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**Catalyst Design: From Molecular  
to Industrial Level**

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**ABSTRACTS**

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### OP-IV-3

## Catalytic Oxidation of 5-Hydroxymethylfurfural over $\text{Au}_{1-x}\text{Ag}_x$ and $\text{Pd}_{1-x}\text{Ag}_x$ Catalysts

Timofeev K.L., Kharlamova T.S., Svetlichnyi V.A., Vodyankina O.V.  
Tomsk State University, Tomsk, Russia  
kvintkl@gmail.com

At present, a large part of valuable organic compounds and fuels is produced from depleting and unsustainable fossil resources, primarily oil, characterized by constantly growing complexity of production technologies and negative environmental impact [1]. Currently, the use of biomass becomes promising due to the high renewability of the feed as well as opportunity to synthesize a wide spectrum of organic compounds and fuels. One of the main advantages of this direction is the presence of valuable side products formed during the refining, e.g., 5-hydroxymethylfurfural (HMF) [2]. The HMF is a multifunctional platform molecule used to synthesize various important compounds ranging from healthcare products to polymers. Among others, the 2,5-furandicarboxylic acid (FDCA) is an important product of the HMF oxidation (Fig. 1) serving as an alternative for terephthalic acid in the synthesis of metal-organic frameworks (MOFs) [3].

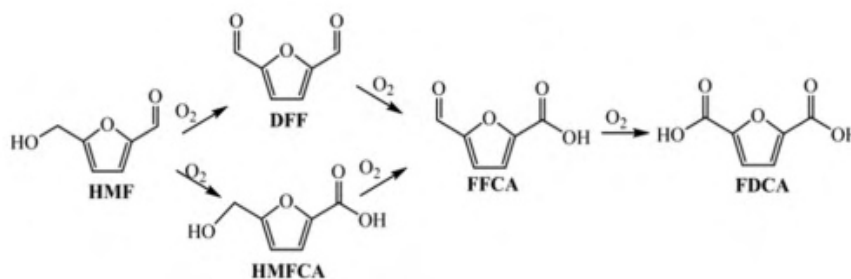


Fig. 1. The proposed scheme of HMF transformations.

Diverse catalytic systems were proposed for the HMF selective oxidation that influence the selectivity towards desired products in the oxidation process [4]. Nevertheless, the factors affecting the pathways of the HMF oxidation over different catalysts are still not clear and require additional studies.

The present work is devoted to the study of the catalytic HMF oxidation with molecular oxygen in water solutions over noble metal ( $\text{Me} = \text{Au}_{1-x}\text{Ag}_x$ ,  $\text{Pd}_{1-x}\text{Ag}_x$ ) nanoparticles (NPs) obtained by laser ablation in liquid (PLAL) and  $\text{Me}@\text{UiO-66}$  composites. The influence of the catalytic experiment conditions such as substrate/catalyst and  $\text{NaOH}/\text{substrate}$  molar ratios, reaction temperature, oxygen pressure was studied.

Table 1 shows a selection of results of the study of catalytic properties under specified conditions (reaction temperature of 100 °C, oxygen pressure of 5 or 10 atm, substrate/catalyst ratio of 100, reaction time of 6 h). The  $\text{Au}_{1-x}\text{Ag}_x$  NPs obtained by LAL show high catalytic activity in a neutral medium, but the main products of the HMF transformations are low-molecular compounds of oxidative decomposition. The  $\text{Pd}_{1-x}\text{Ag}_x$  NPs were characterized by lower activity and relatively high selectivity towards DFF, but the main direction of the HMF transformation is the formation of the C–C oxidative cleavage products. The incorporation of  $\text{Pd}_{1-x}\text{Ag}_x$  NPs into the UiO-66 matrix

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contributes to a noticeable decrease in the activity of bimetallic Me@UiO-66 composite catalysts towards the oxidative C-C cleavage.

Table 1. Catalytic properties of mono- and bimetallic NPs and corresponding UiO-66-supported composites in the HMF oxidation.

Sample	Experimental conditions					HMF conv., %	Selectivity, %			
	Time, h	T, °C	P <sub>O2</sub> , atm	Molar ratio			FDC A	DFF	HMF CA	FFCA* + low molecular weight products
				Sub. /Cat.	NaOH /Sub.					
Pd (abl.)	6	100	5	100	0	24.2	1.0	28.7	4.4	65.9
PdAg (abl.) (0,5:0,5)	6	100	5	100	0	22.2	0.5	6.9	0.7	91.9
Au (abl.)	6	100	5	100	0	77.5	1.0	0.5	2.6	95.9
AuAg (abl.) (0,5:0,5)	6	100	5	100	0	50	1.5	2.2	0.8	95.5
1%Pd-Ag@UiO-66 (0,85:0,15)	6	100	5	100	0	30.8	2.2	66.9	3.5	27.5
1%Au@UiO-66	6	100	10	100	0	35.0	2.7	23.5	1.6	72.3
1%Au@UiO-66	6	100	10	100	2	58.2	0.2	1.1	10.8	87.9
1%AgAu@UiO-66 (0,5:0,5)	6	100	5	100	0	18.6	1.2	13.4	1.1	84.3

\*Selectivity towards FFCA for all samples does not exceed 5% except for 1%Au@UiO-66 in alkali medium (FFCA selectivity is 12–29%).

The results obtained indicate that the main direction of the FDCA formation in the presence of the base is the oxidation of the carbonyl group of HMF to yield HMFCa followed by its consecutive oxidation to FFCA and FDCA (Fig. 1). In the neutral medium, the FDCA formation occurs through the oxidation of the both hydroxyl and carbonyl groups to yield the DFF and HMFCa, respectively, for the Me NPs. The incorporation of Pd<sub>1-x</sub>Ag<sub>x</sub> NPs into the UiO-66 matrix facilitates the FDCA formation in a neutral medium mainly through the DFF, while the contribution of the parallel route through the HMFCa becomes insignificant.

The effect of modification of UiO-66 with NH<sub>2</sub>- and SO<sub>3</sub>-groups on the catalytic properties of the Me@UiO-66 composites and the role of the base agent and its nature in the HMF transformations will be discussed.

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