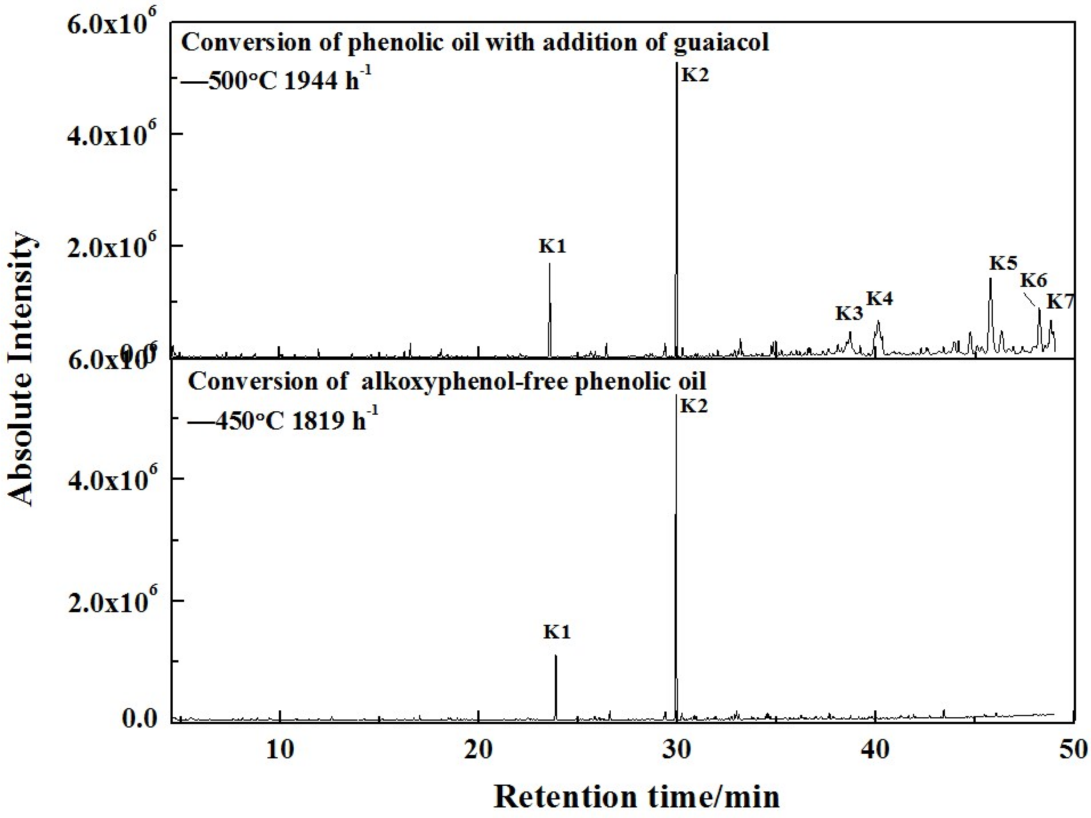

Fig. S1 TICs of the products respectively obtained from the conversion of the phenolic-oil with addition of guaiacol and the alkoxyphenol-free phenolic-oil under catalysis of Al_2O_3

The results show that polyalkylated benzenes including pentamethyl benzene and hexamethyl benzene are much generated in the both conversion systems with and without addition of guaiacol. Comparatively, polyaromatics such as 1,7-dimethy-phenanthrene and 2,3,5-trimethyl-phenanthrene are more generated in the alkoxyphenol-containing reaction system. It indicates that a mere solid acid like Al_2O_3 without loading of any metal salt, tends to promote the deoxygenation and *C*-alkylation of phenols, which is accordant with the results from the conversion of phenol with methanol over Al_2O_3 as reported in literatures [1, 2].

Table S3: Main components of the products from conversions of the phenolic-oils with and without addition of guaiacol

Classification	Number	Substance	Peak Area/%	
			Conversion of the phenolic-oil with addition of guaiacol	Conversion of the phenolic-oil free of alkoxyphenol
Aromatic hydrocarbons	K1	Benzene, pentamethyl-	5.64	12.17
	K2	Benzene, hexamethyl-	20.70	59.71
	K3	Phenanthrene, 2,3-dimethy-	3.99	—
	K4	Phenanthrene, 1,7-dimethy-	7.72	—
	K5	Phenanthrene, 2,3,5-trimethyl-	14.94	—
	K6	Phenanthrene, 2,3,5-trimethyl-	6.57	—
	K7	Anthracene, 1,3,6,8-tetramethyl-	2.89	—

References:

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2. P. S. Landis and W. O. Haag, *J. Org. Chem*. 1963, **28**, 585.