

Synergic effect of polymer-supported bimetallic catalysts in the hydrogenation and isomerization of 1-octene

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Abstract

The catalytic properties of the bimetallic catalysts for the hydrogenation and isomerization of 1-octene were investigated. The PVP–PdCl₂–1/2Co(OAc)₂ bimetallic catalyst reduced by NaBH₄ exhibited a remarkable bimetallic synergic effect under mild conditions of 40°C and 0.1 MPa. The maximum turnover frequency (TOF_{max}, mol H₂/mol Pd min) can be nearly doubled compared with that of the reaction catalyzed by the monometallic catalyst, and simultaneously the isomerization of 1-octene to 2-octene and 3-octene was inhibited significantly. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Polymer-supported bimetallic catalyst; Synergic effect; 1-Octene; Hydrogenation; Isomerization

1. Introduction

It has been known that in the hydrogenation of terminal olefins, the migration of C=C double bond from the terminal to the internal position of the molecule usually exists by using polymer-supported Pd catalysts, and the degree of the isomerization varies with the fundamental chain of the polymer, the coordinative group in the polymer and the reaction conditions [1,2]. In some cases, the terminal olefins can be easily isomerized to the internal olefins, which, in turn, inhibit the hydrogenation of the substrates.

Recently, the multi- or bimetallic synergic effect in homogeneous or polymer-anchored catalysis has attracted much attention, since enhanced reaction rates, selectivities and new types of reactions are expected to arise from the cooperation or successive participation of two or more kinds of metal components [3–11]. In our recent study, we have found that the homogeneous or polymer-anchored bimetallic palladium-based catalysts, prepared by means of adding a second transition metal component to the homogeneous or polymer-anchored monometallic catalyst, can result in a remarkable synergic effect on the reaction rates and the selectivities for the desired product in the hydrogenation of nitrobenzene, hydrodechlorination of organic chlorides, cyclotrimerization of butadiene, oxidization of olefins and carbonyla-

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tion of allyl halides under atmospheric pressure [12–18].

In this paper, we report a remarkable synergic effect of the polymer-anchored bimetallic palladium–cobalt catalyst reduced by NaBH_4 ($\text{PVP-PdCl}_2\text{-Co(OAc)}_2/\text{NaBH}_4$) on the hydrogenation and isomerization of 1-octene for improving the maximum turnover frequency and inhibiting the isomerization of 1-octene.

2. Experimental

2.1. Materials

Poly(*N*-vinyl-2-pyrrolidone) (PVP) is a product of BASF. 1-Octene and other reagents are all of analytical grade. High purity H_2 and Ar (> 99.9%) are used for the catalytic experiments.

2.2. Preparation of the PVP-supported catalysts

To a mixture of 1 ml of 5 mol dm^{-3} HCl and 0.056 g (0.31 mmol) of PdCl_2 , 75 ml of absolute ethanol and 0.724 g of PVP were added. After stirring at room temperature for 48 h, a red-brown solution was obtained (the catalyst PVP-PdCl_2 , 4×10^{-3} mmol Pd ml^{-1} , N/Pd = 20). To the monometallic catalyst, a second transition metal compound (e.g., $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O}$ or $\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$) was added, then stirred at room temperature for 24 h to obtain the polymer-supported bimetallic catalyst ($\text{PVP-PdCl}_2\text{-mMX}$, 4×10^{-3} mmol Pd ml^{-1} , N/Pd = 20, M/Pd = *m*). To the bimetallic catalyst, NaBH_4 ($\text{NaBH}_4:(\text{M} + \text{Pd}) = 5$ (mole ratio)) was added under argon atmosphere, stirred at room temperature for 6 h, then NaBH_4 reduced bimetallic catalyst $\text{PVP-PdCl}_2\text{-mMX}/\text{NaBH}_4$ was obtained.

