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Performance of a bimetallic Pd–In catalyst in the selective liquid-phase hydrogenation of internal and terminal alkynes

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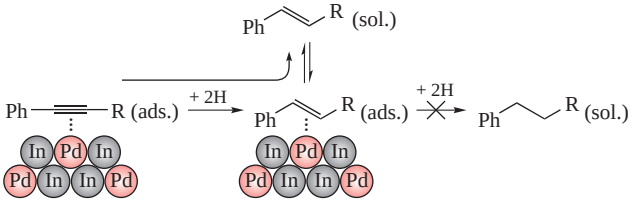
The 1% Pd–1% In/$MgAl_2O_4$ catalyst demonstrated excellent selectivity in the semi-hydrogenation of internal 1-phenylprop-1-yne, which exceeded the selectivity of a commercial Lindlar catalyst and reference monometallic 0.5% Pd/$MgAl_2O_4$ catalyst due to Pd–In alloy formation.



The selective hydrogenation of triple C≡C bonds is an important challenge for fine organic synthesis and industrial chemistry.[1–3] Pd-supported catalysts are traditionally used for the hydrogenation of alkynes providing a favourable activity, but their selectivity is insufficient, especially at high alkyne conversion (> 80–90%).[4] The modification of palladium catalysts by alloying with other metals usually improves their selectivity. The well-known bimetallic compositions for selective alkyne hydrogenation are Pd–Zn,[5,6] Pd–Ag[7,8] and Pd–Cu.[9–11] The Pd–Ga composition was intensively studied in gas-phase and liquid-phase alkyne hydrogenation due to the favorable activity/selectivity parameters.[12–14] Indium is an analogue of Ga; however, the catalytic properties of bimetallic Pd–In systems are still not investigated in detail.[15–18]

This work was focused on studying the performance of a Pd–In catalyst in the liquid-phase hydrogenation of internal (1-phenylprop-1-yne, **1a**) and terminal (phenylacetylene, **1b**) alkynes.[†] The catalyst was obtained *via* the Pd–In$(OAc)_5$ heterometallic acetate complex as a precursor of the active component.[19] Our previous studies demonstrated that this approach enables the formation of highly homogeneous bimetallic nanoparticles in a final catalyst.[6,10,11] The $MgAl_2O_4$ spinel was chosen as a support due to its mechanical strength and base properties, which are preferable for the preparation of highly selective catalysts.[20] The catalyst was characterized in detail by TPR, FTIR-CO and TEM techniques.

The reaction rates were measured by the rate of H_2 uptake at the first (conversion of triple bond to double) and the second (total hydrogenation to alkane) reaction steps. The activity of the catalysts (*A*) was estimated as the reaction rate normalized per 1 mg of the catalyst, (mmol alkyne min^{-1} mg_{Cat}^{-1}). Specific catalytic activity was evaluated by the turnover frequencies at the first (TOF_1) and the second (TOF_2) reaction steps calculated as a ratio of converted substrate molecules (alkyne or alkene, respectively) to the overall Pd atoms in the catalyst per second. In addition, the reaction kinetics was characterized by a TOF_1/TOF_2 ratio.[9] The selectivity of catalysts (*S*) was calculated as a molar ratio of the hydrogenation products ($n_{C_nH_{2n}}$ and $n_{C_nH_{2n+2}}$) in the reaction mixture determined by GC/MS analysis: $S = n_{C_nH_{2n}}/(n_{C_nH_{2n}} + n_{C_nH_{2n+2}})$.

Field emission scanning electron microscopy (FESEM, Hitachi SU8000) was used to characterize Pd and Pd–In catalysts. The images were recorded in the secondary electron mode at an accelerating voltage of 2 kV and a working distance of 5–6 mm. The morphology of the samples was studied with a correction applied to the surface effects of conduction layer sputtering.[21] It was found that the modification of monometallic Pd/$MgAl_2O_4$ with indium results in a moderate grow in the average size of metal particles from 4–4.5 to 5–5.5 nm. TEM analysis shows that the supported Pd–In nanoparticles are uniform and spherical in shape.

