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Effects of potassium promoter on the performance of $PdCl_2$–$CuCl_2$/AC catalysts for the synthesis of dimethyl carbonate from CO and methyl nitrite

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ABSTRACT

The effect of potassium (K) promoter on the catalytic performance of activated carbon (AC) supported Wacker-type catalysts ($PdCl_2$–$CuCl_2$/AC) for the synthesis of dimethyl carbonate (DMC) from CO and methyl nitrite (MN) was investigated by means of N_2 adsorption, H_2-temperature-programmed reduction (H_2-TPR), and X-ray photoelectron spectroscopy (XPS). The experimental results showed that the space time yield of DMC on Wacker-type catalysts with different K promoters ranked in the following order: KCl > KOH > CH_3COOK > K_2CO_3. Especially, the addition of KCl significantly improved the catalytic activities of $PdCl_2$–$CuCl_2$/AC catalyst for DMC synthesis from CO and MN. N_2 adsorption data indicated that the addition of K promoters did not change the textural properties of Wacker-type catalysts greatly. H_2-TPR and XPS results demonstrated that the existence of KCl promoted the reducibility of Cu^{2+} species and increased the proportion of Cu^{2+} species on catalyst surface, which is favorable for oxidizing Pd^0 to active Pd^{2+}. Further, the addition of KCl benefited the reactivity of $PdCl_2$–$CuCl_2$/AC catalyst for DMC synthesis from CO and MN.

1. Introduction

Dimethyl carbonate (DMC) is an environmentally benign chemical product with biodegradability and low toxicity [1]. It has attracted more and more attention and widely used as the methylation or carbonylation agent, solvent, and fuel additive [2–7].

The synthesis of DMC from CO and methyl nitrite (MN) was developed by Ube Industries [8,9]. DMC is synthesized over supported palladium catalysts in the Ube process [10,11]. Among all the supported palladium catalysts, activated carbon (AC) supported Wacker-type catalysts ($PdCl_2$–$CuCl_2$/AC) exhibited excellent catalytic performance for the synthesis of DMC from CO and MN [12,13]. Recently, the potential of various activated carbon supported Wacker-type catalysts promoted by different alkali promoters such as potassium (K) promoters was evaluated in the synthesis of DMC by oxycarbonylation of methanol [14–16]. It is found that the presence of alkali promoters such as CH_3COOK benefits the vapor-phase DMC synthesis reaction and the well-defined $Cu_2Cl(OH)_3$ is supposed to be the active phase [17]. The essential role of alkali promoters may be as a result of electron-donating properties of K, which has an effect upon the electronic environment of palladium and copper active species in the Wacker-type catalyst [14]. Jiang *et al.* [14]. have proved that the catalytic activities of activated carbon supported Wacker-type catalysts promoted by different alkali promoters ranked in the following order: K > Na > Li. And the interaction between CH_3COOK and $CuCl_2$ or $PdCl_2$ during the preparation of catalyst resulted in the formation of KCl species which suppressed the chlorine loss of Wacker-type catalysts. However, it has not yet been reported that the effects of potassium promoters of Wacker-type catalysts on the synthesis of DMC from CO and MN.

In this paper, activated carbon supported Wacker-type catalysts promoted by different K promoters were prepared by different methods and the catalytic activities of catalysts with different mass content of K promoter were evaluated. The effect of different K promoters on the catalytic performance of $PdCl_2$–$CuCl_2$/AC catalysts for DMC synthesis from CO and MN was investigated to explore an effective K promoted $PdCl_2$–$CuCl_2$/AC catalyst for the DMC formation.

