Journal of Catalysis **182,** 456–462 (1999)
Article ID jcat.1998.2344, available online at http://www.idealibrary.com on IDEAL®

Pumice-Supported Cu–Pd Catalysts: Influence of Copper on the Activity and Selectivity of Palladium in the Hydrogenation of Phenylacetylene and But-1-ene

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Received July 30, 1998; revised October 20, 1998; accepted November 4, 1998

Pumice-supported copper–palladium catalysts prepared from organometallic precursor have been tested in the hydrogenation of phenylacetylene and in the hydrogenation/isomerization of the but-1-ene. The structure and catalytic behaviour of the bimetallic catalysts depended on the different temperatures of reduction. The presence of CuO or Cu metal in an alloyed state with Pd influenced the two reactions. The system containing CuO is the most active and selective towards the formation of the monoalkene in the hydrogenation of the highly unsaturated hydrocarbon. The system containing Cu partially alloyed with Pd is more active and selective towards the isomerization of the but-1-ene. The performance in the two reactions is discussed in terms of the electronic effect prevailing when CuO is present and in terms of the geometric ensemble size variation prevailing with the Cu–Pd system. © 1999 Academic Press

Key Words: **selective hydrogenation of alkyne derivatives; Pd–Cu/pumice catalysts; structure/activity relationship.**

1. INTRODUCTION

In the hydrogenation of highly unsaturated hydrocarbons, high selectivity to alkenes is required for making linear polyolefines (1, 2). Palladium is one of the most frequently used metals in such processes since it has the unique ability to selectively hydrogenate alkynes and alkadienes to olefines (3, 4). However, upon ageing, a buildup of carbonaceous material on the support is responsible for the decreased selectivity of alkynes to alkene (5–7). Among the factors controlling the activity and selectivity, formation of the β-hydride phase occurring preferentially on large particles is considered to enhance the activity and decrease the selectivity to the alkene (8). Controversies exist regarding the size effect of palladium particles in catalytic hydrogenation. In different studies on the hydrogenation of but-1-yne opposite results were found: the amount of but-1-ene produced without further hydrogenation was found to be either higher (9) or lower (10) on highly dispersed particles. A study on the hydrogenation of acetylene on alumina-supported Pd catalysts under industrial conditions with high H_2/C_2H_2 ratio has detected a decrease of specific activity and an increase in the selectivity to ethylene with increasing metal dispersion (11). In a recent study on the same reaction under the same conditions, but using pumice-supported Pd catalyst, a decrease in activity and a constant selectivity upon varying the dispersion have been found (12).

Addition of a small amount of a second metal is a way to increase the selectivity of the system to alkenes (13). The consequent changes in activity and selectivity are explained in terms of different ensemble requirements for parallel/consecutive reaction paths and also in terms of the so-called ligand effect (14). The "ensemble size effect" refers to the number of surface atoms which are needed for the activation of the organic substrate. The ligand effect generally refers to the electronic influence exercised by the neighbours of "ligands" of a particular surface atoms. The Cu–Pd system is an interesting combination from a physical standpoint since the two metals have similar surface free energies and they form a continuous series of face-centred-cubic substitutional solid solutions up to a Cu content of about 40 at% (15). Supported Cu–Pd catalysts have been widely investigated in the hydrogenation of different substrates (5, 16–18). It has been found that copper addition to Pd catalysts markedly improves the catalytic selectivity for partial hydrogenation of alkadienes and also alkynes while decreasing the activity (5, 16). Detailed structural studies have also found a variety of surface and bulk structures of the bimetallic catalysts as a function of the preparation procedure and also of the type of interaction with the support (19, 20).

