Tin–Chromium-modified Nickel/Activated Carbon Catalyst for Vapor-phase Carbonylation of Methyl Acetate to Acetic Anhydride

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In the present work, a series of Ni/AC, Ni–Sn/AC, and Ni–Sn–Cr/AC catalysts were prepared by incipient wetness impregnation. Activity tests were performed in a continuous flow fixed-bed reactor. The conversion of methyl acetate and selectivity of acetic anhydride reached 81.1 and 38.8% respectively over the screened Ni–Sn–Cr/AC catalyst under optimal reaction conditions. Catalysts were characterized by means of BET and XRD.

Carbonylation of methyl acetate (MeOAc) provides an alternative promising method for the preparation of acetic anhydride (AcOAc). Compared with conventional industrial routes, carbonylation of MeOAc to AcOAc is totally dependent on relatively abundant coal and natural gas resources rather than scarce oil reserves.[1] Therefore, much interest has been concentrated on screening efficient catalysts for carbonylation of MeOAc. A number of catalysts have been tested. Above all, rhodium-based catalysts have been investigated in detail and have been found to be most active and selective.[2] However, in view of catalyst cost, the high price of rhodium due to its scarcity constricts its industrial application. Thus, exploration of effective nonnoble metal catalysts has attracted much more attention. Nickel catalysts have been found to be much more effective than other nonnoble metal catalysts under mild reaction conditions. Kelkar et al.[3] and Gong et al.[4] have investigated liquid-phase carbonylation of MeOAc to AcOAc with nickel complex catalysts. However, liquid-phase carbonylation suffers from complicated separation of catalyst and product as well as corrosive attack to reactor, which can be avoided in vapor-phase reaction. However, up to now, few effective nonnoble metal catalysts used in vapor-phase carbonylation of MeOAc to AcOAc have been reported. Although, Shikada et al.[5] have reported a Ni/AC (activated carbon) catalyst used in vapor-phase carbonylation of MeOAc, little catalyst characterization was reported and catalytic activity could be improved. Herein, we report the first time that Ni–Sn–Cr/AC catalyst was employed in vapor-phase carbonylation of MeOAc to AcOAc.

The Ni/AC, Ni–Sn/AC, and Ni–Sn–Cr/AC catalysts were prepared by incipient wetness impregnation. First, commercial activated carbon (GH-9A) was refluxed with dilute nitric acid for 4 h, then washed with deionized water to pH 7, and dried at 120 °C for use. A typical catalyst preparation process is described as follows: first, proper quantities of $Ni(NO_3)_2\cdot6H_2O$ were dissolved in distilled water to obtain an aqueous solution of mixture. Second, the prepared activated carbon (20–40 mesh) was added to the solution and stored for 10 h, followed by drying at 120 °C. Finally, the catalyst was calcined under N_2 atmosphere at 600 °C for 4 h. Then, the Ni/AC catalyst was obtained. For preparing modified catalysts, one aqueous solution of $Ni(NO_3)_2\cdot6H_2O$ and $SnCl_4\cdot5H_2O$, and the other aqueous solution composed of $Ni(NO_3)_2\cdot6H_2O$, $SnCl_4\cdot5H_2O$, and $Cr(NO_3)_3\cdot9H_2O$ were prepared, following the aforementioned procedure, the Ni–Sn/AC and Ni–Sn–Cr/AC catalysts were obtained. And no further pretreatment to all catalysts were performed prior to characterization and activity test. In this paper, catalysts with different metal loading are described as *x*%Ni–*y*%Sn–*z*%Cr/AC (w/w).

Carbonylation of MeOAc to AcOAc was carried out in a continuous flow fixed-bed reactor ($\phi17 \times 450$ mm). In a typical experiment, 5 mL of catalyst diluted with 5 mL of porcelain was loaded. The liquid substrate consisting of MeOAc and methyl iodide (CH_3I, used as promoter) was continuously injected into the preheater by a syringe pump, and a gas mixture of CO and H_2 from gas cylinders controlled by a mass flow meter was simultaneously fed into the preheater, mixed with MeOAc and CH_3I sufficiently, and then flowed into the reactor jointly. The liquid products collected with a cold trap were analyzed by gas chromatography (GC-9A) using a flame ion detector (FID) and a Propark Q column. The feed and effluent gas were analyzed by gas chromatography (GC-9560) equipped with a FID and a GDX-502 column, at the same time H_2, CO, CH_4, and CO_2 were analyzed by a gas chromatography (GC-4000A), using thermal conductivity detector and a carbon molecular sieve column.