2.3. General procedure for 1-octene hydrogenation

A 65 ml three-necked and jacketed bottle fitted with a silicon rubber septum was evacu-

ated and connected to a constant pressure gas burette containing H_2 . Then 10 ml of absolute ethanol and 1 ml of the catalyst solution (4×10^{-3} mmol Pd) was introduced through the silicon rubber septum via a syringe successively. After the catalyst was reduced by H_2 in-situ (if using NaBH_4 reduced catalyst, it did not need to be reduced by H_2) for 10 min, the substrate was added. Samples were removed via a syringe for GC analysis at the given time. The reaction was monitored by the H_2 uptake.

2.4. General procedure for 1-octene isomerization

A 65 ml three necked and jacketed bottle fitted with a silicon rubber septum was evacuated and connected to a constant pressure gas burette containing Ar. Then 10 ml of absolute ethanol and 1 ml of the catalyst solution (4×10^{-3} mmol Pd, unreduced or reduced by H_2 or by NaBH_4) was introduced through the silicon rubber septum via a syringe successively. After 10 min, the substrate was added under argon. Samples were removed via a syringe for GC analysis at the given time.

3. Results and discussion

The PVP-supported mono- and bimetallic catalysts were used in the hydrogenation of 1-octene. The experimental results are listed in Table 1. It can be seen from Table 1 that the monometallic catalyst PVP-PdCl_2 is active to the hydrogenation of 1-octene. The maximum turnover frequency (TOF_{max} , mol $\text{H}_2/\text{mol Pd min}$) is 106, and the conversion of 1-octene is up to 94.8% in 170 min, but there is a serious isomerization of 1-octene to 2-octene and 3-octene during the hydrogenation process, and the relative concentration of 2-octene and 3-octene in the end product is about 8%. While the monometallic catalysts PVP-CuCl_2 , PVP-Ni(OAc)_2 and PVP-Co(OAc)_2 reduced by H_2 or NaBH_4 are all inactive for the hydrogenation of 1-octene under mild conditions of 40°C and

Table 1
Hydrogenation of 1-octene catalyzed by PVP–PdCl₂–mMX

Catalyst	TOF _{max} (min ⁻¹) ^c	Product composition (%)			Conversion of 1-octene ^e (%)
		1-Octene	Octane	2-Octene and 3-octene ^d	
PVP–PdCl ₂ ^a	106	5.2	87.0	7.8	94.8 (170)
PVP–PdCl ₂ –CuCl ₂ ^a	nil	–	–	–	–
PVP–PdCl ₂ –Ni(OAc) ₂ ^a	84	5.2	88.7	6.1	94.8 (170)
PVP–PdCl ₂ –Co(OAc) ₂ ^a	110	4.8	89.2	6.0	95.2 (170)
PVP–CuCl ₂ ^a	nil	–	–	–	–
PVP–Ni(OAc) ₂ ^a	nil	–	–	–	–
PVP–Co(OAc) ₂ ^a	nil	–	–	–	–
PVP–PdCl ₂ ^b	122	4.9	90.1	5.0	95.1 (170)
PVP–PdCl ₂ –CuCl ₂ ^b	48	13.8	64.0	22.2	86.2 (170)
PVP–PdCl ₂ –Ni(OAc) ₂ ^b	145	1.2	97.3	1.5	98.8 (170)
PVP–PdCl ₂ –2Co(OAc) ₂ ^b	105	3.9	94.0	2.1	96.1 (170)
PVP–PdCl ₂ –Co(OAc) ₂ ^b	169	0	100	0	100 (160)
PVP–PdCl ₂ –1/2Co(OAc) ₂ ^b	195	0	100	0	100 (150)
PVP–PdCl ₂ –1/4Co(OAc) ₂ ^b	158	0.8	98.7	0.5	99.2 (170)
PVP–CuCl ₂ ^b	nil	–	–	–	–
PVP–Ni(OAc) ₂ ^b	nil	–	–	–	–
PVP–Co(OAc) ₂ ^b	nil	–	–	–	–

Reaction conditions: 0.1 MPa; 40°C; absolute ethanol, 10 ml; Pd ($n_M:n_{Pd} = m$), 4×10^{-3} mmol; 1-octene, 4 mmol.

