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Selective Liquid Phase Hydrogenation of Aromatic Nitro Compounds in the Presence of Fe–Cu Nanoparticles

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Abstract—Fe—Cu bimetallic oxide nanoparticles supported on silica gel that catalyze the hydrogenation of nitrobenzene to aniline and of dinitrobenzenes to phenylenediamines under relatively mild reaction conditions (200°C, p_{H_2} 1.3 MPa, 4 h, and 700 rpm) are synthesized. The catalytic properties of supported bimetallic Fe—Cu catalysts depend on the synthesis procedure, sample composition, and conditions of thermal treatment. There is a synergistic effect of interaction between Cu and Fe in the hydrogenation of nitrobenzene, 1,3-dinitrobenzene, and 1,4-dinitrobenzene in the presence of a bimetallic Fe—Cu catalyst obtained via coprecipitation.

Keywords: $Fe-Cu/SiO_2$ catalysts, selective hydrogenation, nitrobenzene, dinitrobenzene, bimetallic nanoparticles

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INTRODUCTION

The catalytic reduction of nitro groups in aromatic mono- and dinitro compounds on heterogeneous catalysts is a key method of preparation of aromatic amines in laboratories and industry [1-3]. Aromatic amines are also widely used to synthesize different fine chemicals, dyes, urethanes, and pharmaceuticals [4, 5]. The most effective heterogeneous catalysts for the hydrogenation of mono and dinitro compounds are systems based on noble metals, particularly Pt [6-8], Pd [9–11], Ru [12], and others (e.g., Ni) [13–16]. Despite their high efficiency, these catalysts have considerable disadvantages (large amounts of active components, high costs, and rapid deactivation of an active surface). Nickel-containing systems require high temperatures, high hydrogen pressures, and long reaction times [15, 16].

Despite the growing scientific interest in the transition from precious metals to more affordable, efficient and environmentally friendly iron-based catalytic systems, currently there are only few publications on hydrogenation of nitro compounds on iron-containing systems [17-19]. It should be noted that hydrazine hydrate was used as a reducing agent in these studies.

For example, 8% Fe_2O_3/C supported catalysts were used for the selective reduction of nitrobenzene [17]. Hydrazine hydrate was used as a source of hydrogen. Under mild conditions (atmospheric pressure, 60°C, 90 min), $\sim 100\%$ selectivity towards aniline and 95% conversion of nitrobenzene were achieved.

Metallic iron immobilized in an ionic liquid (ImmFe-IL) was used as a catalyst in the hydrogenation of *p*-dinitrobenzene. The resulting product was *p*-nitroaniline with a selectivity of 99% at 88% conversion of *p*-DNB [18]. The reaction proceeded for 12 h at 110°C in ethylene glycol in the presence of hydrazine hydrate.

It is therefore of interest to obtain iron-containing catalytic systems that would be active in the liquidphase reduction of nitro compounds using hydrogen as a reducting agent under relatively mild reaction conditions.

The aim of this work was to study the catalytic properties of bimetallic iron-copper catalysts in the selective reduction of nitro groups in nitrobenzene, 1,3-dinitrobenzene, and 1,4-dinitrobenzene to form corresponding amines.

EXPERIMENTAL

Bimetallic Fe–Cu catalysts supported on a SiO₂ (KSKG silica, $S_{sp} = 108 \text{ m}^2 \text{ g}^{-1}$, $V_{pore} = 1.05 \text{ cm}^3 \text{ g}^{-1}$, $D_{pore} = 26 \text{ nm}$, Khimmed, Russia) were synthesized in two different ways: via the co-deposition of Cu and Fe precursors (Cu(NO₃)₂ and Fe(NO₃)₃) by deposition—precipitation with urea (DPU), and the sequential

