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Direct vapor-phase carbonylation of methanol at atmospheric pressure on activated carbon-supported $NiCl_2$–$CuCl_2$ catalysts

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Abstract

In this paper, a series of metallic chloride catalysts supported on activated carbon are prepared. The results show that $NiCl_2$/C has a high conversion of methanol, and $CuCl_2$/C has a high selectivity to methyl acetate for methanol vapor-phase carbonylation without addition of any promoter in the feed. The results show that $NiCl_2$–$CuCl_2$/C has a higher activity and selectivity of methanol carbonylation than $NiCl_2$/C, and the yield of methyl acetate increased by 25%. The optimum component of composite catalyst is 5% $NiCl_2$ and 15% $CuCl_2$. This novel $NiCl_2$–$CuCl_2$/C catalyst has high activity and good stability for methanol vapor-phase carbonylation. The reaction conditions are optimized as follows: reaction temperature of 573 K, methanol concentration of 14.5 mol% and carbon monoxide space velocity of 3000 L/(kg_{cat} h). Under the optimum conditions, methanol conversion of 34.5% and carbonylation selectivity of 94.7 mol% are obtained. Structures of catalysts are characterized with SEM-EDS and XRD.

Keywords: Methanol; Vapor-phase carbonylation; Activated carbon supported $NiCl_2$–$CuCl_2$ catalyst; Metallic chloride; Methyl acetate

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1. Introduction

Although iodide-promoted Rh-catalyzed carbonylation of methanol is one of the most successful examples of homogeneous catalysis employed industrially today, it is affected by the disadvantages associated with a very noble rhodium, and a highly corrosive reaction medium due to the use of methyl iodide as a promoter [1]. Many research efforts have been indulged in the search for an appropriate catalyst to carry out vapor-phase carbonylation under atmospheric pressure, for example, supported rhodium complexes, and Ni/C, Ni–Sn/C catalysts. Nickel-based catalyst was found to exhibit satisfactory activity and selectivity for the carbonylation of methanol [2–6]. Methyl iodide was found to be essential in the cases. The rate-determining step of the reaction was discovered to be the cleavage of the C–I bond of methyl iodide. There has been very little success in finding heterogeneous or homogeneous catalysts that can operate effectively without a halide promoter. According to the known carbonylation mechanism, the initial step is that methyl iodide (CH_3I) directly carbonylates with carbon monoxide to form CH_3COI which further interacts with methanol (MeOH) to form methyl acetate (AcOMe) and HI, and then MeOH reacts with HI to form CH_3I. Thus, it seems likely that methanol does not carbonylate directly with CO during the catalytic cycle, and therefore this carbonylation reaction is indirect catalytic carbonylation. Without any halide in the feed as the promoter, direct carbonylation of methanol is presented [7–9]. In this paper, a series of metallic chloride catalysts supported on activated carbon are prepared. The results show that $NiCl_2$/C has a high conversion of methanol, and $CuCl_2$/C has a high selectivity to methyl acetate for methanol vapor-phase carbonylation without addition of any promoter in the feed. This novel $NiCl_2$–$CuCl_2$/C catalyst has high activity and good stability for methanol vapor-phase carbonylation.

2. Experimental

2.1. Catalysis preparation

Activated carbon supported $NiCl_2$–$CuCl_2$ catalysts (denoted as $NiCl_2$–$CuCl_2$/C) were prepared by impregnating activated carbon with $NiCl_2\cdot6H_2O$ and $CuCl_2\cdot2H_2O$ ethanol solution for 2 h at 343 K. Then the catalyst precursor was

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dried in an air oven for 12 h at 393 K. Prior to the catalytic tests, the dried catalysts were treated in situ with N_2 at 673 K for 2 h. Activated carbon (olive-based carbon, particle size 20–40 mesh, specific surface area 1000 m^2/g) was purchased from Shanghai Tangxin Activated Carbon Co. Ltd., and $NiCl_2 \cdot 6H_2O$ (AR, 99%) and $CuCl_2 \cdot 2H_2O$ (AR, 99%) were purchased from Guangzhou Chemical Reagent Company. The loading of $NiCl_2$ and $CuCl_2$ was 3–15 and 5–17 wt.%, respectively.

