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CuPt/MFI CATALYSTS FOR PROPANE DEHYDROGENATION

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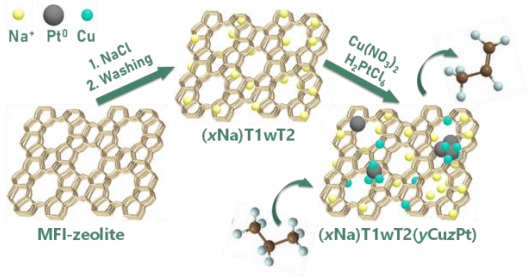
Abstract

The neutralization of MFI zeolite acid sites with NaCl using an impregnation–calcination–washing (ICW) method followed by the co-impregnation of the zeolite support with $Cu(NO_3)_2$ and H_2PtCl_6 yields highly active and stable CuPt/MFI catalysts for propane dehydrogenation. The presence of acid sites in the initial zeolite strongly affects the Pt dispersion as well as the overall activity and stability of the catalysts. The CuPt/MFI catalysts with the zeolite SiO_2/Al_2O_3 molar ratio of 80 demonstrated stable operation (deactivation constant of 0.0035 h^{-1}) at 540 °C, 0.1 MPa, weight hourly space velocity (WHSV) of 28 h^{-1} for 35 h.



Key words: propane dehydrogenation, zeolite, platinum, CuPt nanoparticles, impregnation–calcination–washing method.

Introduction

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 propylene compared to the traditional pyrolysis and catalytic cracking [2]. The use of copper as a promoter enhances the selectivity and stability of Pt-based catalysts for PDH owing to the formation of Cu–Pt alloys or solutions [3, 4]. Although the addition of Cu improves the selectivity, it leads to a decrease in the platinum dispersion due to surface coverage by Cu [5]. A wide range of supports for Pt systems such as Al_2O_3, SiO_2, mixed oxides and zeolites have been proposed [6]. When utilizing acidic zeolites as platinum supports, it is 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 ICW method involving the use of a large amount of NaCl followed by the removal of its excess through washing [8, 9] was used to reduce the acidity of MFI zeolites.

Results and discussion

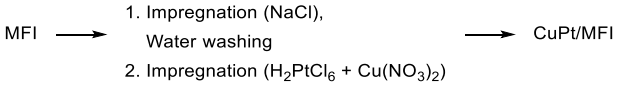
CuPt propane dehydrogenation catalysts were prepared in two steps. First, the zeolite acid sites were neutralized with NaCl using the ICW method. Then the zeolite support was co-impregnated with $Cu(NO_3)_2$ and H_2PtCl_6 (Scheme 1). The impact of various factors in their preparation (SiO_2/Al_2O_3 and Cu/Pt ratios, calcination temperatures at different stages, treatment order) on the catalytic properties was investigated.

The samples obtained were designated as (*x*Na)T1wT2(*y*CuzPt) 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" means a water washing step.

The detailed experimental procedures are given in the Electronic supplementary information (ESI).

No reflections attributed to Pt were observed on the XRD patterns 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 the zeolite surface (Fig. S1 in the ESI).

The performance of CuPt/MFI catalysts is significantly influenced by the concentration of the zeolite acid sites. The platinum dispersion, measured by CO chemisorption, increased 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 was observed when the zeolite calcination temperature reached 500 °C post introducing NaCl excess (Fig. 1b). At this point, Na^+ cations largely neutralized 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 resulted in an increase in the remaining acid sites, which contributed to the Pt dispersion and catalyst activity.



Scheme 1. Synthesis of CuPt/MFI catalysts.

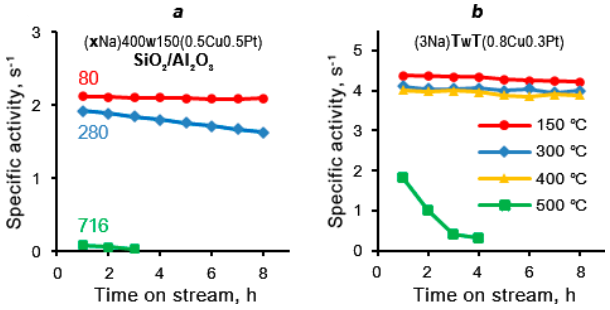


Figure 1. Effect of the SiO_2/Al_2O_3 molar ratio in the zeolite, the reaction conditions: WHSV = 28 h^{-1}, 540 °C, 0.1 MPa (***a***). Effect of the calcination temperature on the catalyst activity and stability, the reaction conditions: WHSV = 28 h^{-1}, 570 °C, 0.1 MPa (***b***).

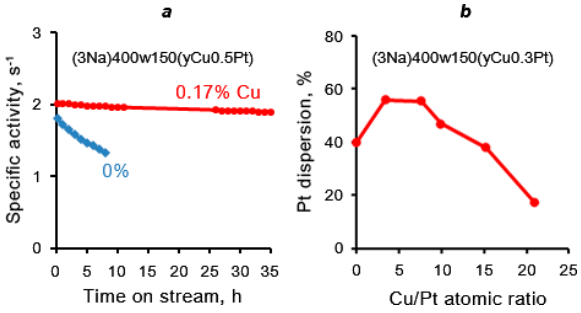


Figure 2. Activity of the CuPt/MFI-80 catalysts with and without Cu (***a***). Effect of the Cu/Pt atomic ratio on the Pt dispersion (***b***). The reaction conditions: WHSV = 28 h^{-1}, 540 °C, 0.1 MPa.

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

Catalyst	WHSV, h^{-1}	*T*, °C	C_3H_6 yield, %	Feed composition	Pt, %	Time on stream, h	Specific activity, s^{-1} [a]	Deactivation constant, h^{-1}	IP[b]	Ref.
0.1Pt0.4CuK@S-1	5.4	550	40	C_3H_8/N_2 = 1/3	0.16	73	1.73	0.005	355	[10]
0.1Pt10Cu/Al_2O_3	4	550	19	$C_3H_8/H_2/N_2$ = 8/8/34	0.1	12	0.91	0.012	76	[11]
(3Na)w(0.17Cu0.5Pt)	28	540	27.5	Pure C_3H_8	0.55	35	2.02	0.0035	577	this work
(3Na)w(0.3Cu0.1Pt)	28	570	30.1	Pure C_3H_8	0.09	8	12.08	0.020	600	this work

[a] specific activity is defined as the moles of C_3H_6 formation per Pt g-atom per second;
[b] IP is the specific activity/deactivation constant [9].

The addition of copper dramatically enhanced the catalyst stability (Fig. 2a). The optimal Cu/Pt atomic ratios for CuPt/MFI-80 catalysts ranged from 1 to 10, ensuring that platinum was well-dispersed on the zeolite surface (Fig. 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. MFI-80-(3Na)400w150(0.3Cu0.1Pt) catalyst showed seven times higher specific activity (12 s^{-1}) (Fig. S2 in the ESI) than the best earlier reported CuPt/MFI catalyst, 0.1Pt0.4CuK@S-1, which was prepared by introducing platinum and copper during the synthesis of silicalite-1 [10].

Conclusions

Hence, a precise control over the acidity (through the SiO_2/Al_2O_3 ratio, calcination temperatures) and the Cu/Pt ratio is crucial to achieve the high Pt dispersion and active and stable CuPt/MFI catalyst for PDH. The ICW method provides a simple and convenient way to enhance the Pt dispersion as well as the activity and stability of PDH catalysts.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the experimental section, XRD patterns, and specific activity of the resulting catalysts in PDH. For ESI, see DOI: 10.32931/io2509a.

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