No.	Catalyst	X, %	Product	γ, %
Nitrobenzene as a substrate				
1	6Fe-DPU-300C	20	Aniline	100
2	6Fe-SI-300C	17	Aniline	100
3	3Cu-DPU-300C	73	Aniline	100
4	6Fe-3Cu-SI-300C	56	Aniline	100
5	6Fe-3Cu-DPU-300C	98	Aniline	100
6	6Fe-3Cu-DPU-300H	72	Aniline	100
7	3Fe-6Cu-DPU-300C	45	Aniline	100
8	6Fe-6Cu-DPU-300C	52	Aniline	100
9	6Fe-1Cu-DPU-300C	23	Aniline	100
1,3-Dinitrobenzene as a substrate				
10	6Fe-DPU-300C	54	Nitroaniline	55
11	3Cu-DPU-300C	27	Nitroaniline	34
12	6Fe-3Cu-DPU-300C	100	Phenylenediamine	82
13	6Fe-3Cu-SI-300C	100	Phenylenediamine	45
1,4-Dinitrobenzene as a substrate				
14	6Fe-DPU-300C	60	Nitroaniline	44
15	3Cu-DPU-300C	20	Nitroaniline	30
16	6Fe-3Cu-DPU-300C	100	Phenylenediamine	87
17	6Fe-3Cu-DPU-300H	57	Nitroaniline	80
18	6Fe-3Cu-SI-300C	100	Phenylenediamine	55

Table 1. Catalytic properties of Fe–Cu/SiO₂ catalysts in the hydrogenation of nitro compounds $R-NO_2 \xrightarrow{Fe-Cu/SiO_2} R-NH_2$

Reaction conditions: 200°C, $p_{\text{H}_2} = 1.3$ MPa, 700 rpm, 4 h, THF, and n_{sub} : $n_{\Sigma \text{Me}} = 9$; S is the selectivity; X is conversion of substrate.

impregnation onto the outer surface of a carrier from a solution of $(NH_4)_3[Fe(C_2O_4)_3] \cdot 3H_2O$ and then Cu(NO₃)₂ with intermediate drying of an iron-containing sample (SI). The procedure for synthesizing the samples was thoroughly described in [20]. The samples were dried at 80-100°C and then calcined in air for 4 h at 300°C after deposition of the precursors. The temperature of calcination was chosen according to the results from thermal analysis of the samples. The calcined samples were reduced at 300°C for 2 h in a hydrogen flow. The reduction temperature was selected according to the results of temperature-programmed reduction with hydrogen (TPR-H₂). Fe/SiO₂ and Cu/SiO₂ monometallic catalysts were also synthesized by similar procedures to compare their catalytic properties.

The copper content in the bimetallic samples was 1, 3, and 6 wt %, while those of iron were 3 and 6 wt %. The calcined samples are denoted as C; the reduced, as H. The catalysts were characterized using TEM, DRIFTS-CO, and XRD.

The catalytic activity of the synthesized catalysts in the reaction of liquid-phase hydrogenation of aromatic nitro compounds ($C_{NO_2} = 0.16$ M in THF and n_{NO_2} : $n_{\Sigma\text{Me}} = 9$) was studied at an initial hydrogen pressure of 1.3 MPa, a temperature of 200°C, and intensive stirring at 700 rpm. The reaction time was 4 h.

RESULTS AND DISCUSSION

The synthesized monometallic and bimetallic iron-copper catalysts were studied in the liquid-phase hydrogenation of nitro compounds to obtain amines under relatively mild reaction conditions. Table 1 shows the results from catalytic tests.

Our results indicate that the calcined monometallic iron-containing samples have low acivity: the maximum conversion of nitrobenzene was only 17-20% after 4 h of the reaction (Table 1, entries 1 and 2). The efficiency of the monometallic copper catalyst obtained via deposition was several times higher: the conversion of nitrobenzene was 73% for the same reaction time.

The catalytic properties of Fe–Cu bimetallic samples depend mainly on the synthesis method. A synergistic effect of the interaction between Cu and Fe in hydrogenation of nitrobenzene was observed for the sample obtained via co-precipitation and hydrolysis of urea (6Fe-3Cu-DPU-300C). Its efficiency was approximately two times higher than that of the catalysts prepared by sequential impregnation (-6Fe-3Cu-SI-300C). The conversion of nitrobenzene on the 6Fe-3Cu-DPU-300C sample was 98% with a quantitative yield of aniline. The same tendency is typical of hydrogenation of dinitrobenzenes. The samples obtained via DPU were the ones most effective in the hydrogenation of 1,3-dinitrobenzene and 1,4-dinitrobenzene. There was full conversion of the initial substrates with high selectivity for phenylenediamines (82 and 87%, respectively) after 4 h of the hydrogenation of 1,3-dinitrobenzene and 1,4-dinitrobenzene on 6Fe-3Cu-DPU-300C catalyst (Table 1, entries 12 and 16). The low selectivity of the samples obtained via SI, determined internal standard method, in the hydrogenation of dinitrobenzenes, was probably due to side reactions with formation of condensation products not detectable via GLC. The differences in the catalytic activity of the Fe-Cu samples depending on the method of synthesis can be matched to the physicochemical characterization data for these samples. TPR-H₂ and SEM-EMF studies indicate that the preparation Fe-Cu-SI samples leads to weakly interacting particles of iron and copper oxides, while the DPU method allows the preparation of Fe-Cu-O bimetallic mixed oxide phases [20, 21]. As a result, the best way to obtain active and highly selective iron-copper catalysts is the coprecipitation of metal precursors via urea hydrolysis.