^aThe catalyst was reduced by H₂.

^bThe catalyst was reduced by NaBH₄.

^cCalculated from the amount of dihydrogen uptake.

^dThe separation of the peaks for 2-octene and 3-octene in GC is not good enough to make individual quantitative determination.

^eThe conversion based on the data of GC analysis at the time indicated in parentheses (in minutes).

0.1 MPa. It also has been found by other persons of our group that PVP–CuCl₂, PVP–Ni(OAc)₂ and PVP–Co(OAc)₂ reduced by H₂ or NaBH₄ have no catalytic hydrogenation activities under the same reaction conditions. However, when we use the bimetallic catalysts obtained by adding one second transition metal component (e.g., CuCl₂ · 2H₂O, Ni(OAc)₂ · 4H₂O or Co(OAc)₂ · 4H₂O) to the monometallic catalyst PVP–PdCl₂ and then using H₂ or NaBH₄ to reduce the catalysts, respectively, it shows that both the PVP-supported Pd–Co and Pd–Ni bimetallic catalysts reduced by NaBH₄ can exhibit remarkable synergic effect on the inhibition of 1-octene isomerization, and the Pd–Co bimetallic catalyst is better. Furthermore, the TOF_{max} changes with the Pd/Co ratio. When the hydrogenation reaction is catalyzed by the PVP–PdCl₂–1/2Co(OAc)₂ catalyst, the TOF_{max} can be nearly doubled compared with that of the reaction catalyzed by the corresponding monometallic catalyst PVP–

PdCl₂, moreover, 1-octene can be fully hydrogenated to octane after 150 min, and no 2-octene and 3-octene exist in the end product.

Table 2 gives the results of the hydrogenation of 2-octene by using PVP–PdCl₂ and PVP–PdCl₂–1/2Co(OAc)₂ as the catalysts. It shows that there is no obvious synergic effect when the PVP–PdCl₂–1/2Co(OAc)₂ catalyst reduced by H₂ or NaBH₄ is used since the TOF_{max} is nearly the same as that using H₂ or NaBH₄

Table 2
Hydrogenation of 2-octene catalyzed by PVP–PdCl₂ and PVP–PdCl₂–1/2Co(OAc)₂

Catalyst	Reducer	TOF _{max} (min ⁻¹)
PVP–PdCl ₂	H ₂	32
PVP–PdCl ₂	NaBH ₄	34
PVP–PdCl ₂ –1/2Co(OAc) ₂	H ₂	35
PVP–PdCl ₂ –1/2Co(OAc) ₂	NaBH ₄	30

Reaction conditions: 0.1 MPa; 40°C; Pd (Pd:Co = 1:0.5 (mole ratio)), 4×10^{-3} mmol; absolute ethanol, 10 ml; 1-octene, 4 mmol; reaction time, 60 min.

reduced PVP–PdCl₂ monometallic catalyst. Up to now, it is only an experimental finding that the PVP–PdCl₂–1/2Co(OAc)₂ bimetallic system shows a synergic effect for the hydrogenation of 1-octene, but not for 2-octene. Further experiments are in progress to explain this experimental phenomenon.

