

## Application of Silica-supported Fe–Cu Nanoparticles in the Selective Hydrogenation of *p*-Dinitrobenzene to *p*-Phenylenediamine

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Received June 16, 2016

**Abstract**—Supported bimetallic Fe–Cu/SiO<sub>2</sub> materials are synthesized, and their catalytic activity in hydrogenation of dinitrobenzene to phenylenediamine at 145–180°C and 1.3 MPa hydrogen pressure is studied for the first time. The best results (89% selectivity toward *p*-phenylenediamine at complete conversion of *p*-dinitrobenzene) are obtained for the sample synthesized via co-deposition with subsequent calcination at 300°C. The sample contains 7% iron and 3% copper. The formation of separate phases of metal oxides (for the catalysts prepared by impregnation) and mixed bimetallic oxide phases (in case of co-deposition procedure) in calcined samples is revealed via thermoprogrammed reduction with hydrogen.

**Keywords:** Fe–Cu catalysts, dinitrobenzene hydration, phenylenediamine

**DOI:** 10.1134/S0036024417020285

### INTRODUCTION

Aromatic amines obtained via the catalytic reduction of corresponding nitrocompounds are widely used in the synthesis of different compounds for fine organic synthesis and pharmaceutical industry [1, 2]. Nickel-containing catalysts, as well as catalysts based on platinum-group metals [3–8] are the most commonly used for the selective hydrogenation of dinitrobenzene (DNB) to phenylenediamine (PhDA). The main drawback of these catalysts is a high content of the active components and their toxicity. The development and investigation of more effective and environmentally safe catalytic systems remain important goals of modern catalysis [9]. In particular, the catalysts containing iron are of great interest, due to their relatively high activity in hydrogenation reactions, abundance, low cost, and low toxicity [10].

The goal of this work was to study the effects of the preparation procedure of the supported bimetallic Fe–Cu/SiO<sub>2</sub> catalysts and the conditions of the thermal treatment on the catalytic activity and selectivity of *p*-phenylenediamine formation from *p*-dinitrobenzene.

### EXPERIMENTAL

Supported bimetallic Fe–Cu catalysts were synthesized via the consecutive impregnation of a carrier

by solutions of metal salts (CIm) and by the co-deposition of precursors of both metals onto the carrier using urea (CoD). KSKG silica gel ( $S_{sp} = 108 \text{ m}^2 \text{ g}^{-1}$ ;  $V_{por} = 1.05 \text{ cm}^3 \text{ g}^{-1}$ ;  $D_{por} = 26 \text{ nm}$ ) was used as the carrier. Copper nitrate, ammonium trioxalatoferrate (NH<sub>4</sub>)<sub>3</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] · 3H<sub>2</sub>O (98%, Acros Organics) (impregnation method) and iron (III) nitrate (co-deposition method) were used as the initial compounds. Once the metal precursors were supported, the samples were dried at 60–110°C and then calcined at 300°C. The calcined samples were reduced in a H<sub>2</sub> flow at 300°C. We selected the temperatures on the basis of thermal analysis and TPR-H<sub>2</sub> data for the samples. The synthesized materials were marked as xFeyCu–N–M, where *x* and *y* are the mass percentage of Fe and Cu, respectively; N is the method of synthesis; and M is the conditions of thermal treatment. The samples were characterized by TPR-H<sub>2</sub> using the technique described in [11].

The catalytic hydrogenation was conducted in a 100 mL autoclave in the temperature range of 145–180°C and initial hydrogen pressure of 1.3 MPa. The autoclave was charged with 30 mL of 0.08 M DNB solution in tetrahydrofuran and 0.2 g of catalyst. Eicosan (0.100 g) was added as an internal standard. The samples of the reaction mixture were analyzed by gas-liquid chromatography.