Pd–In alloying in Pd–In/$MgAl_2O_4$ was revealed through a comparative study of Pd/$MgAl_2O_4$ and Pd–In/$MgAl_2O_4$ by the FTIR spectroscopy[‡] of chemisorbed CO. Three typical absorption bands were observed in the spectra (Figure 1). A band at 2177 cm^{-1} corresponds to CO molecules adsorbed on low-coordinated Al^{3+} cations (Lewis acid sites). This band completely disappears after vacuum treatment, which is typical of weakly adsorbed CO. A strong band at 2096–2068 cm^{-1} is attributable to the linear form

[†] The 1% Pd–1% In/$MgAl_2O_4$ catalyst was prepared by the incipient wetness impregnation of $MgAl_2O_4$ (Sasol, Germany, 40 m^2 g^{-1}) with a Pd–In$(OAc)_5$ complex solution in dilute acetic acid (pH 2.8). After drying at room temperature, the catalyst was reduced for 1 h at 550 °C in a 5 vol% H_2/Ar mixture. Reduction temperature was determined by temperature-programmed reduction (TPR) method. A 5% Pd–PbO/$CaCO_3$ commercial Lindlar catalyst (Sigma-Aldrich) and monometallic 0.5% Pd/$MgAl_2O_4$ were used as reference samples.

Hydrogenation was carried out in a stainless-steel autoclave-type reactor at 10 atm of H_2, 25 °C in *n*-hexane (98%, Merck) as a solvent. The alkyne/Pd ratio was about 4000. The GC/MS analysis of the reaction products was performed on a Maestro-2 gas chromatograph (Interlab, Russia) equipped with an HP5-MS capillary column (5% phenyldimethylsiloxane) 30 m in length and 0.25 mm in ID with a film thickness of 0.25 μm.

[‡] FTIR spectra were recorded on a Protege460 spectrometer, Nicolet, 400–6000 cm^{-1} range, resolution of 4 cm^{-1}. The samples were alternately vacuum-treated and treated with H_2 (30 Torr) at 450 °C for 2 h for removing adsorbed gases and water from the surface, as well as to complete reduction. CO adsorption was carried out at 25 °C and an equilibrium pressure of 20 Torr followed by desorption in a vacuum at 25 and 100 °C.

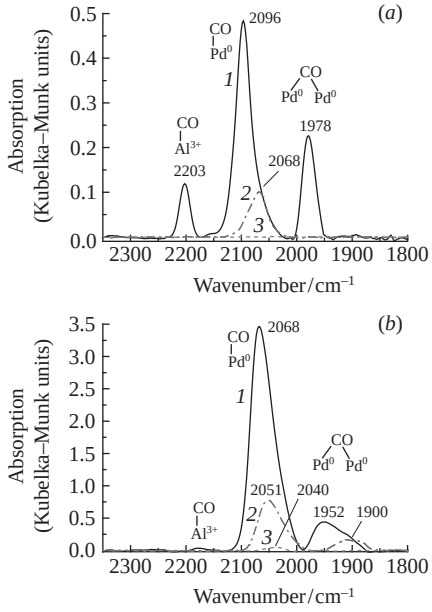


Figure 1 FTIR-CO spectra for (*a*) 0.5% Pd/Al_2O_3 and (*b*) 1% Pd–1% In/$MgAl_2O_4$ catalysts (20 Torr, 20 °C): (*1*) adsorption, (*2*) desorption at 25 °C and (*3*) desorption at 100 °C.

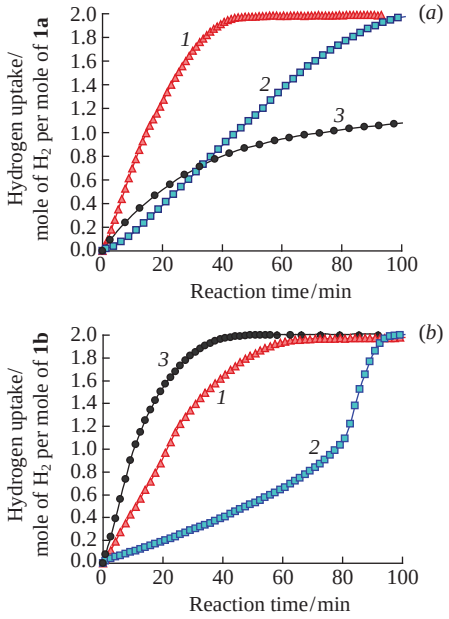


Figure 2 Hydrogen uptake *vs.* reaction time for (*1*) $Pd/MgAl_2O_4$, (*2*) Pd–In/$MgAl_2O_4$ and (*3*) Lindlar catalysts in liquid-phase hydrogenation of (*a*) **1a** and (*b*) **1b**.

