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| D:\Rinat\Rinat\доки\журнал\статьи\logo.jpg | CuPt/MFI CATALYSTS FOR PROPANE DEHYDROGENATION | | |
| Cite this: *INEOS OPEN*,  **20XX**, *X (X)*, XX–XX  DOI: 10.32931/ioXXXXx  *Received XX Month 20XX,*  *Accepted XX Month 20XX*  http://ineosopen.org | | M. A. Kashkina,\*a,b A. B. Ponomaryov, a A. V. Smirnov,b E. V. Pisarenko,с and M. V. Shostakovskya | |
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| Abstract  The neutralization of MFI-zeolite acid sites with NaCl using impregnation-calcination-washing (ICW) method followed by co-impregnation of zeolite support with Cu(NO3)2 and H2PtCl6 yields highly active and stable CuPt/MFI catalysts for propane dehydrogenation. The presence of acidic sites in initial zeolite critically impacts the Pt dispersion as well as the overall activity and stability of catalysts. CuPt/MFI catalysts with zeolite SiO2/Al2O3 molar ratio of 80 have demonstrated a stable operation (deactivation constant of 0.0035 h-1) at 540°C, 0.1 MPa, weight hourly space veloсity (WHSV) of 28 h-1 for 35 h. | | |  |
| **Key words:** propane dehydrogenation, zeolite, platinum, CuPt nanoparticles, ICW method | | | |

Propylene is among the most important compounds in the chemical industry and is extensively used for the production of monomers, polymers, and basic organic chemicals [1]. The propane dehydrogenation (PDH) process is a cost-effective industrial method for producing of propylene compared to traditional pyrolysis and catalytic cracking [2]. The use of copper as a promoter enhances selectivity and stability of Pt-based catalysts for PDH due to the formation of Cu-Pt alloys or solutions [3,4]. Although the addition of Cu increases selectivity, it leads to decreasing of platinum dispersion due to surface coverage by Cu [5]. A wide range of supports for Pt systems, such as Al2O3, SiO2, mixed oxides and zeolites, have been proposed in the literature [6]. When utilizing acidic zeolites as platinum supports, it's essential to suppress their acidity to prevent side reactions such as cracking, olefin oligomerization, and aromatization. Alkali metals are efficient in suppressing the zeolite acidity [7]. In this work, the impregnation-calcination-washing (ICW) method involving the use of a large amount of NaCl followed by the removal of its excess through washing [8,9] was used for decreasing acidity of MFI-type zeolites.

CuPt propane dehydrogenation catalysts were prepared in two steps. First, zeolite acid sites were neutralized with NaCl using ICW method. Then zeolite support was co-impregnated with Cu(NO3)2 and H2PtCl6 (Scheme 1). The impact of various factors in their preparation (SiO2/Al2O3 and Cu/Pt ratios, calcination temperatures at different stages, treatment sequences) on the catalytic properties was investigated.



Scheme 1. Scheme of the synthesis of CuPt/MFI catalysts

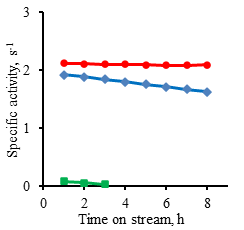
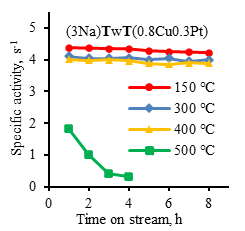
The obtained samples were designated as (*x*Na)T1wT2(*y*Cu*z*Pt) where *x*, *y*, and *z* represent Na, Cu, and Pt content in wt.%, respectively. T1 stands for the calcination temperature post NaCl impregnation, T2 is the calcination temperature post washing, and "w" signifies a water washing step.

More experimental details are given in the Electronic supplementary information (ESI).

No reflections attributed to Pt are present on the XRD pattern of the samples both with and without Cu, which indicates that Pt particles are too small to be detected by XRD analysis and platinum is well dispersed on zeolite surface (Fig. S1).