The isomerization of 1-octene with mono- and bimetallic catalysts reduced by different reducing agents under argon atmosphere were studied. Pd catalysts are usually active for the isomerization of alkene [2]. Fig. 1 shows that in C₂H₅OH solution, 1-octene can be isomerized to 2-octene and 3-octene under argon atmosphere, so the content of 1-octene in the end product decreases. The isomerization rate differs from the catalyst being used and the reducing agent. When the unreduced PVP–PdCl₂ monometallic catalyst is used, 1-octene content in the product decreases to 38% after 170 min. When PVP–PdCl₂–1/2Co(OAc)₂ bimetallic catalyst reduced by H₂ is used, 1-octene in the product decreases to 66% after 170 min, while PVP–PdCl₂–1/2Co(OAc)₂ catalyst reduced by NaBH₄ is inert for the isomerization of 1-octene,

and the content of 1-octene remains unchanged in 170 min. A possible explanation is that the valence state and the structure of the catalytic active species of the bimetallic catalyst can affect its catalytic property because the reduction abilities of H₂ and NaBH₄ are different. Pd²⁺ can be reduced to zero-valence state by H₂, while Co²⁺ cannot be reduced by H₂. However, when NaBH₄ is used as the reducing agent for the bimetallic PVP–PdCl₂–1/2Co(OAc)₂ catalyst, PVP-protected superfine particles of palladium boride–cobalt boride could be formed with higher catalytic activity than those reduced by H₂ for the isomerization of 1-octene.

The results obtained from the above experiments show that the PVP–PdCl₂–1/2Co(OAc)₂ bimetallic catalyst, obtained by adding the second transition metal component Co(OAc)₂·4H₂O to the monometallic catalyst PVP–PdCl₂ and then using NaBH₄ as the reducing agent, exhibits a remarkable synergic effect for the hydrogenation of 1-octene under mild conditions. It can increase the rate of hydrogenation of 1-octene, and simultaneously inhibit the iso-

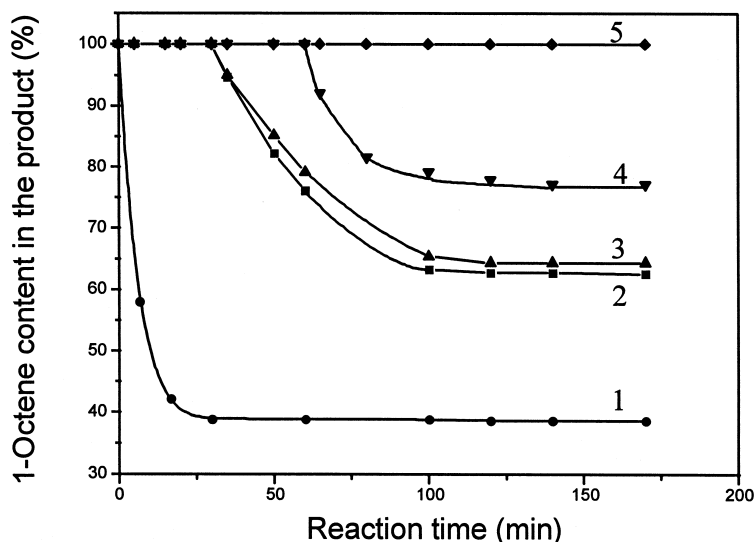


Fig. 1. Isomerization of 1-octene with mono- and bimetallic catalysts reduced by different reducing agents under argon atmosphere. Catalyst: (1) PVP–PdCl₂ not being reduced; (2) PVP–PdCl₂ reduced by H₂; (3) PVP–PdCl₂–1/2Co(OAc)₂ reduced by H₂; (4) PVP–PdCl₂ reduced by NaBH₄; (5) PVP–PdCl₂–1/2Co(OAc)₂ reduced by NaBH₄. Reaction conditions: 0.1 MPa; 40°C; Pd, 4 × 10⁻³ mmol; absolute ethanol, 10 ml; 1-octene, 4 mmol.

merization of 1-octene to 2-octene and 3-octene. It has been shown that in the selective hydrogenation of butadiene in crude 1-butene using organic membrane catalytic reactor, the PVP–PdCl₂–1/2Co(OAc)₂ catalyst reduced by NaBH₄ also inhibits the isomerization of 1-butene to 2-butene, which in turn improves the selectivity for 1-butene [19].

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