Development of a Zirconia-Supported Palladium Catalyst for Decarbonylation of Furfural into Furan

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Abstract: A zirconia-supported Pd catalyst was developed for furfural decarbonylation into furan to be applied to THF production process. The catalyst improved with the addition of potassium maintained high activity at a low hydrogen concentration over a prolonged period of time. This catalyst was more durable to the reaction in the absence of hydrogen than other catalysts whereas deactivation was not observed for the reaction of benzaldehyde without hydrogen. The factor for superior performance was discussed by considering the effects of hydrogen and the added alkaline on the interaction of Pd surface with furan ring.

Keywords: Furfural, Furan, Decarbonylation, Palladium, Zirconia, Hydrogen Effect.

1. Introduction

Furfural-based THF production is a most feasible process for chemicals production from renewable feedstocks. Although one of the problems standing in the way of application to practical process was poor durability of catalysts for furfural decarbonylation into furan, we have recently found that zirconia-supported Pd catalysts exhibit high and durable performance for furfural decarbonylation at a low hydrogen concentration under industrially advantageous conditions. The catalyst improved with addition of potassium showed highly stable performance, and no deactivation was observed after several tens of hours. In this study, characterizations of the catalysts and the reaction under specific conditions were carried out to investigate the mechanism of catalyst deactivation for furfural decarbonylation. We wish to discuss the effects of hydrogen and the added alkaline in relation to the interaction of Pd surface with furan ring, and the potency of zirconia support that enhances these effects on Pd.

2. Experimental

Commercially available monoclinic ZrO2 pellet (Saint-Gobain Norpro SZ31164) was used as zirconia support. Silica and γ-alumina pellet were also employed as comparative supports. The pellets were broken and sieved into the size of 600-1000 μm for catalyst preparations. The loading of Pd (1wt%) was performed by the incipient-wetness impregnation of Pd(NO3)2/HNO3 solution. After drying and calcination in air at 500°C for 4 h, the catalysts were finally reduced in an H2 stream at 450°C for 2 h. The vapor-phase decarbonylation of furfural was conducted using a fixed bed flow reactor at atmospheric pressure. In all experiments of this study, the furfural purified by distillation was employed, and its purity was more than 99.6%. The catalyst bed was heated to reaction temperature in a stream of mixture of H2 and N2, and then the furfural was introduced through a vaporizer with H2 and N2 into the reactor. Effluent gas from the reactor outlet was analyzed by an on-lined TCD-GC. The TPO analysis for the catalysts was performed using another flow reactor equipped with an ANELVA M-400 QMS.

3. Results and discussion

Fig. 1 shows the time course of furfural conversion for the reaction over metal oxide-supported Pd catalysts. The zirconia-supported Pd catalysts exhibited high activity for furfural decarbonylation at a low concentration of hydrogen, giving the desired product, furan, in more than 99% selectivity at 260°C. The catalyst improved by the addition of potassium, Pd(1wt%)-K(1wt%)/ZrO2, maintained high performance
whereas the activity of other supported Pd catalysts dropped within several hours at a low concentration of hydrogen.

It has been known that accompanying hydrogen, dispensable stoichiometrically in decarbonylation reaction, improves catalyst durability for fufural decarbonylation though the mechanism of this positive effect is still unclear.[1,2] In our experiments, stopping hydrogen feed during the reaction resulted in rapid decrease in the activity for alumina-supported and silica-supported Pd catalysts. However, the zirconia-supported Pd catalyst with potassium showed remarkable durability in the absence of hydrogen, regaining the activity after reintroducing hydrogen (Fig. 2). The durability order for the catalysts in the absence of hydrogen was coincident with the longevity order in the presence of hydrogen, suggesting that deactivation mechanism for the catalysts is essentially same regardless whether hydrogen is present or not.

We also performed similar experiments using benzaldehyde to examine the transition of catalyst activity with and without hydrogen. In contrast to fufural decarbonylation, the deactivation by cutting hydrogen off was not observed for benzaldehyde decarbonylation into benzene even for Pd/SiO₂. This clearly indicates that the deactivation for fufural decarbonylation is ascribed to the interaction of Pd surface with furan ring.

The difference in electronic properties of Pd between Pd/ZrO₂ and Pd-K/ZrO₂ was revealed in the TPO analysis. As shown in Fig. 3, the oxygen consumption peak in the TPO profile appeared at a higher temperature for the latter catalyst, proving that the added alkaline makes impacts on the electronic properties of Pd to resist oxidation.

### 4. Conclusions

The obtained results lead the conclusion that the added alkaline and hydrogen stabilize metallic state of Pd and prevent from interacting with the furan ring which blocks active sites and triggers irreversible deactivation during the reaction. The superior performance of zirconia-supported Pd catalysts should be attributed to assistance capability of zirconia for maintaining the electronic state of Pd.

### References


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**Fig. 1** Furfural decarbonylation over supported Pd catalysts. Temp., 260 °C; cat., 0.75 g; WHSV, 4 h⁻¹; fufural conc., 29%; H₂/furfural, 0.06.

**Fig. 2** Effect of H₂ on fufural decarbonylation over ZrO₂-supported Pd catalysts. Reaction conditions are same as those for Fig. 1.

**Fig. 3** TPO profiles for ZrO₂-supported Pd catalysts. 2.7 % O₂; 20 Nml/min; heating rate, 20 °C/min.