

NOTES

Structure Sensitivity of Acetylene–Ethylene Hydrogenation over Pd Catalysts

Pd-Based catalysts are used for the selective hydrogenation of alkynes and alkadienes to the corresponding alkenes on a large scale. Addition of Pb and Zn (Lindlar type catalysts) to Pd (1–4), and alloying of Pd with Ag (5), Cu (6), Pb (7) improve the selectivity of alkyne hydrogenation. The presence of organic bases, organic sulfides, or CO in the reaction mixture (3) is known to inhibit hydrogenation of the alkene formed. Although structure sensitivity in alkene hydrogenation has been systematically investigated, only a few studies have been devoted to the effect of metal dispersion on the selectivity of hydrogenation of an alkyne–alkene mixture. In the hydrogenation of mixtures of *cis*-di-*t*-butylacetylene with cyclopentene or with *cis*-di-*t*-butylethylene (8, 9) the competitive reactivity of di-*t*-butylacetylene is increased with catalyst dispersion. By increasing the dispersion of the supported metal catalyst the preference of the *cis* isomer formation (10) from 3-hexyne was enhanced. In liquid phase the rate of 1-butyne hydrogenation and the selectivity of the reaction toward 1-butene formation were observed to decrease with the dispersion of the Pd/Al₂O₃ catalysts employed (11).

The work described in this article aimed to investigate the effect of Pd dispersion on the competitive hydrogenation of a mixture containing 0.3% C₂H₂, 0.5% H₂ balanced by C₂H₄ over Pd/alumina as catalyst. In particular, attempts have been made to clarify the extent of ethane formation produced directly from acetylene (intrinsic selectivity of the ethane formation) and that from ethylene in the presence of acetylene with the

use of [¹⁴C]C₂H₂. Isotopic labeling techniques have unambiguously demonstrated that ethane is generally formed from both acetylene and ethylene (12–19).

Details of the catalyst preparation for samples denoted by A, D, E, and H and listed in Table 1 have already been published (19). Catalyst B was prepared by impregnation of γ -Al₂O₃ (24 m² g⁻¹) with PdCl₂ solution, calcined in air at 573 K and reduced at 473 K in a stream of H₂. Catalysts C and F were prepared by impregnation and by ion exchange using Pd(NH₃)₄Cl₂, respectively. All samples except A and B, were reduced with N₂H₄ at ambient temperature. The samples were then oxidized at 393 K overnight and reduced *in situ* by the incoming reaction mixture. Samples A and B were reduced in a stream of H₂ and treated in He at 373 K prior to the catalytic runs.

Dispersion of the Pd/Al₂O₃ samples was determined by olefin titration (20), by O₂ chemisorption measurements at room temperature and at 673 K (21), and by CO chemisorption. The data are presented in Table 1.

The product selectivity and the rate of acetylene transformation have been measured after 0.5 h on stream in a gradientless flow reactor at atmospheric pressure. (In the reactor the rate of back-mixing was ca. 15–20 liters min⁻¹.) The overall selectivity of ethane formation (produced from both C₂H₂ and C₂H₄), $S_{C_2H_6}$, was calculated from the GLC analysis in conformity with previous papers. The intrinsic selectivity of ethane formation, i.e., the amount of C₂H₆ that is produced directly from acetylene,

TABLE 1
Characterization of Pd Catalysts

Catalysts	Dispersion (%)		
	D_I	D_{II}	D_{III}
A Pd-black	2.2 ^a	—	—
B 8.7 wt% Pd/Al ₂ O ₃	—	7.2	5.5
C 1.2 wt% Pd/Al ₂ O ₃	—	26.5	—
D 0.4 wt% Pd/Al ₂ O ₃	53	37.5	—
E 0.017 wt% Pd/Al ₂ O ₃	46	—	54.1
F 0.07 wt% Pd/Al ₂ O ₃	—	57.2	65.8

Note. D_I , from ethylene titration I; D_{II} , from O₂ chemisorption; D_{III} , CO chemisorption assuming Pd/CO = 1.2.

^a Inferred from BET measurements.

$S_{C_2H_6}^I$, was inferred from the radioactivity of the products. The radioactivity of C₂H₆ reflects essentially the intrinsic route of ethane formation from [¹⁴C]C₂H₂ because as soon as the intermediate [¹⁴C]C₂H₄ is desorbed from the surface it is immediately diluted by the large excess of C₂H₄ in the gas phase (the relative specific activity of C₂H₄, $\rho_{C_2H_4}/\rho_{C_2H_2}^0$, should be less than 0.3/99.2). The hydrogenation of gas-phase C₂H₄ does not, therefore, contribute significantly to the radioactivity of C₂H₆ as long as the conversion for C₂H₄ remains low. With tail-end mixtures this requirement is ensured.

