



Short communication

Catalytic aromatization of methyl bromide to aromatics over bimetallic CuO-ZnO/HZSM-5

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ARTICLE INFO

Keywords:

CH₃Br
Aromatization
CuO-ZnO
Acidity
Aromatics

ABSTRACT

The catalytic conversions of CH₃Br into aromatics over HZSM-5, CuO/HZSM-5, ZnO/HZSM-5 and CuO-ZnO/HZSM-5 were investigated to study the synergistic effect of CuO and ZnO. The results showed that the yield of aromatics decreased in the order of 2%CuO-3%ZnO/HZSM-5 (27.4%) > 5%CuO/HZSM-5 (19.3%) > HZSM-5 (14.4%) > 5%ZnO/HZSM-5 (6.0%) at 360 °C under the same condition, and the bimetallic 2%CuO-3%ZnO/HZSM-5 gave 33.0% aromatic yield at 380 °C. The addition of ZnO promoted the catalytic activity of CuO in CH₃Br aromatization to aromatics. The higher strong acidity significantly improved the hydrogen-transfer and aromatization reaction, increasing the yield of aromatics.

1. Introduction

Aromatics play a significant role in the chemical industry. With dramatic diminishing fossil resources and the continuous increasing demand for crude oil, the conversion of biomass into aromatics has attracted increasing attention. Methane (CH₄) is the simplest hydrocarbon and the main component of natural gas and biogas, and the conversion of biomass to biomethane has received increasing attention [1]. Thus, the conversion of CH₄ to aromatics is regarded as a promising research topic.

Although CH₄ is a significantly promising and economical feedstock, the direct and efficient conversion of CH₄ to chemicals remains a huge challenge due to its high C–H bond strength, negligible electron affinity, large ionization energy and low polarizability [2]. The dehydrogenation and aromatization of CH₄ on modified HZSM-5 to produce aromatics was reported [3]. However, the high amount of coke made the catalyst deactivation occurred fast, resulting in low methane conversion (10%). To solve this problem, the syngas route was proposed: methane to syngas to methanol to aromatics [4–8]. However, the yield of aromatics through this syngas route is not satisfactory [9].

In recent years, many efforts have been devoted to activate CH₄ using Cl₂ or Br₂ to produce methyl halide intermediates [10–13]. Thus, a two-step reaction has been proposed: conversion of CH₄ to CH₃X over a suitable catalyst and catalytic transformation of CH₃Br or CH₃Cl to higher hydrocarbons or aromatics. Although monohalogenated

methane (CH₃-X) is similar to methanol (C-OH) in chemical structure, the reaction thermodynamics and possible mechanisms are more complex than those for methanol [14,15]. Previous reports have focused mainly on the conversion of CH₃Cl [16,17], but little reports have studied the conversion of CH₃Br into aromatics. Yin et al. [9,18] investigated the catalytic conversion of CH₃Br to aromatics over PbO-modified HZSM-5, which was effective for CH₃Br aromatization. However, the toxicity of Pb to the environment limits the industrial development of this catalyst and the catalyst deactivated rather rapidly.

In this article, HZSM-5 (Z5), 5%ZnO/HZSM-5 (ZnO/Z5-5), 5%CuO/HZSM-5 (CuO/Z5-5) and 2%CuO-3%ZnO/HZSM-5 (CuZnO/Z5-2/3) were prepared and applied to the conversion of CH₃Br to aromatics. The influence of different metal oxides and synergistic effect of CuO and ZnO on the CH₃Br conversion and aromatic yield were studied. The effects of the temperature and CH₃Br flow rate on the aromatic yield were investigated, and the stability of selected catalyst was also evaluated.