2.2. Carbonylation reaction

Methanol carbonylation was carried out in a fixed bed Pyrex reactor (20 mm i.d.) with a continuous flow system at atmospheric pressure. The amount of the catalyst used was 2 g. Pure N_2 was fed to reactor while the catalyst bed was heated from room temperature to reaction temperature before starting the catalytic reaction. The purity of CH_3OH and CO is 99.5 and 99.9%, respectively. Carbon monoxide was saturated with methanol by bubbling the gas into a reservoir, which was kept at a suitable temperature to attain the desired methanol concentration in the reactant flow. The flow rates of the gases were set by means of mass-flow controllers. The effluent gas from the reactor was sampled by a sampling valve and was immediately analyzed by a gas chromatograph equipped with a flame ionization detector.

The system allowed the separation of methane, ethene, dimethyl ether (DME), methanol, methyl acetate and acetic acid. Methanol conversion (X) and selectivity (S_i) for the reaction are defined as

$$X = \frac{\sum X_i N_i}{\sum X_i N_i + X_0} \times 100\%, \qquad S_i = \frac{X_i N_i}{\sum X_i N_i} \times 100\%$$

where X_0 = content of efflux of methanol (mol%); X_i = content of efflux of product i (mol%); N_i = number of methyl group in product i.

2.3. Characterization

A X-ray diffractometer (D/max-A, Japan) was used for X-ray diffraction (XRD) analysis. The radiation source was Cu Kα, and the applied current and voltage were 30 mA and 30 kV, respectively. During the analysis, the sample was scanned from 10° to 60°. The surface morphology and elemental analysis were characterized with a scanning electron microscopy (SEM, LEO1530VP, LEO Company) and energy dispersive X-ray (EDX, INCA300, OXFORD Company) instruments.

3. Results and discussion

3.1. Methanol carbonylation over the different catalysts

Table 1 shows that $NiCl_2/C$ has a high conversion of methanol, and $CuCl_2/C$ has a high selectivity to methyl acetate for methanol vapor-phase carbonylation without addition of any promoter in the feed. A series of supported bimetallic chloride catalysts are also prepared. The results show that $NiCl_2$–$CuCl_2/C$ has a higher activity and selectivity of methanol carbonylation than $NiCl_2/C$, and the yield of methyl acetate increased by 25%. The optimum component of composite catalyst is 5% $NiCl_2$ and 15% $CuCl_2$. This novel $NiCl_2$–$CuCl_2/C$ catalyst has high activity and good stability for methanol vapor-phase carbonylation.

3.2. Effect of reaction conditions

Table 2 shows the effect of reaction temperature on the activity and selectivity. Data for temperature examinations are collected with the 5% $NiCl_2$–15% $CuCl_2/C$ catalyst on stream for at least 4 h. The data are considered as steady-state activity. The selectivity to methyl acetate decrease with the decrease of the temperature, the conversion of methanol increases with the increase of the temperature. A maximum of carbonylation activity is reached at 573 K. From Table 2, we can see that DME is formed as the main byproduct; methane is formed at a lower extent. Methanol carbonylation is found to be a very selective reaction to methyl acetate at lower temperature ($T < 573$ K). Higher temperatures lead a sharp decrease of the carbonylation selectivity and to an increase of DME selectivity.

Tables 3 and 4 show the effect of carbon monoxide space velocity and methanol concentration on the carbonylation of methanol.

Table 1
Catalytic performance for methanol carbonylation on the different metal chloride supported catalysts

Catalyst	Methanol, X (%)	S_i (mol%)			AcOMe, Y (mol%)
		CH_4	DME	AcOMe	
10% $NiCl_2/C$	43.3	4.0	36.9	59.1	25.6
10% $CuCl_2/C$	29.8	3.3	19.0	77.7	23.1
3% $NiCl_2$–17% $CuCl_2/C$	40.3	1.4	26.2	72.2	29.1
5% $NiCl_2$–15% $CuCl_2/C$	46.9	1.3	27.8	70.9	33.3
10% $NiCl_2$–10% $CuCl_2/C$	48.0	1.4	33.1	66.5	31.9
15% $NiCl_2$–5% $CuCl_2/C$	50.1	1.5	37.0	61.5	30.8

Reaction conditions: $T = 573$ K; $P = 0.1$ MPa; $CH_3OH\% = 8.4$ mol%; CO GHSV = 750 L/(kg_{cat} h); time on stream = 3 h; X: conversion, S: selectivity, Y: yield (XS_{AcOMe}), DME: dimethyl ether, AcOMe: methyl acetate.

Table 2
Effect of reaction temperature on the carbonylation of methanol

Reaction temperature (K)	Methanol, X (%)	S_i (mol%)			AcOMe, Y (mol%)
		CH_4	DME	AcOMe	
533	28.2	0.1	3.4	96.5	27.2
553	34.8	0.1	5.7	94.3	32.8
573	38.1	0.2	6.1	93.7	35.7
593	40.1	0.4	11.5	88.1	35.3

Reaction conditions: $P = 0.1$ MPa, $CH_3OH\% = 8.4$ mol% and CO GHSV $= 3000$ L/(kg$_{cat}$ h).