The structural properties of catalysts were measured by isothermal adsorption of N_2 using a Micromeritics Tristar 3000 nitrogen physisorption apparatus. X-ray diffraction (XRD) patterns were obtained on a Bruker Advanced X-ray Solutions/D8-Advance using Cu Kα radiation.

The results of vapor-phase carbonylation of MeOAc to AcOAc over different catalysts are summarized in Table 1. The Ni/AC catalysts with different Ni loading did not show high conversion for MeOAc and high selectivity to AcOAc. And the Ni–Sn/AC catalysts showed a little improvement on the catalytic activity compared to Ni/AC catalysts. But the addition of Cr to Ni–Sn/AC catalyst resulted in a much more significant enhancement in catalytic activity. Consequently, the trimetallic catalyst Ni–Sn–Cr/AC could be the best choice for the carbonylation of MeOAc. Effects of metal loading on catalytic activity of Ni–Sn–Cr/AC catalysts were investigated and indicated that conversion of MeOAc and selectivity of AcOAc could reach 30.8 and 74.9% respectively over 9%Ni–12%Sn–6%Cr/AC catalyst with reaction conditions a. Furthermore, with optimized reaction conditions b, the selectivity of AcOAc could be markedly improved to 81.1% accompanied by a great increase in conversion of MeOAc.

The XRD patterns of different catalysts are illustrated in Figure 1. The crystalline phase of 9%Ni/AC catalyst was mainly composed of Ni^0, verified by the peaks at $2\theta = 44.5$, 52.3, and

Table 1. Catalytic performance of different catalysts for vapor-phase carbonylation of MeOAc to AcOAc

		Conversion[c]/%	Selectivity[d]/%		
Entry	Catalyst	MeOAc	AcOAc	AcOH	CH_4
1[a]	7%Ni/AC	11.3	56.8	41.7	1.5
2[a]	9%Ni/AC	12.5	57.6	41.2	1.2
3[a]	7%Ni–8%Sn/AC	18.9	61.3	37.8	0.9
4[a]	9%Ni–10%Sn/AC	21.7	63.5	35.7	0.8
5[a]	9%Ni–6%Cr/AC	20.6	62.7	36.4	0.9
6[a]	9%Ni–11%Sn–3%Cr/AC	28.5	72.3	27.3	0.4
7[a]	9%Ni–12%Sn–4%Cr/AC	31.9	70.2	29.3	0.5
8[a]	9%Ni–12%Sn–6%Cr/AC	30.8	74.9	24.6	0.5
9[b]	9%Ni–12%Sn–6%Cr/AC	38.8	81.1	18.1	0.8

Reaction conditions: [a]$CO:H_2 = 11:1$, $MeOAc:CH_3I = 7:1$, $CO:MeOAc = 4:1$, $T = 200\,°C$, $P = 5.3\,MPa$, $GHSV = 1200\,h^{-1}$, reaction duration 7 h; [b]$CO:H_2 = 8:1$, $T = 205\,°C$, others as the same as a. [c]Conversion (mol %) = converted AcOMe/injected AcOMe, [d]Selectivity (mol %) = [(product, mol h^{-1}) × (no. of methyl groups in the molecule)]/[(reacted AcOMe, mol h^{-1}) × 2].