2. Results and discussion

2.1. Catalyst characterization

The textural properties of the catalysts are shown in Fig. 1 and Table 1. All the Z5 catalysts exhibited type I N₂ adsorption-desorption isotherms without distinct hysteresis loops because of their uniform

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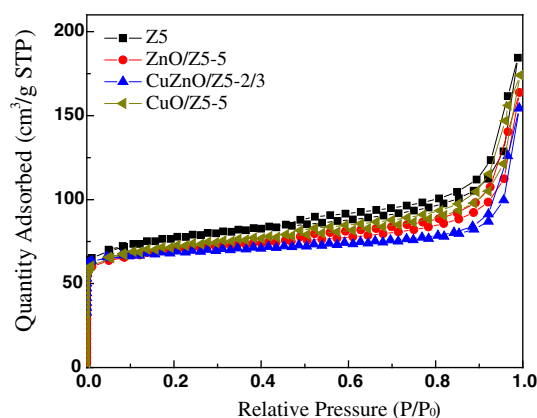


Fig. 1. N_2 adsorption and desorption isotherms of the HZSM-5 (Z5), 5%Zn/HZSM-5 (ZnO/Z5-5), 5%Cu/HZSM-5 (CuO/Z5-5) and 2%Cu-3%Zn/HZSM-5 (CuZnO/Z5-2/3).

Table 1

Textural properties of the HZSM-5 (Z5), 5%Zn/HZSM-5 (ZnO/Z5-5), 5%Cu/HZSM-5 (CuO/Z5-5) and 2%Cu-3%Zn/HZSM-5 (CuZnO/Z5-2/3).

Catalyst	S_{BET} (m^2/g)	S_{Micro} (m^2/g)	V_{total} (cm^3/g)	V_{Micro} (cm^3/g)
Z5	242.3	153.5	0.098	0.080
ZnO/Z5-5	217.7	149.5	0.127	0.078
CuO/Z5-5	225.5	145.4	0.092	0.076
CuZnO/Z5-2/3	231.1	149.0	0.090	0.077

S_{BET} , BET surface area; S_{Micro} , micropore surface area; V_{total} , total volume; V_{Micro} , micropore volume.

microporous structures [19]. Compared with the pure Z5 catalyst, the modified Z5 catalysts showed slight decreases in surface areas and pore volumes because of the metal oxides deposited in the channels of Z5, which resulted in blockage of pores. The S_{BET} was in the order of CuZnO/Z5-2/3 > CuO/Z5-5 > ZnO/Z5-5, meaning that the addition of ZnO in the CuO improved the dispersion of the Cu in the Z5 and reduced the blockage caused by metal oxides deposition.

The acidities of Z5, ZnO/Z5-5, CuO/Z5-5 and CuZnO/Z5-2/3 were characterized by NH_3 -TPD, and the results are shown in Fig. 2 and Table S1. For each profile, normalization by processing 1 g of catalyst was carried out. Two NH_3 desorption peaks were observed at 150–200 °C and 450–500 °C, which are usually assigned to weak and strong acid sites, respectively [20]. It was quite interesting to find that the strong acid sites was only observed for the CuO/Z5-5 and CuZnO/Z5-2/3 catalysts while Z5 and the ZnO/Z5-5 only showed weak acid sites. The number of strong acid sites in CuZnO/Z5-2/3 was higher than

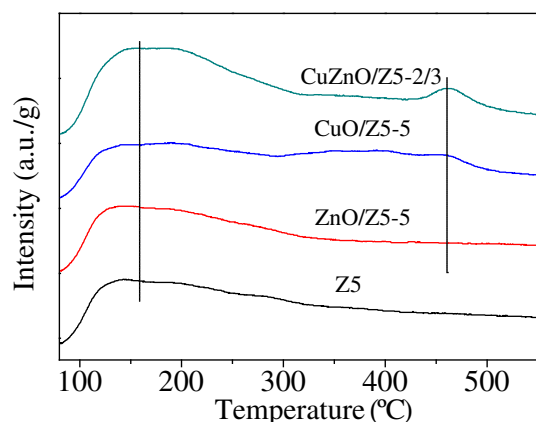


Fig. 2. NH_3 -TPD curves of HZSM-5 (Z5), 5%Zn/HZSM-5 (ZnO/Z5-5), 5%Cu/HZSM-5 (CuO/Z5-5) and 2%Cu-3%Zn/HZSM-5 (CuZnO/Z5-2/3).

that in CuO/Z5-5. Thus, it was concluded that the combination of CuO and ZnO increased the strength of the acid sites to an extent.

The EELS line scan analysis and EDS mapping of CuZnO/Z5-2/3 are shown in Fig. S1. The highly dispersion and uniform of the CuO and ZnO on the Z5 support were observed, which support the dispersion of the metal sites in the XRD results as shown in Fig. S2. The average particle size of the CuO/ZnO active components was approximately 20 nm.