Table 3
Effect of CO GHSV on the carbonylation of methanol

CO GHSV (L/(kg$_{cat}$ h))	Methanol, X (%)	S_i (mol%)			AcOMe, Y (mol%)
		CH_4	DME	AcOMe	
750	46.9	1.3	28.8	70.9	33.3
1500	40.7	0.4	13.4	86.2	35.1
3000	38.1	0.2	5.1	93.7	35.7
3750	36.4	0.1	2.9	97.0	35.3
4500	34.1	0.1	2.0	97.7	33.3

Reaction conditions: $T = 573$ K, $P = 0.1$ MPa, $CH_3OH\% = 8.4$ mol%.

Table 4
Effect of methanol concentration on the carbonylation of methanol

Methanol, C_0 (mol%)	Methanol, X (%)	S_i (mol%)			AcOMe, Y (mol%)	STY (mol/(kg$_{cat}$ h))
		CH_4	DME	AcOMe		
8.4	38.1	0.2	6.1	93.7	35.7	2.0
14.5	34.5	0.1	5.2	94.7	32.7	3.2
22.5	26.4	0.1	3.9	96.0	25.3	3.8

Reaction conditions: $T = 573$ K; $P = 0.1$ MPa; CO GHSV $= 3000$ L/(kg$_{cat}$ h); STY (space–time yield) $=$ AcOMe mol/(kg$_{cat}$ h).

The reaction conditions are optimized as follows: reaction temperature of 573 K, methanol concentration of 14.5 mol% and carbon monoxide space velocity of 3000 L/(kg$_{cat}$ h). Under the optimum conditions, methanol conversion of 34.5%, carbonylation selectivity of 94.7 mol%, and AcOMe space–time yield of 3.2 mol/(kg$_{cat}$ h) are obtained.

Fig. 1 shows that the carbonylation selectivity on novel catalyst steadily increases with the time on stream. The activation process lasts for about 2.5 h, and the yield of methyl acetate reaches a maximum at the end of the activation. No obvious deactivation is observed for the catalyst over 15 h at 573 K. After the reaction time exceeds 18 h, the conversion of methanol decreases obviously with the increase of the reaction time, but the selectivity to methyl acetate maintains constant exceeding 95%. These results are better

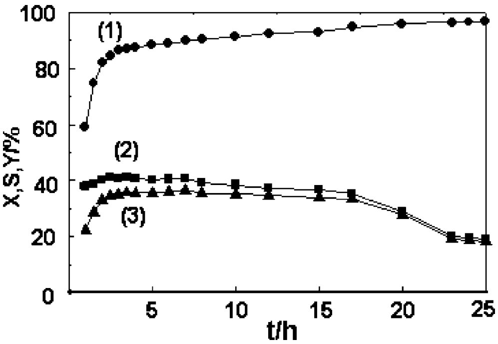

Fig. 1. The stability of $NiCl_2$–$CuCl_2$/C catalyst for methanol carbonylation. Reaction conditions: $T = 573$ K, $P = 0.1$ MPa, $CH_3OH\% = 8.4\%$ and CO GHSV $= 1500$ L/(kg$_{cat}$ h). (1) Selectivity to methyl acetate; (2) conversion of methanol; (3) yield of methyl acetate.

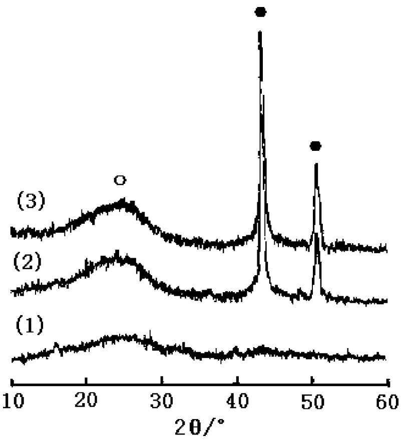

Fig. 2. XRD of catalysts: (1) before reaction; (2) reaction for 6 h; (3) reaction for 24 h. (○) Carbon; (●) Cu.