Table 2. Structural properties of 9%Ni/AC, 9%Ni–12%Sn/AC, and 9%Ni–12%Sn–6%Cr/AC

Catalyst	BET surface area/$m^2\,g^{-1}$	Total pore volume/$cm^3\,g^{-1}$	Average pore diameter/nm
9%Ni/AC	1048.8	0.552	2.105
9%Ni–10%Sn/AC	956.7	0.502	2.101
9%Ni–12%Sn–6%Cr/C	799.7	0.434	2.17

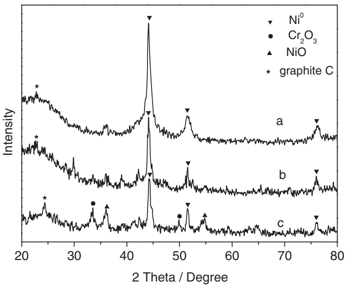

Figure 1. XRD patterns for: a 9%Ni/AC, b 9%Ni–12%Sn/AC, c 9%Ni–12%Sn–6%Cr/AC.

77.2° obviously. Besides diffraction peaks of Ni^0, the crystalline phases of 9%Ni–12%Sn–6%Cr/AC catalyst were mainly composed of NiO and Cr_2O_3. However, the diffraction peak of Sn was detected on neither Ni–Sn/AC nor Ni–Sn–Cr/AC catalyst. The XRD pattern of NiO was detected at $2\theta = 36.1$ and 54.8°, the diffraction peak at $2\theta = 33.4$ and 49.9° could be resolved to Cr_2O_3. The Cr_2O_3 could be due to decomposition of $Cr(NO_3)_3{\cdot}9H_2O$ during the process of catalyst calcination. The NiO could be ascribed to decomposition of $Ni(NO_3)_2{\cdot}6H_2O$. As a result, Ni^0 detected could be attributed to reduction of NiO by activated carbon during the catalyst calcination under N_2 atmosphere. It is obvious that the diffraction intensity of Ni^0 diffraction peak decreased sharply accompanied by introduction of Sn and Cr. Thus, it could be concluded that the addition of Sn and Cr facilitated uniform dispersion of Ni^0 phase over activated carbon, which could partly correspond to higher activity of Ni–Sn–Cr/AC catalyst. In addition, a synergetic effect among Ni, Sn, and Cr could improve activity of Ni–Sn–Cr/AC catalyst as well.

Table 2 shows the structural properties of different catalysts. It is obvious that the surface area of catalysts decreased gradually with addition of Sn and Cr. However, according to Table 1, the activities of three catalysts were totally reversed proportion to their surface area. It could be concluded that improvement of catalytic activity as a result of addition of Sn and Cr was independent of change of surface area of catalysts. In addition, the total pore volume of catalysts exhibited a descending trend following the increase of Sn and Cr, which could be attributed to certain active components transferred into pore space of activated carbon in the process of catalyst calcination. However, pore diameter of different catalysts hardly changed, which may have less effect on catalytic activity.

In conclusion, Ni–Sn–Cr/AC catalyst was first used for vapor-phase carbonylation of MeOAc to AcOAc. Promising results were attained over 9%Ni–12%Sn–6%Cr/AC catalyst under optimized reaction conditions. Ni^0 formed in the process of catalyst calcination and was kept in reduced state owing to the H_2 atmosphere during the reaction. The high catalytic activity of Ni–Sn–Cr/AC catalyst could be partly related to homogeneous dispersion of Ni^0 caused by addition of Sn and Cr as well as a synergetic effect among Ni, Sn, and Cr. Although, the mechanism of the improvement of catalytic activity with addition of Sn and Cr needs to be further investigated, this work provides an efficient method for synthesis of AcOAc.

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References

1 J. R. Zoeller, V. H. Agreda, S. L. Cook, N. L. Lafferty, S. W. Polichnowski, D. M. Pond, *Catal. Today* **1992**, *13*, 73.
2 M. J. Howard, M. D. Jones, M. S. Roberts, S. A. Taylor, *Catal. Today* **1993**, *18*, 325.
3 A. A. Kelkar, R. S. Ubale, R. V. Chaudhari, *J. Mol. Catal.* **1993**, *80*, 21.
4 J. F. Gong, Q. H. Fan, D. Z. Jiang, *J. Mol. Catal., A* **1999**, *147*, 113.
5 T. Shikada, H. Yaglta, K. Omata, K. Fujimoto, H. Tominaga, *Ind. Eng. Chem. Res. Dev.* **1985**, *24*, 521; K. Fujimoto, T. Shikada, M. Miyauchi, H. Tominaga, *Chem. Lett.* **1983**, 1157.

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