2.2. Aromatization of CH_3Br

2.2.1. Aromatization of CH_3Br with different catalyst composition

The catalytic aromatization of CH_3Br was conducted over the series of catalysts. Table 2 lists the results of CH_3Br conversions and product distributions for the series of catalysts under the same condition. It was found that Z5, ZnO/Z5-5, CuO/Z5-5 and CuZnO/Z5-2/3 all showed higher than 96% of CH_3Br conversions. The activity of the catalysts decreased in the order of CuZnO/Z5-2/3 (27.4%) > CuO/Z5-5 (19.3%) > Z5 (14.4%) > ZnO/Z5-5 (6.0%). The bimetallic CuZnO supported catalyst showed a higher yield of aromatics than the mono-metallic catalysts at a given conversion. The addition of ZnO inhibited the catalytic activity of Z5 but promoted the catalytic activity of CuO/Z5. The $C_2 \sim C_5$ alkanes and $C_7 \sim C_9$ aromatics were the major products. The CuZnO/Z5-2/3 and CuO/Z5-5 gave the higher selectivity of heavy aromatics ($C_{\geq 10}$) while the Z5 and ZnO/Z5-5 gave higher selectivity of light aromatics (C_6-C_8). The yields of different alkanes and alkenes over CuZnO/Z5-2/3 and CuO/Z5-5 were higher than Z5 and ZnO/Z5-5. It was also found that more hydrocarbons were obtained, more aromatics were produced.

It was reported that [9,21] during this reaction, the CH_3Br was firstly activated by both basic and acidic sites and converted to the CH_2 : and HBr, and then the CH_2 : was reacted with each other to form the light olefins ($C_2=$, $C_3=$, $C_4=$...). At last, the aromatics were formed through steps of C propagation and alkylation at acidic sites. Thus, the variations of the aromatic yields were mainly resulted from the changes of acidity, which affected both the conversion of CH_3Br to CH_2 : and HBr and aromatization of olefins to aromatics. It was reported that the formation of aromatics from light hydrocarbons were significant influenced by the acidity of catalyst, especially the strong acidity [22] by Diels-Alder cyclization and dehydrogenation-aromatization. From the results of the NH_3 -TPD, the CuO/Z5-5 and CuZnO/Z5-2/3 possess typical profiles with both weak and strong acid sites, while Z5 and ZnO/Z5-5 only showed weak acid sites. The number of strong acid sites in CuZnO/Z5-2/3 was higher than that in CuO/Z5-5, indicating that the

Table 2

Conversion of CH_3Br and product distributions of aromatics and hydrocarbons over HZSM-5 (Z5), 5%Zn/HZSM-5 (ZnO/Z5-5), 5%Cu/HZSM-5 (CuO/Z5-5) and 2%Cu-3%Zn/HZSM-5 (CuZnO/Z5-2/3). Reaction conditions: catalyst loading = 10 g, $T = 360$ °C, CH_3Br flow rate = 40 mL/min, and of N_2 flow rate = 5 mL/min.

Compound		Z5	ZnO/Z5-5	CuO/Z5-5	CuZnO/Z5-2/3
CH_3Br	Conversion (%)	98.3	98.7	97.1	96.9
Aromatics	Yield (%)	14.4	6.0	19.3	27.4
	C_6 selectivity (%)	2.8	0.9	1.3	0.8
	C_7 selectivity (%)	22.4	15.7	19.3	14.2
	C_8 selectivity (%)	37.1	37.8	33.8	29.6
	C_9 selectivity (%)	14.9	25.1	19.3	21.0
	C_{10} selectivity (%)	6.6	5.9	9.0	12.7
	$C_{\geq 10}$ selectivity (%)	16.3	14.8	17.2	21.6
Alkanes	C_2H_6 yield/%	1.0	0.8	0.7	0.3
	C_3H_8 yield/%	10.6	6.3	14.0	14.7
	C_4H_{10} yield/%	9.1	8.3	16.6	20.8
	C_5H_{12} yield/%	2.8	3.4	7.5	8.5
	C_6H_{14} yield/%	2.3	4.1	1.6	1.7
	C_{2-4} yield/%	0.2	0.2	0.5	0.5
Alkenes					

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