Bimetallic alloy palladium catalysts for acetylation of propene: Study on the promotion mechanism

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Highlights

- Effects of PdM (Cu, Au, Sb) bimetallic catalysts on the acetoxylation reaction were studied
- The promoting effects of Sb on the catalytic performance of Pd catalysts was revealed
- The structural properties of the active PdSb nanoalloy particles were illustrated

1. Introduction

Acetoxylation is an industrial oxidative esterification process, and widely used in the production of valuable intermediates with an environmental-friendly process.[1,2] A typical industrial catalyst for the acetoxylation reaction is the Pd-M (M is the second metal) bimetallic catalysts with the addictive of potassium acetate (KOAc), which also suffers from low activity, selectivity, and stability. Furthermore, the active center, reaction mechanism, and deactivation mode are still controversial and plausible. In this work, a series of bimetallic catalysts were prepared and tested for the acetoxylation of propene, with effects of the second metal and KOAc on the catalyst performance were explored in details.

2. Methods

The bimetallic catalysts were prepared by an impregnation method.[3] The reaction was carried out in a fixed-bed reactor. A typical reaction condition is: the feed molar ratio of oxygen/acetic acid/propylene = 1 : 2.5 : 9, reaction temperature of 150°C, reaction pressure of 6 bar, and a gas hourly space velocity (GHSV) of 3000 h^{-1}. All the gas compositions after reaction were analysed with an online gas chromatograph equipped with both FID and TCD detectors.

3. Results and discussion

Generally, the single Pd catalyst showed low activity and selectivity for the acetoxylation reaction of propene, which is usually correlated with the strong adsorption of propene and acetic acid on the Pd atom (Figure 1a). Therefore, a series of transition metals were alloyed with Pd to modify the adsorption and reaction behaviors of feedstocks and products on Pd. Au and Cu showed little effect on the catalytic performance of Pd catalysts, while PdSb exhibited a higher activity and selectivity for the acetoxylation of propene compared with the single Pd catalysts. The molar ratio between Pd and Sb was also optimized, with the best catalytic activity achieved on Pd : Sb of 2 : 1, which could be due to the appropriate adsorption strength of feedstocks and products on the catalyst surface. The effect of KOAc, which could also adjusted the adsorption behavior and prevent the excessive oxidation of propene and acetic acid, was shown in Figure 1c. A volcano curve of the catalytic activity was observed with the optimized KOAc contents of 10 wt%. To sum up, allyl acetate selectivity of 96.2% and space-time yield of 1.73 h^{-1} were obtained on Sb-10%KOAc/α-Al_2O_3, which are much higher than that on Pd catalyst (selectivity of 94.6% and space-time yield of 0.77 h^{-1}).

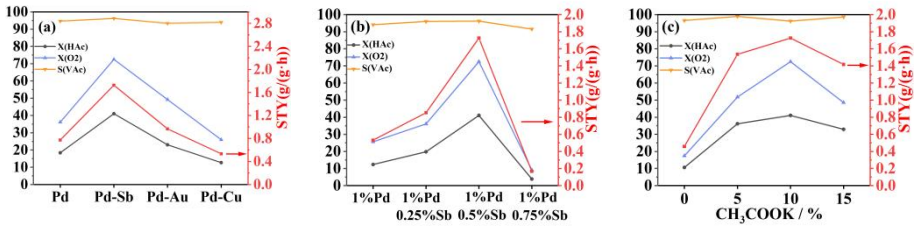

Figure 1. Effect of (a) the bimetallic PdM (M = Sb, Au, Cu) catalysts, (b) molar ratio between Pd and Sb, and (c) amounts of CH_3COOK on the acetoxylation of propene.

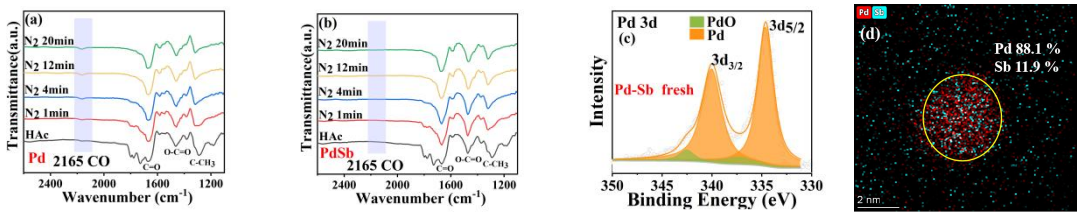

Figure 2. In situ DRIFTS spectra of the adsorption of acetic acid on (a) Pd and (b) Pd-Sb catalysts, (c) XPS of the Pd 3d state on PdSb, and (d) elemental map in a nanoparticle of the fresh Pd-Sb catalyst.

The in situ DRIFTS of the adsorption of acetic acid was also performed (Figure 2a,b). A characteristic peak of CO at 2165 cm^{-1} was observed on the Pd catalyst, while that is absent on the PdSb catalyst, which evidenced the inhibition of excessive oxidation of acetic acid and improvement of allyl acetate selectivity on PdSb. The XPS of fresh PdSb was shown in Figure 2c. The binding energies of 334.6 eV and 340.0 eV are attributed to Pd^0 $3d_{5/2}$ and $3d_{3/2}$ of the Pd 3d state respectively, while 337.3 eV and 342.5 eV are assigned to Pd^{2+} $3d_{5/2}$ and $3d_{3/2}$.[4] The Pd^0/Pd^{2+} ratio increased from 70.1/29.9 in Pd to 86.7/13.3 in PdSb, which may suggest the reasonable active center of Pd^0. Furthermore, the elemental map of an alloy nanoparticle on the fresh bimetallic PdSb catalyst displayed that the particle size was about 3 nm and the atomic percentages of Pd and Sb in an active center were 88.1 and 11.9%, respectively.

4. Conclusions

A series of PdM bimetallic catalysts were tested for the acetoxylation fo propene, with the best activity were achieved on the PdSb bimetallic catalyst. The present of Sb could effectively inhibit the excessive oxidation of acetic acid and advance the activity and the selectivity of allyl acetate. The active center was suggested to be the PdSb nanoalloy particles with the size of ~3 nm and the atomic percentages of Pd and Sb being 88.1 and 11.9%. The highest allyl acetate selectivity of 96.2% and space-time yield of 1.73 h^{-1} were obtained on $Pd_{88}Sb_{12}$-10%KOAc/α-Al_2O_3.

References

[1] Jenq Renn Chen, Chien May Lee, Process Safety Progress. 24 (2005) 280-286.

[2] Marcin B, Stanis Aw L, Journal of Advanced Oxidation Technologies. 18 (2015) 303-314.

[3] Nakaya Y, Hayashida E, Shi R, Journal of the American Chemical Society. 145 (2023) 2985-2998.

[4] Ding D, Xu X, Tian P, Chinese Journal of Catalysis. 39 (2018) 673-681.

Keywords

Pd-Sb catalyst; Acetoxylation; Allyl acetate.