

Conversion of lignin-derived carboxylic acids into valuable chemicals under catalysis by *in situ* generated MoO_x and WO_x

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Materials

Molybdenum hexacarbonyl (LLC ‘Redkino experimental plant’, Redkino, Russia, 36.5–37.5 wt% of Mo) and tungsten hexacarbonyl (LLC ‘Redkino experimental plant’, Redkino, Russia, 51–52% wt% of W) were used as precursors for *in situ* synthesis of catalysts. Terephthalic acid (Polyef, Blagoveshchensk, Russia, pure), phthalic acid (Reachim, Russia, pure), isophthalic acid (Reachim, Russia, pure), 2,5-dihydroxybenzoic acid (Sigma-Aldrich, USA, 98%), 2,5-dihydroxyterephthalic acid (Sigma-Aldrich, USA, 98%), and 1,2,4,5-benzenetetracarboxylic acid (Sigma-Aldrich, USA, 96%) were used as substrates. Dodecane (Component-reaktiv, Moscow, Russia, >99%) was used as a solvent. Acetone (Component-reaktiv, Moscow, Russia, >99.5%) and petroleum ether 40/70 (Component-reaktiv, Moscow, Russia, tech.) were used for catalyst washing. Dimethyl sulfoxide (Component-reaktiv, Moscow, Russia, >99.8%) was used to remove unreacted substrates.

Catalytic tests

The MoO_x and WO_x catalysts were formed *in situ* from their carbonyls (Mo(CO)₆ or W(CO)₆) during hydrodeoxygenation of the aromatic acids. A mixture of the corresponding carbonyl, substrate (100 mg), and dodecane (1.5 g) were placed into an autoclave reactor. The reaction was conducted at a constant stirring speed of 900 rpm. The molar ratio of substrate/metal was 5. The hydroprocessing of aromatic acids was carried out at 350 °C, 5 MPa H₂, and for 6 h. In the case of 2,5-dihydroxybenzoic acid and 1,2,4,5-benzenetetracarboxylic acid, the additional experiments were conducted at the different reaction time (350 °C, 5 MPa H₂, 0.5–6 h). After cooling the reactor to ambient temperature, the liquid reaction products were separated by centrifugation. The solid was washed with DMSO to remove unreacted substrates. The catalyst samples were washed with acetone and petroleum ether 40/70 and dried in Ar atmosphere.

Product analysis

A gas chromatography–mass spectrometer (Thermo Scientific ISQ 7000 GC-MS) equipped with a capillary column (Restek 5XI-17SIL MS CAP, 30 m × 0.25 mm × 0.25 μm) was employed to identify liquid reaction products. A gas chromatograph (Crystallux 4000 M) equipped with a flame ionization detector and capillary column (Optima-1, 25 m × 0.32 mm × 0.35 μm) was used to quantify liquid reaction products.

The conversion of substrates and product selectivity were calculated using the following equations:

$$\text{Conversion (\%)} = \frac{\text{mole of substrate consumed}}{\text{initial mole of substrate}} \times 100\%$$

$$\text{Product selectivity (\%)} = \frac{\text{mole of product}}{\sum \text{moles of all products}} \times 100\%$$

Table S1 Hydrodeoxygenation of aromatic acids with different substituents over *in situ* MoO_x and WO_x. Reaction conditions: 350 °C, 5 MPa H₂, 6 h.

2,5-dihydroxybenzoic acid 1	<i>In situ</i> MoO_x	<i>In situ</i> WO_x
<i>Reaction products</i>	Selectivity, %	
Benzene	35	14
Cyclohexane	56	1
Toluene	5	4
Phenol	2	79
Cresols	2	2
<i>Conversion, %</i>	97	92
2,5-dihydroxyterephthalic acid 2	<i>In situ</i> MoO_x	<i>In situ</i> WO_x
<i>Reaction products</i>	Selectivity, %	
Benzene	21	21
Cyclohexane	70	1
Toluene	3	3
Phenol	0	70
Cresols	6	5
<i>Conversion, %</i>	87	85

Table S2 Hydrodeoxygenation of phthalic, isophthalic and 1,2,4,5-benzenetetracarboxylic acids over *in situ* MoO_x and WO_x. Reaction conditions: 350 °C, 5 MPa H₂, 6 h.

Phthalic acid 3	<i>In situ</i> MoO_x	<i>In situ</i> WO_x
<i>Reaction products</i>	Selectivity, %	
Benzene	1	10
Toluene	61	44
<i>o</i> -Xylene	38	15
Benzoic acid	1	24
<i>o</i> -Methylbenzoic acid	0	8
<i>Conversion, %</i>	94	91
Isophthalic acid 4	<i>In situ</i> MoO_x	<i>In situ</i> WO_x
<i>Reaction products</i>	Selectivity, %	
Benzene	0	3
Toluene	9	25
<i>o</i> -Xylene	7	4
<i>m</i> -Xylene	80	52
<i>p</i> -Xylene	1	2
Benzoic acid	1	3
<i>m</i> -Methylbenzoic acid	2	11
<i>Conversion, %</i>	96	94
1,2,4,5-Benzenetetracarboxylic acid 5	<i>In situ</i> MoO_x	<i>In situ</i> WO_x
<i>Reaction products</i>	Selectivity, %	
Toluene	5	20
Xylenes	32	64
Trimethylbenzene	50	14
Tetramethylbenzene	13	2
<i>Conversion, %</i>	92	88