Heterogeneously catalysed Cyclotrimerisation of Ethyne to Benzene over Supported Palladium Catalysts

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The cyclotrimerisation of ethyne to benzene over supported Pd particles under conditions of catalytic turnover is described; the results are in excellent accord with data from single crystal studies.

The low temperature conversion of ethyne to benzene was first demonstrated as a surface reaction under ultra high vacuum conditions on single crystal Pd(111) almost simultaneously by Tysoe *et al.*[1] and by Sesselmann *et al.*[2] Molecular beam studies indicate that the reaction proceeds *via* a C_4 intermediate[3] and the synthesis of furan following ethyne chemisorption on oxygen-precovered Pd(111) reveals the stoichiometry of this intermediate to be C_4H_4.[4] Here we describe the conversion of ethyne to benzene over high-area supported Pd particles, under conditions of true catalytic turnover, a process which has not been previously demonstrated. The concurrent formation of buta-1,3-diene (butadiene) and butene provides strong evidence that a C_4H_4 intermediate is also involved under these conditions. The reaction also appears to be structure sensitive in agreement with predictions from single crystal measurements.[5,6] These three observations demonstrate that in this case there is a direct correspondence between single crystal data obtained under idealised conditions of low pressure and the behaviour of practical catalysts operated at pressures some 10^{12} times higher.

Catalysts containing between 2 and 5% w/w Pd supported on Aerosil silica (Degussa) or titania (Degussa) were prepared by impregnation with $PdCl_2$. Catalysts containing 10% w/w Pd supported on alumina and charcoal were obtained from Baker Platinum Division and Maybridge Chemical Company, respectively. The samples were loaded into a quartz tube microreactor and pretreated in flowing oxygen at 473 K, before being reduced in hydrogen at either 473 K or 773 K, followed by purging with helium at 773 K. The effluent flow was analysed with a multiplexed quadrupole mass spectrometer and palladium surface areas were determined by CO chemisorption followed by temperature programmed desorption. Research grade ethyne (Cambrian) was further purified by passing through a cold trap after which no impurities (and especially no benzene) could be detected by mass spectrometry.

On switching the gas feed from helium to ethyne, above 480 K, a high level of benzene synthesis was immediately observed, which fell off with time to a considerably lower steady-state level. Below 480 K no benzene was detected. This behaviour was observed with all the samples employed, including those supported on charcoal and TiO_2, and a typical reaction profile for a Pd/Al_2O_3 sample is shown in Fig. 1*A*. In addition to benzene, butadiene and butene were also detected as products. Both exhibited the same time profile as benzene (Fig. 1*A*), but the signals at m/z 54 and 56 can be assigned with certainty to butadiene and butene on the basis of known fragmentation patterns. No C_3 or C_5 products were detected. The fall from the initial high rate of benzene production to its steady-state level correlated with a rise in the amount of unreacted ethyne to its maximum level (Fig. 1*A*). In addition to benzene and the C_4 products, ethene was also detected. However, in contrast to the formation of benzene, ethene production was observed at significantly lower reaction temperatures. Fig. 1*B* shows the time evolution of the ethene yield for a Pd/SiO_2 sample maintained at 390 K, on switching the gas feed to ethyne. Initially no ethyne was detectable whilst a considerable amount of ethene was formed; the onset of ethyne detection correlated with the maximal rate of ethene formation and the decrease in the level of ethene production mirrored the increase in the amount of unreacted ethyne.

CO chemisorption measurements carried out by both frontal chromatography and temperature programmed desorption (TPD) methods indicated that CO adsorption was completely inhibited once the activity towards ethene and benzene synthesis had reached a steady-state level. This contrasts with the amount of chemisorption which occurred on the freshly reduced catalyst (Fig. 2*A*). Both the CO chemisorption capacity and the very high transient degree of benzene formation could be restored by flowing O_2 over the sample at 670 K for 3 h, followed by reduction in H_2 at 770 K. When a sample that had been exposed to ethyne for several hours at 540 K was heated in a flow of O_2 to 670 K, CO_2

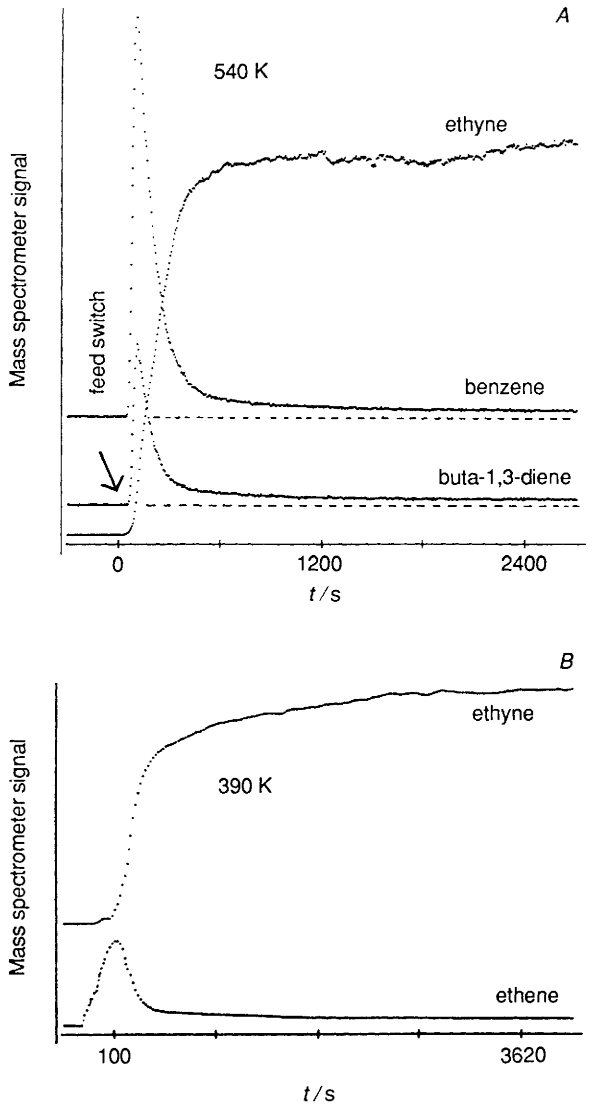

Fig. 1 *A*: Time variation in benzene, buta-1,3-diene and ethyne production on switching gas feed from He to ethyne at 540 K; Pd/Al_2O_3 catalyst. *B*: Variation in ethene and ethyne production on switching gas feed from He to ethyne at 390 K; Pd/SiO_2 catalyst