of CO adsorbed on top of Pd atoms. A band within a lower frequency region (<980–1950 cm^{-1}) corresponds to the bridged forms of adsorbed CO. Note that In does not adsorb CO under our experimental conditions.[22]

Evidence for Pd–In alloy formation in Pd–In/$MgAl_2O_4$ was obtained by a comparison of the spectra of adsorbed CO on monometallic and bimetallic catalysts. For a monometallic catalyst, the bridged to linear bonded CO intensity ratio ($I_{bridged}/I_{linear}$) is 0.32, while this ratio for Pd–In/$MgAl_2O_4$ is lower (0.16) by a factor of 2. This implies that the probability of CO bonding in the bridged form is strongly diminished on the surface of Pd–In/$MgAl_2O_4$, as compared to $Pd/MgAl_2O_4$ indicating the 'dilution' of multiatomic Pd centers by In atoms. Moreover, upon CO desorption from a monometallic sample, the band of linearly adsorbed CO is shifted toward lower frequency from 2096 to 2068 cm^{-1}, which is consistent with expectations for coverage dependent CO coupling effects. On the other hand, for a bimetallic sample, the coverage dependent shift is significantly less pronounced and does not exceed ~15 cm^{-1}.

Both observations are in line with the results obtained by Meriaudeau[23] and allow us to conclude that Pd atoms on the surface of Pd–In/$MgAl_2O_4$ become separated by In atoms, and isolated Pd atoms prevail on the catalyst surface, which suppresses dipole-dipole interaction between CO molecules and reduces the probability of bridge-bonded CO adsorption.

The influence of indium on the performance of a Pd catalyst in alkyne selective hydrogenation can be disclosed by comparing the characteristics of monometallic and bimetallic Pd–In samples (Figures 2, 3 and Table 1).

A comparison of the kinetic profiles of H_2 uptake for $Pd/MgAl_2O_4$ and Pd–In/$MgAl_2O_4$ indicates that the reaction rate for hydrogenation of **1a** (Scheme 1) is apparently lower for the bimetallic sample [Figure 2(*a*)]. An analysis of kinetic parameters (Table 1) shows that modification with In decreases TOF in triple bond and double bond hydrogenation by factors of ~6 and ~4.4, respectively. As a result, TOF_1/TOF_2 decreases from 1.6 to 1.2. Despite a slightly lower TOF_1/TOF_2 ratio for Pd–In/$MgAl_2O_4$, the detailed analysis of a relationship between **1a** conversion and selectivity in alkene formation [Figure 3(*a*)] reveals significant improvement of the selectivity for Pd–In catalyst, as compared to the reference monometallic $Pd/MgAl_2O_4$ within the whole range of **1a** conversion. This result can be qualitatively rationalized in the framework of a classical model proposed by Bond[24] and adopted to the hydrogenation of substituted alkynes in a liquid phase (Scheme 1).

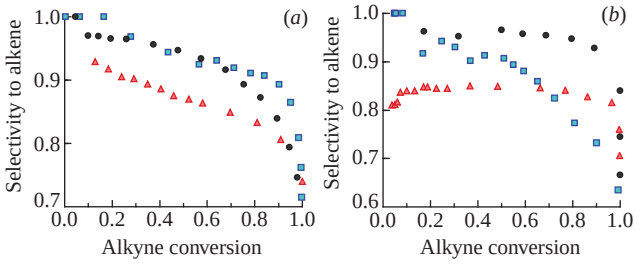
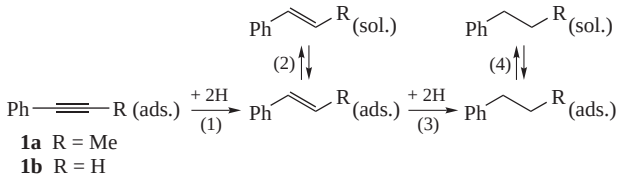


Figure 3 Selectivity to alkene *vs.* the alkyne conversion for (▲) $Pd/MgAl_2O_4$, (■) Pd–In/$MgAl_2O_4$ and (●) Lindlar catalysts in alkyne hydrogenation for (*a*) **1a** and (*b*) **1b**.

Table 1 Kinetic parameters of synthesized catalysts for liquid-phase alkyne hydrogenation (P_{H_2} = 10 bar, 25 °C).