The performance of CuPt/MFI catalysts is significantly influenced by the zeolite acidic site concentration. The platinum dispersion, measured by CO chemisorption, increases with higher acidity of the initial zeolites, leading to improved activity and stability of the catalysts (Fig. 1a). A sharp decrease in the activity and stability of the catalysts is observed when zeolite calcination temperature reaches 500 °C post introducing NaCl excess (Fig. 1b). At this point, the Na+ cations largely neutralize the zeolite acidity, while they compete with Pt for acid sites, negatively affecting the distribution of platinum. Conversely, reducing the calcination temperature to 150 °C results in the increase of the remaining acidic sites which contribute to Pt dispersion and catalyst activity.

Figure 1. a) Effect of SiO2/Al2O3 molar ratio in zeolite, reaction conditions: WHSV = 28 h-1, 540 °C, 0.1 MPa. b) Effect of calcination temperature on catalyst activity and stability, reaction conditions: WHSV = 28 h-1, 570 °C, 0.1 MPa.



(***x***Na)400w150(0.5Cu0.5Pt)

**SiO2/Al2O3**

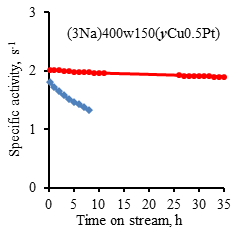
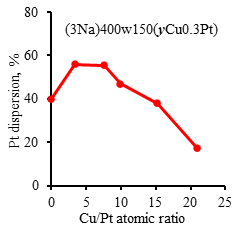
**80**

**280**

**716**

**a**

**b**



**0.17% Cu**

**0% Cu**

**a**

Figure 2. a) Activity of CuPt/MFI-80 catalysts with and without Cu. b) Effect of Cu/Pt atomic ratio on Pt dispersion. Reaction conditions: WHSV = 28 h-1, 540 °C, 0.1 MPa.

The addition of copper dramatically enhances catalyst stability (Figure 2a). The optimal Cu/Pt atomic ratios for CuPt/MFI-80 catalysts range from 1 to 10, ensuring that the platinum is well-dispersed on the zeolite surface (Figure 2b). With an increase in the Cu/Pt ratio, copper atoms may obstruct specific platinum sites, diminishing the availability of Pt and causing a decrease in the activity and stability of the catalysts.

Table 1 summarizes the data on the CuPt catalysts for propane dehydrogenation reported to date in comparison with some catalysts prepared in the present study. The MFI-80-(3Na)400w150(0.3Cu0.1Pt) catalyst showed 7 times higher specific activity (12 s-1) (Fig. S2) compared to the best CuPt/MFI catalyst in the literature, 0.1Pt0.4CuK@S-1, which was prepared by introducing platinum and copper during the synthesis of silicalite-1 [10].

Hence, precise control of acidity (through SiO2/Al2O3 ratio, calcination temperatures) and the Cu/Pt ratio is crucial to achieve high Pt dispersion and active and stable CuPt/MFI catalyst for PDH. ICW method provides simple and convenient way to enhance Pt dispersion as well as activity and stability of PDH catalysts.

**b**

Table 1. Comparison of the catalytic performance of CuPt propane dehydrogenation catalysts.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Catalyst | WHSV, h-1 | Т, °С | C3H6 yield, % | Feed composition | Pt , % | Time on stream, h | Specific activity, s-1a | Deactivation constant, h−1 | IPb | Ref. |
| 0.1Pt0.4CuK@S-1 | 5.4 | 550 | 40 | C3H8/N2 = 1/3 | 0.16 | 73 | 1.73 | 0.005 | 355 | [10] |
| 0.1Pt10Cu/Al2O3 | 4 | 550 | 19 | C3H8/H2/N2 = 8/8/34 | 0.1 | 12 | 0.91 | 0.012 | 76 | [11] |
| (3Na)w(0.17Cu0.5Pt) | 28 | 540 | 27.5 | Pure C3H8 | 0.55 | 35 | 2.02 | 0.0035 | 577 | This work |
| (3Na)w(0.3Cu0.1Pt) | 28 | 570 | 30.1 | Pure C3H8 | 0.09 | 8 | 12.08 | 0.020 | 600 | This work |

a Specific activity is defined as the moles of C3H6 formation per Pt g-atom per second. b IP=specific activity/deactivation constant [9].

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