## Catalytic performance of Fe–Cu catalysts and the results from TPR

Catalyst	$T_{\text{react}}, ^\circ\text{C}$	$t, \text{min}$	$S_{\text{PhDA}}, \%$	$t_1, \text{min}$	$S_{1 \text{ PhDA}}, \%$	$T_{\text{TPR}}, ^\circ\text{C}$	$\text{H}_2 : \text{M}$
7Fe2Cu-CIm-300C	166	105	53	130	55	150–270 270–500	0.66 (Cu) 0.55 (Fe)
7Fe2Cu-CIm-300C-H	165	240	1.4	600	25.4		
7Fe3Cu-CoD-300C	145	145	10.7	460	89	150–300 300–500	2.15 (Cu) 0.89 (Fe)
7Fe3Cu-CoD-300C-H	175	400	5	–	–		
7Fe3Cu-CoD-110B	166	65	8.8	175	68	200–320 320–500	2.49 (Cu) 0.86 (Fe)
3.3Cu-CoD-110B	169	240	0	–	–	220–400	1.51 (Cu)
7Fe-CoD-110B	166	330	63*	–	–	230–500	0.66 (Fe)

$t$ ,  $S_{\text{PhDA}}$  are the reaction time and  $p$ -PhDA selectivity corresponding to complete conversion of  $p$ -DNB;  $t_1$ ,  $S_{1 \text{ PhDA}}$  are the reaction time and  $p$ -PhDA selectivity at complete conversion of  $p$ -NA.

\* $p$ -DNB conversion is 81%.

## RESULTS AND DISCUSSION

All synthesized bimetallic Fe–Cu catalysts are active (see table) in the liquid-phase hydrogenation of  $p$ -DNB to  $p$ -PhDA (as opposed to monometallic catalysts). Hydrogenation proceeds via formation of  $p$ -nitroaniline ( $p$ -NA) (Fig. 1). The catalysts obtained by co-deposition are more active and selective toward PhDA than catalysts obtained by impregnation. Analysis of the reaction mixtures obtained over the catalysts prepared by impregnation reveals that DNB conversion calculated on the basis of the internal standard, generally exceeds the values calculated on basis of catalyze composition; this is the evidence of the formation of products that are not detected by GLC, explaining the low selectivity of these catalysts. The hydrogen reduction of the calcined 7Fe3Cu-CoD-

300C sample obtained via co-deposition slowed down the hydrogenation reaction (especially of the intermediate NA). A drop in both activity and selectivity toward PhDA (2 times) is observed for the reduced 7Fe2Cu-CIm-300C-H sample. It should be noted that 7Fe3Cu-CoD-110B sample only dried after co-deposition displayed substantial catalytic activity (table). This sample was much more active and selective than the monometallic samples obtained under the same conditions and used as references.

The TPR studies of the samples of calcined catalysts showed the presence of different supported phases. The character, temperature, and degree of reduction of the metals in bimetallic samples depend largely on the preparation procedure used.

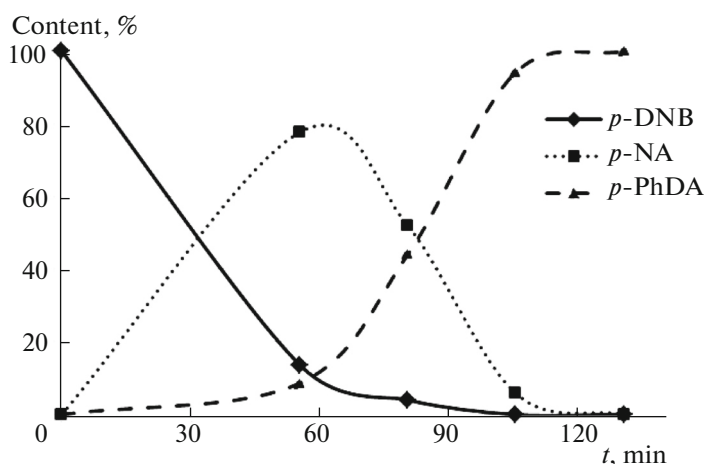


Fig. 1. Dependences of catalyze composition on the reaction time in the presence of the calcined catalyst 7Fe2Cu-CIm-300C, obtained by sequential impregnation.