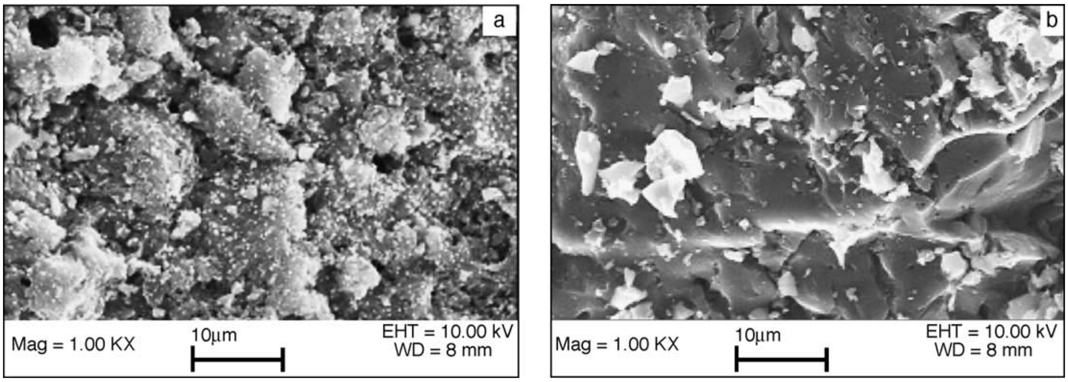

Fig. 3. SEM of catalysts: (a) before reaction; (b) after reaction for 24 h.

than that of sulfided CoMo/C catalyst (methanol conversion of 20%, carbonylation selectivity of 50 mol%, space–time yield of 0.15 mol/(kg$_{cat}$ h)) and $RhW_{12}PO_{40}/SiO_2$ catalyst (methanol conversion of 40%, carbonylation selectivity of 50 mol%) used in the literatures [10,11]. At the temperature of 573 K, the methyl acetate yield dropped rapidly to <1% over 6 h for the reported $RhW_{12}PO_{40}/SiO_2$ catalyst and the carbonylation activity dropped to zero over 20 h for the reported Cu/MOR catalyst [12]. This result suggests that the novel $NiCl_2$–$CuCl_2$/C catalyst may be promising for methyl acetate production from the carbonylation of methanol at atmospheric pressure, without requiring methyl iodide as promoter.

3.3. *Structure characterization*

Fig. 2 shows the XRD patterns of $NiCl_2$–$CuCl_2$/C catalyst. A broad XRD peak attributed to activated carbon support around $2\theta = 24^\circ$ was observed on the sample. Before reaction, $NiCl_2$–$CuCl_2$/C catalyst seemed to be non-crystalline structure, the average atomic ratio of Cl/(Ni + Cu) obtained by EDX elemental analysis was 1.8. After 6 h reaction, strong peaks of XRD attributed to metal copper, the average atomic ratio of Cl/(Ni + Cu) decreased to 0.7. After 24 h reaction, the atomic ratio of Cl/(Ni + Cu) was found to be 0.5. The results show that the peak intensity of Cu^0 crystalline phase enhances with the reaction time increases, the atomic ratio of Cl/(Ni + Cu) reduces with the reaction time increases. But the peak of Ni^0 crystalline phase has not been found. If catalyst was reduced in H_2 to form bimetallic catalyst, the selectivity of carbonylation product was zero. It showed that the crystalline catalyst of Ni^0 and Cu^0 had little carbonylation activity.

Fig. 3 shows SEM image of $NiCl_2$–$CuCl_2$/C catalyst. In the SEM image of the catalyst before reaction, the particles of metal chloride are deposited uniformly on the activated carbon, and the average diameter of particle is 0.5 μm. From the fact that diffraction peaks of Ni and Cu compounds in XRD results were not observed at all, these particles were found to be minor part on this catalyst. This suggests that $NiCl_2$ and $CuCl_2$ on the catalyst before reaction were highly dispersed on the activated carbon surface. But during the reaction, a structural change was clearly observed. In the SEM image of the sample after 24 h, the particles are agglomerated to 4 μm. This structural change seems to be related to the decrease of Cl/(Ni + Cu) atomic ratio from 1.9 to 0.5, and furthermore, to the reaction time dependence of catalytic activity in carbonylation of methanol.

4. Conclusions

1. A series of metallic chloride catalysts supported on activated carbon are prepared. The results show that $NiCl_2$/C has a high conversion of methanol, and $CuCl_2$/C has a high selectivity to methyl acetate for methanol vapor-phase carbonylation without addition of any promoter in the feed.
2. This novel $NiCl_2$–$CuCl_2$/C catalyst has high activity and good stability for methanol vapor-phase carbonylation; the optimum component of composite catalyst is 5% $NiCl_2$ and 15% $CuCl_2$.

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