Substrate	Catalyst	A_1/μmol of alkyne (alkene) min^{-1} mg^{-1}_{Cat}	A_2/μmol of alkyne (alkene) min^{-1} mg^{-1}_{Cat}	TOF_1/ s^{-1}	TOF_2/ s^{-1}	TOF_1/TOF_2
1-Phenyl-prop-1-yne **1a**	0.5% $Pd/MgAl_2O_4$	7.36	4.53	2.61	1.61	1.6
	1% Pd–In/$MgAl_2O_4$	2.42	2.0	0.43	0.36	1.2
	Lindlar	2.15	0.08	0.07	0.003	26.1
Phenyl-acetylene **1b**	0.5% $Pd/MgAl_2O_4$	8.27	4.70	2.93	1.67	1.8
	1% Pd–In/$MgAl_2O_4$	0.97	7.96	0.17	1.41	0.1
	Lindlar	9.06	4.35	0.32	0.15	2.1



1a R = Me
1b R = H

Scheme 1

According to this reaction scheme, selectivity in alkyne hydrogenation is governed by two possibilities: (1) a chemisorbed alkene intermediate remains on the surface long enough to be hydrogenated to alkane, or (2) the desorbed alkene can re-adsorb in competition with alkyne. These two possibilities were termed mechanistic and thermodynamic factors, respectively.[24]

In the hydrogenation of **1a**, $Pd/MgAl_2O_4$ demonstrates ~90% selectivity to alkene even at the early stage of the reaction, when **1a** conversion is low and re-adsorption of alkene at step (2) (thermodynamic factor) can be neglected (initial selectivity). This observation suggests the direct hydrogenation of a chemisorbed alkene intermediate [step (3)] over monometallic Pd (mechanistic factor), which reduces selectivity below 100% at a low **1a** conversion. For the Pd–In catalyst, the initial selectivity amounts to 100% implying the suppression of reaction (3) by In. This suggests that, on the In-modified catalyst, the rate of alkene desorption at step (2) prevails over the rate of hydrogenation of adsorbed alkene intermediate at step (3), which improves initial alkene selectivity (see Scheme 1).

As conversion of **1a** increases [Figure 3(*a*)], selectivity decreases for both $Pd/MgAl_2O_4$ and $Pd–In/MgAl_2O_4$. However, for the bimetallic Pd–In catalyst, the observed decline in alkene selectivity is evidently more gradual than that for the monometallic sample, which is particularly evident at high **1a** conversions. Since a thermodynamic factor prevails over a mechanistic one at high alkyne conversions, this allows us to hypothesize that the introduction of In affects alkyne and alkene adsorption energies favoring high surface coverage by alkyne even at a high alkene conversion. It should be mentioned that the $Pd–In/MgAl_2O_4$ catalyst demonstrates evidently higher selectivity, as compared to that of the commercial Lindlar catalyst, and better utilization of Pd as evidenced by higher TOF values (Table 1). This fact is in a good agreement with literature data indicating that the presence of Pb in the Lindlar catalyst structure substantially decreases the catalytic activity though improves the target selectivity.[25–27]

In the case of hydrogenation of **1b**, a negative effect of In on the reaction rate at step (1) is even more evident than in **1a** hydrogenation (see Figure 2). TOF_1 over bimetallic catalyst is lowered by a factor of 17, as compared to monometallic $Pd/MgAl_2O_4$ (0.17 *vs.* 2.93, respectively). However, at step (2), TOF_2 remains essentially identical for bimetallic and monometallic catalysts (1.47 and 1.67, respectively), which is in contrast to **1a** hydrogenation. As a result, the kinetic profile of hydrogen uptake for $Pd–In/MgAl_2O_4$ exhibits pronounced upward bending after the consumption of 1 equiv. of hydrogen, and the TOF_1/TOF_2 ratio decreases from 1.8 for monometallic to 0.1 for bimetallic catalyst (Table 1).

A comparison between the alkene selectivity–alkyne conversion plots for monometallic and bimetallic catalysts reveals significant improvement of alkene selectivity at a low alkyne conversion for $Pd–In/MgAl_2O_4$ [Figure 3(*b*)]. The increase in selectivity is analogous to that observed in 1-phenylprop-1-yne hydrogenation [*cf.* Figures 3(*a*) and 3(*b*)] and attributable to the suppression of the direct hydrogenation of a chemisorbed alkene intermediate over the In-modified catalyst. However, as **1b** conversion increases, alkyne selectivity over Pd–In catalyst declines steeply implying that, unlike internal **1a** hydrogenation, in hydrogenation of terminal **1b**, alkene effectively competes with alkyne for surface adsorption sites.

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