The rate and selectivity data at comparable 60–70% conversions are summarized in Table 2. The turnover number (TON) of acetylene hydrogenation at 298 K was observed to be in the range of 5.89×10^{-3} – $2.62 \times 10^{-2} \text{ s}^{-1}$. The TON has slightly increased with dispersion which might indicate that on small crystallites acetylene chemisorbs in a less crowded manner, i.e., the probability of the hydrogen chemisorption at gaps in the adsorbed layer of hydrocarbon might increase, as others have suggested. The site blocking effect of acetylene or surface oligomers at the very beginning of the reaction with the large Pd crystallites might also give some explanation for the low value of TON with samples A and B.

The crystallite size as shown by the data in Table 2 affects the selectivity of the direct route of ethane formation; as the dispersion increases from about 2 to 60% the value of $S_{C_2H_6}^I$ decreases by a factor of 3–4. In considering the reasons for this change of $S_{C_2H_6}^I$ one might suggest the following explanations: (i) decrease of Pd-hydride formation with increasing dispersion, or (ii) the mode of C₂H₂ chemisorption is influenced by the size of the crystallites.

The detrimental effect of the β -hydride phase on the selectivity of acetylene hydrogenation has already been demonstrated by Palczewska *et al.* (22, 23) who observed a direct correlation between the β -hydride phase and the selectivity for ethane formation. At high dispersion the formation of a hydride phase is eliminated to a large extent (24, 25) and the presence of acetylene and ethylene (26), owing to the reduction of the virtual pressure of H₂ at the surface of Pd, inhibits its formation as well.

The observed change of the intrinsic selectivity with dispersion might also be interpreted by the assumption that the dispersion affects the mode of C₂H₂ chemisorption. On low index faces of Pd (poorly dispersed samples) acetylene might interact with several adjacent Pd atoms. Delocalised chemisorption might lead to a longer residence time on the surface and therefore the adsorption in the hollows on the (111) or (100) faces might facilitate the rupture of the C–H bond (27). As has been

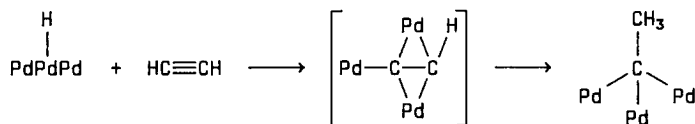
TABLE 2
Rate and Selectivity Data at 300 K

Catalyst	TON (s ⁻¹)	Ethane selectivity ^a (%)		
		$S_{C_2H_6}^I$	$S_{C_2H_6}$	$S_{C_2H_6}-S_{C_2H_6}^I$
A	5.89×10^{-3}	10.9	53.1	42.2
B	8.36×10^{-3}	17.5	67.2	49.7
C	1.05×10^{-2}	—	34.5	—
D	9.4×10^{-3} – 1.2×10^{-2}	8.2	21.0	12.8
E	4.48×10^{-2}	4.9	18.2	13.3
F	2.62×10^{-2}	3.8	15.3	11.5

^a Ethane formed \times 100/acetylene consumed.

pointed out (17, 27), reactive adsorption of acetylene with adsorbed hydrogen originating from the dissociative adsorption of acet-

ylene results in the formation of alkylidene species whose hydrogenation yields ethane exclusively.



With increasing dispersion a second type of adsorption might become manifest; the delocalized Pd-C bond becomes localized as the coordinative unsaturation of surface sites increases. These structures might resemble those of dinuclear and mononuclear organometallic alkyne complexes (28, 29). Owing to steric reasons the C-H bond might not be readily accessible on edges and corners, and this is indicated by the *cis* preference in the hydrogenation of 3-hexyne.

As shown by the last two columns in Table 2, the larger part of the ethane stems from the hydrogenation of ethylene. Hydrogenation of ethylene on the support (18) might not be a controlling factor. This phenomenon was observed to be operative on aging (19) and the hydrogenation is likely to be assisted by the surface polymer formed (13-15, 19, 30). The experiments with Pd black (16, 17) have demonstrated that surface sites on which ethylene hydrogenation occurs can be eliminated in the presence of large partial pressure of acetylene. This observation as well as the previous studies (12-15) confirm that the strength of complexing of acetylene will decide whether or not ethylene is hydrogenated in the presence of acetylene. The selectivity of ethane formation from ethylene was observed to decrease with dispersion. In principle the strength of complexing of acetylene should increase with decreasing dispersion because on face and edge sites alkynes might complex in a bridge-bonded fashion whereas alkene cannot coordinate in this way. Apparently, owing to the dissociative adsorption of acetylene and formation of alkylidene species the effective acetylene

coverage which inhibits adsorption of ethylene is lower on poorly dispersed samples than on highly dispersed ones.

In conclusion, the results presented in Table 2 show that in the hydrogenation of a typical industrial mixture some limited structure sensitivity can be observed. At low dispersion the ease of the dissociative chemisorption of acetylene and the presence of a hydride phase may account for the alkane formation. At medium dispersion the mechanism of acetylene chemisorption and the more effective complexing of C_2H_2 may be responsible for the selective formation of ethylene.

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