Our catalytic tests also showed that the catalytic properties of bimetallic catalysts depend on the composition and heat treatment conditions. A bimetallic sample with 6 wt % iron and 3 wt % (6Fe-3Cu-DPU-300C) shows the best catalytic properties in the hydrogenation of nitrobenzene. Changing the composition of the samples sharply reduced their activity in the hydrogenation of nitrobenzene.



Fig. 1. (Color online) DRIFT spectra of $Fe-Cu/SiO_2$ samples near valence vibrations of adsorbed CO: (1) 6Fe-3Cu-SI-300C and (2) 6Fe-3Cu-DPU-300C.

Our study showed that the conditions of heat treatment also have a strong effect on the activity and selectivity of formation of the target product. The reduction of the 6Fe-3Cu-DPU-300C calcined sample in hydrogen sharply lowers its activity in the hydrogenation of nitrobenzene and 1,4-dinitrobenzene (Table 1, entries 6 and 17). The activity of the 6Fe-3Cu-DPU-300H reduced sample was halved, but no target product (phenylenediamine) formed. TPR-H₂ data for Fe-Cu bimetallic samples [20] indicate that the reduction of calcined samples with hydrogen at 300°C results in the full reduction of copper-containing oxide phase particles. A comparison of physicochemical properties and data on catalytic activity shows that the reduction to Cu⁰ is undesirable. The phases most active in hydrogenation of nitro group are obviously



Fig. 2. TEM micrographs of (a) 6Fe-3Cu-SI-300C and (b) 6Fe-3Cu-DPU-300C samples.

highly dispersed copper oxide nanoparticles, which have a developed area of contact with iron oxide nanoparticles or copper ions stabilized in the phases of the Cu–Fe–O system.

The state of metals in the Fe–Cu/SiO₂ bimetallic samples was studied via the IR spectroscopy of adsorbed CO. A comparative analysis showed that the DRIFT-CO spectra at 20°C of the samples synthesized via sequential impregnation and DPU contained narrow bands at 2123–2128 cm⁻¹ with different intensities (Fig. 1). These bands were attributed to valence vibrations of the C=O bonds in carbon monoxide molecules adsorbed on copper cations (Cu²⁺–CO) [22]. It is known that CO reduces the supported Cu²⁺ cations to Cu⁺ even at room temperature during adsorption on copper-containing catalysts [22].

X-ray diffraction study of calcined bimetallic samples showed that there were only reflections of the SiO₂ support on the X-ray diffraction patterns, indicating that X-ray amorphous deposited phases of both iron and copper appeared, the deposited metals were highly dispersed, and the particles were small. TEM studies of the samples obtained by different means confirmed that nanoparticles less than 10 nm in size predominantly formed (Fig. 2).

CONCLUSIONS

We showed for the first time that Fe–Cu oxide nanoparticles deposited on silica gel catalyze the hydrogenation of nitrobenzene to aniline and of dinitrobenzenes to phenylenediamines under relatively mild conditions: 200°C and an initial hydrogen pressure of 1.3 MPa. The catalytic properties of deposited Fe-Cu bimetallic catalysts depend on the synthesis procedure, sample composition, and conditions of heat treatment. Catalysts reduced in hydrogen are less active. A sample synthesized via the coprecipitation of metal precursors and the hydrolysis of urea with subsequent calcination in air at 300°C with 6 wt % iron and 3 wt % copper had the best selectivity towards aniline, 1,3-phenylenediamine, and 1,4-phenylenediamine (over 82%) upon the full conversion of nitrobenzene and dinitrobenzenes.

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