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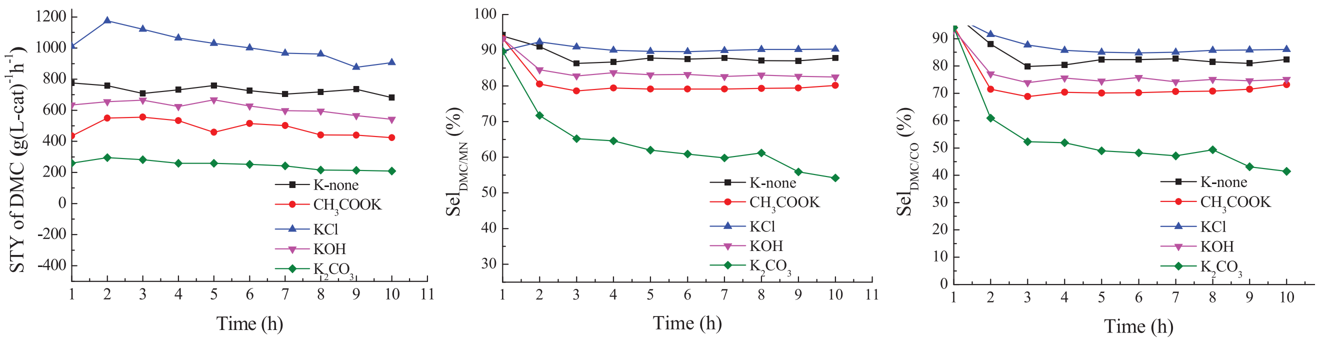

Fig. 1. Catalytic activities of $PdCl_2$–$CuCl_2$/AC catalysts with different K promoters (K loading 1.0 wt%).

2. Experimental

Catalyst preparation: The AC supported Wacker-type catalysts were prepared by a two-step impregnation method. 0.057 g KCl was dissolved in 5 mL distilled water and KCl aqueous solution was added drop by drop to activated carbon. After impregnated for 24 h at room temperature, the sample was dried at 373 K for 4 h and the obtained sample is labeled as AC–KCl. $PdCl_2$–$CuCl_2$/AC catalyst with KCl promoter prepared by the incipient wetness impregnation method (IWI) is as follows: 7 mL of methanol solution of $PdCl_2$ and $CuCl_2$ was added by drops to AC–KCl, impregnating at room temperature for 24 h, drying at 373 K for 4 h and calcining at 473 K for 4 h. And the obtained catalyst is labeled as IWI-$PdCl_2$–$CuCl_2$–KCl/AC. $PdCl_2$–$CuCl_2$/AC catalyst with KCl promoter prepared by the excessive impregnation method is as follows: AC–KCl was added into 50 mL of methanol solution of $PdCl_2$ and $CuCl_2$ and stirred for 4 h, followed by removing solvent by vacuum evaporation at 323 K, drying at 373 K for 4 h and calcining at 473 K for 4 h. And the obtained catalyst is labeled as $PdCl_2$–$CuCl_2$–KCl/AC. $PdCl_2$–$CuCl_2$/AC catalysts with different K promoters (KOH, CH_3COOK and K_2CO_3) were also prepared by the excessive impregnation method and are labeled as $PdCl_2$–$CuCl_2$–KOH/AC, $PdCl_2$–$CuCl_2$–CH_3COOK/AC and $PdCl_2$–$CuCl_2$–K_2CO_3/AC, respectively. The loadings of Cu and Pd for all catalysts were 1.2 and 1.0 wt%, respectively.

Catalyst characterization: Textural properties of different K promoters modified AC supported Wacker-type catalysts were measured with N_2 adsorption and desorption on a Micromeritics ASAP 2020 apparatus at 77 K. H_2-temperature-programmed reduction (H_2-TPR) experiments were carried out on the Micromeritics AutoChem 2920 apparatus. The catalyst surface copper species were analyzed by X-ray photoelectron spectroscopy (XPS), which was carried out on a Perkin-Elmer PHI 1600 ESCA system.

Activity test and product analysis: The DMC synthesis from CO and MN over AC supported Wacker-type catalyst was conducted at 0.2 MPa, 393 K in a continuous flow fixed-bed reactor. 2 mL of catalyst (20–40 mesh) sample were loaded in the middle of fix-bed. The inlet gas was composed of CO, MN and N_2, the volume ratio of CO/MN was 1.0. The gas hourly space velocity (GHSV) of the reaction was 4000 h^{-1}. The products were analyzed by Agilent 4890A GC equipped with a FID detector.