formation commenced at ≈480 K, with almost complete conversion of O_2 to CO_2 occurring at 670 K (Fig. 2*B*). After O_2 treatment for 3 h at 670 K, essentially no CO_2 was detected.

Taken together, these observations strongly suggest that the high initial level of benzene synthesis can be attributed to efficient cyclotrimerisation of ethyne on the clean Pd surface. They also indicate that the reduction in this activity corresponds to a gradual loss of exposed Pd metal area, due to carbon deposition on the surface as a result of ethyne dehydrogenation, a process which is also responsible for the initially high level of ethene formation. Thus the much smaller level of steady-state conversion of ethyne to benzene actually occurs on a extensively carbided Pd surface. Furthermore, the synthesis of the C_4 species, butadiene and butene, and the absence of any C_3 or C_5 products is a strong indication that the cyclisation of ethyne proceeds through a C_4 intermediate. This conclusion is in excellent accord with the results of electron spectroscopic studies on model systems under conditions of ultra high vacuum.[3,4,7] Such work has established the key role of a cyclic C_4 intermediate, but the present results provide the first evidence that such a species is indeed present at the surface of a practical working catalyst.

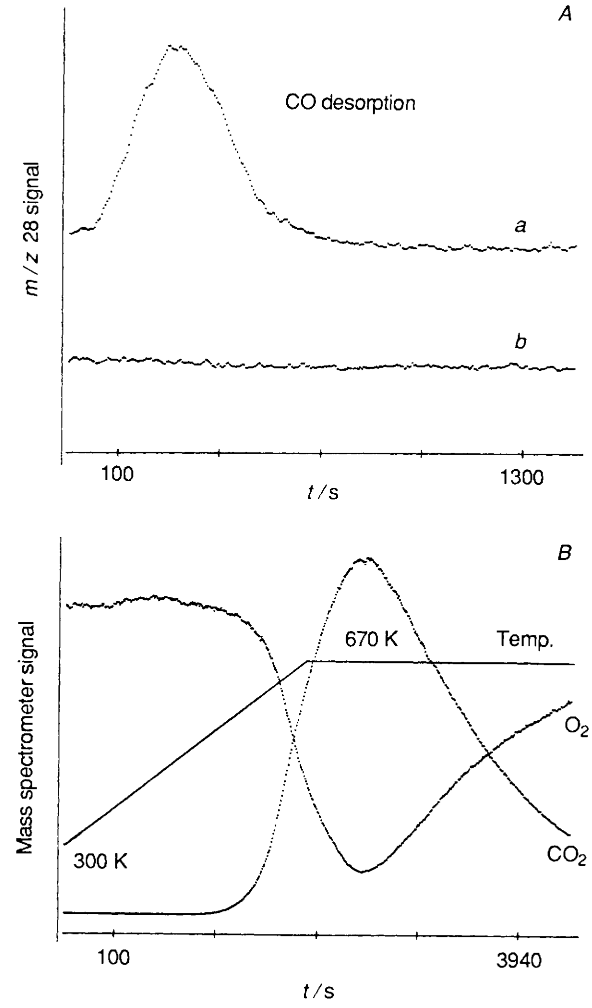

Fig. 2 *A*: CO thermal desorption spectra in the interval 200–500 K (temperature ramp continued to 720 K). Heating rate 12 K/min; Pd/SiO_2 catalyst. *a*: Freshly reduced catalyst; *b*: after exposure to ethyne at 540 K. *B*: Temperature programmed oxidation of Pd/Al_2O_3 catalyst after exposure to ethyne at 540 K. Temperature ramp 300–670 K at 10 K/min then maintained at 670 K for 1 h under oxygen flow

In the present case, measurements made with different Pd loadings suggest that the cyclotrimerisation of ethyne is structure sensitive, *i.e.* reaction rate depends on details of the metal surface geometry. Higher metal loadings (larger particle sizes, lower metal areas) resulting in a higher steady-state level of benzene formation. This is the opposite of what would be expected on a naive basis, but is in excellent agreement with single crystal measurements[5,6] which show that the cyclisation reaction occurs preferentially on the (111) plane of Pd; such planes will predominate on large metal particles but not on small ones. Finally, when a small amount of H_2 was introduced with the ethyne feed, an *increase* in the steady state turnover to benzene was observed; eventually a C_2H_2/H_2 ratio was reached at which the activity was decreased, *i.e.* there exists an optimum C_2H_2/H_2 composition at which selectivity towards cyclisation to benzene is maximal. As expected, the hydrogenation of ethyne to ethene increases markedly with increasing H_2 content.

In summary, it has been demonstrated that ethyne to benzene conversion over Pd can be operated as a genuine catalytic process. Furthermore, we conclude that there is a useful and detailed correspondence between, on the one hand, structure and reactivity data obtained with model systems,[7] and, on the other hand, the behaviour of a practical catalyst under working conditions.

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