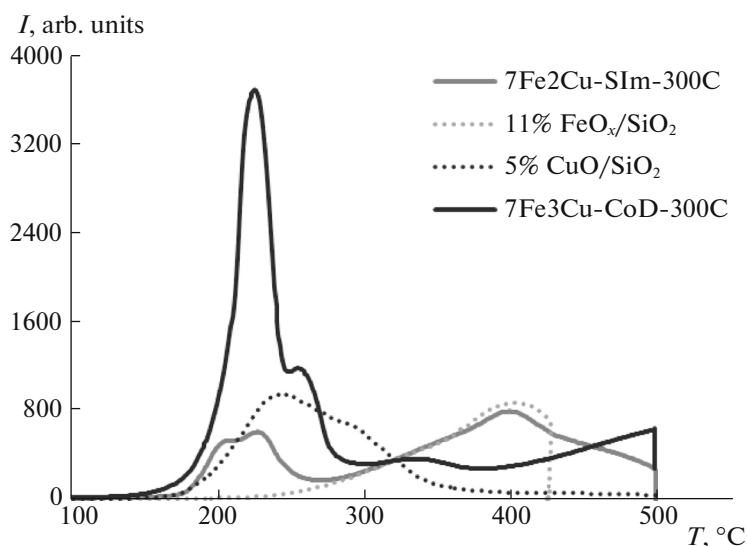


Fig. 2. TPR- $H_2$  curves of bimetallic Fe–Cu samples calcined at 300°C and monometallic samples used as reference.

Analysis of the TPR curve shows that Cu and Fe were present mostly in the form of individual oxides in the bimetallic sample obtained via impregnation. Two intense signals are seen on the TPR curve of the 7Fe2Cu-CIm-300C sample (Fig. 2). The initial profile of the first signal within 150–250°C matches that of the reduction of CuO nanoparticles in the reference monometallic sample. The shape and position of the second peak within 350–420°C matches that of the TPR curve of the reference sample containing iron oxide nanoparticles. The calculated corresponding hydrogen : metal molar ratios (table) is the evidence of the total reduction of copper to metallic state and the partial reduction of iron oxide.

The TPR curve of the sample obtained via co-deposition differs substantially from that of the sample obtained by impregnation. A double signal of high intensity is seen on the TPR curve of the sample 7Fe3Cu-CoD-300C (Fig. 2); a decrease in the intensity of the signal of hydrogen consumption by the iron-containing phases, as well as the signal shift toward lower temperatures, are observed. Such behavior could be due to the formation of mixed bimetallic phases with higher contents of iron ions. The  $H_2$  : Cu ratio for the first peak, which is exaggerated by 300%, also confirms the formation of mixed oxides (the table).

Our data shows that reduction in hydrogen at 300°C should lead to the complete reduction of particles of copper-containing oxide phases in the samples calcined at 300°C. A comparison with the results on catalytic performance shows that reduction to  $Cu^0$  is

undesirable. The most active centers of nitrogroup hydrogenation are supposed to be the highly dispersed CuO nanoparticles that possess the developed contact area with the iron oxide nanoparticles.

## CONCLUSIONS

It was shown for the first time that Fe–Cu oxide nanoparticles supported on silica gel catalyze the hydrogenation of dinitrobenzene to nitroaniline and then to phenylenediamine under relatively mild conditions: 145–170°C and an initial hydrogen pressure of 1.3 MPa. The catalytic properties of the supported bimetallic Fe–Cu catalysts depend on the method of synthesis and the conditions of thermal treatment. The catalysts reduced in hydrogen are less active. The best selectivity towards *p*-PhDA (89%) at complete conversion of *p*-NA was obtained with the sample synthesized by co-deposition of metal precursors with urea, followed by calcination in air at 300°C; the sample contains 7 wt % of iron and 3 wt % of copper.

## ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation, project no. 14-50-00126.

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*Translated by P. Vlasov*