3. Results and discussion

Fig. 1 shows the catalytic performance of $PdCl_2$–$CuCl_2$/AC catalysts with different K promoters, which were CH_3COOK, KCl, KOH and K_2CO_3. From Fig. 1, it is obviously noted that the space time yield (STY) of DMC was around 900 g (L-cat)$^{-1}$ h^{-1} over $PdCl_2$–$CuCl_2$–KCl/AC catalysts, while it was only around 700 g (L-cat)$^{-1}$ h^{-1} over $PdCl_2$–$CuCl_2$/AC without any K promoter. Comparatively, the STY of DMC over $PdCl_2$–$CuCl_2$/AC catalysts promoted by KOH, CH_3COOK and K_2CO_3 was much lower, only around 550, 400 and 200 g (L-cat)$^{-1}$ h^{-1}, respectively. The results showed that the STY of DMC and the selectivity of DMC based on MN and CO on $PdCl_2$–$CuCl_2$/AC catalysts with different K promoters ranked in the following order: KCl > KOH > CH_3COOK > K_2CO_3. Especially, the addition of KCl promoter significantly improved the catalytic activities of $PdCl_2$–$CuCl_2$/AC catalyst for DMC synthesis from CO and MN. Therefore, the addition of K promoters in the form of KCl can significantly enhance the catalytic activities of DMC synthesis from CO and MN.

Textural properties of activated carbon and $PdCl_2$–$CuCl_2$/AC catalysts with different K promoters are listed in Table 1. It is noted that the specific surface area, pore volume and average pore diameter of all the catalysts were slightly changed, suggesting that the structure and physical properties of $PdCl_2$–$CuCl_2$/AC catalysts with different K promoters were similar. Therefore, the different K promoters had negligible effect on the textural properties of K promoters modified $PdCl_2$–$CuCl_2$/AC catalysts.

H_2-TPR profiles of $PdCl_2$–$CuCl_2$/AC catalysts with different K promoters are illustrated in Fig. 2. It can be seen that there is one

Table 1
Textural properties of the catalysts.

Samples	Specific surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Average pore diameter (nm)
AC	1662.2	0.36	2.80
$PdCl_2$–$CuCl_2$/AC	1600.9	0.30	2.80
$PdCl_2$–$CuCl_2$–KCl/AC	1609.3	0.33	2.63
$PdCl_2$–$CuCl_2$–KOH/AC	1562.1	0.28	2.65
$PdCl_2$–$CuCl_2$–CH_3COOK/AC	1540.6	0.26	2.74
$PdCl_2$–$CuCl_2$–K_2CO_3/AC	1578.8	0.25	2.69

Catalyst: Pd loading 1.0 wt%, Cu loading 1.2 wt% and K loading 1.0 wt%.

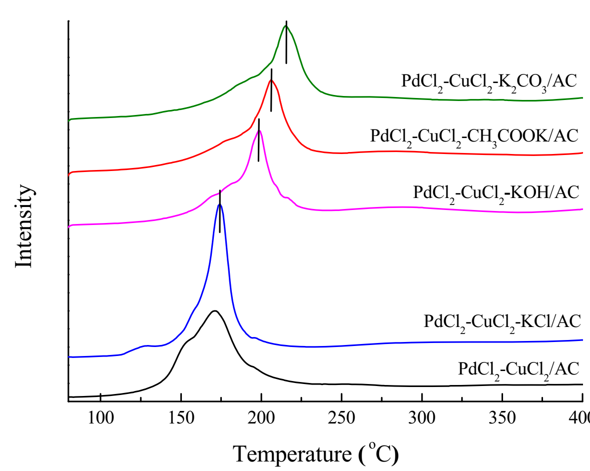

Fig. 2. H_2-TPR profiles of $PdCl_2$–$CuCl_2$/AC catalysts with different K promoters.