Recent investigations on palladium catalysts supported on pumice have shown a beneficial effect of this type of support in the selective hydrogenation of 1,3-cyclooctadiene (21) and phenylacetylene (22). An enhanced activity and selectivity of the pumice-supported palladium was observed, even at metal dispersion above 30% when usually,

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0021-9517/99 $30.00

with other Pd catalysts, a decrease of activity occurs. Moreover, this type of catalyst did not show any ageing phenomena during the hydrogenation of acetylene in ethylene feedstocks (12). The peculiar behaviour of the pumice-supported catalysts was attributed to an increased electron density on the metal (23, 24). A charge donation from the support to the palladium was ascribed to the presence of the alkali ions into the structure of the pumice, as indicated by X-ray photoelectron spectroscopy (XPS, 25). Since the electron enrichment of the metal is larger on smaller particles, the decrease in activity of the pumice-supported catalysts, which occurs at metal dispersion above 30%, is attributed to an insufficient activation of the electron rich substrate instead of being assigned to an increased strength of the bond between the substrate and the metal as indeed claimed for other supported Pd catalysts (26).

On the basis of the above considerations new pumice-supported Cu–Pd catalysts were prepared with the aim of taking advantage of the combination of the properties of the support with those of a bimetallic system (27). The characterisation study, described previously, has shown through XPS and X-ray diffraction (XRD) techniques that the preparation methods involving different reduction temperatures produced significant changes in the surface and structure of the systems (27). These catalysts have been tested in the selective liquid phase hydrogenation of phenylacetylene considered a "structure insensitive" reaction (22) and in the gas phase isomerization–hydrogenation of but-1-ene, where the relative extent of the two processes is "structure sensitive" (28). The comparison with the catalytic behaviour of corresponding monometallic Pd catalysts and the relationship between activity/selectivity and structural properties are described in the present study.

2. EXPERIMENTAL

2.1. *Catalyst Preparation*

The pumice (5 m^2/g) supported catalysts were prepared from organometallic precursors. The adopted procedure is aimed at reaching a higher copper dispersion (29). The monometallic palladium catalysts were prepared from pentane solution of $Pd(C_3H_5)_2$ according to a previous method (30); then they were subsequently reduced in a stream of H_2 between 258 and 298 K. Then the obtained Pd catalysts were contacted with the green-brown solution of (E)-2-ethyl-1-hexenyl-copper (I) (31) of known concentration in $(C_2H_5)O$ under nitrogen at a temperature of 258 K under stirring for 3 h. The anchored copper was reduced under hydrogen between 258 K and room temperature (27). The chemical composition of the catalysts was determined by atomic absorption spectroscopy. Henceforth, the figures preceding the metal in the notation of the catalysts indicate the corresponding weight percentage.

2.2. *Structural Analyses*

The XRD measurements performed with a Philips X-ray diffractometer using Nickel-filtered Cu$K\alpha$ radiation allowed us to obtain the crystallite sizes as well as the lattice parameters of the metal phase (27). X-ray photoelectron spectroscopy measurements performed with a Kratos ES 300 ESCA instrument working in fixed analyser transmission (FAT) mode at pass energy of 40 eV gave information on the chemical state of the Cu–Pd system and also on segregation processes. The spectra were generated by Al$K\alpha$ X rays ($h\nu = 1486.6$ eV, 150 W). Details on the experimental setup and on the analyses of the data have been described (27).

2.3. *Catalytic Reactions*

Hydrogenation of phenylacetylene was performed in a mechanically stirred tank reactor as reported previously (22). The reactor was connected to an inert gas-vacuum line and to a H_2 line. A constant atmospheric hydrogen pressure was used during the reaction. A side arm closed by a silicon septum allowed the injection of reagents and withdrawal of samples for GC analyses. Constant temperature (298 ± 0.1 K) was ensured by a thermostat. The absence of any influence of diffusion effects under operating conditions was adequately checked (22). The initial reagent concentration of the phenylacetylene in THF was always 2.5×10^{-1} M, and the amount of catalyst was always set so that the initial ratio between the reagent moles and the total Pd atoms would be equal to 1000. The reaction was started without preconditioning and also with $\frac{1}{2}$ h preconditioning of the system THF—catalyst with hydrogen and/or phenylacetylene. With all the bimetallic catalysts an induction period of about 10 min was observed without preconditioning and with phenylacetylene preconditioning. On the contrary after the H_2 preconditioning no induction period was detected. Kinetic analyses were performed with a Dani 3800 HRPTV GC equipped with a Supelco capillary column SPB1701 and with a DANI68/10 FID detector. This system was linked to a Shimadzu C-R1B Chromatopac integrator.

The catalytic hydrogenation–isomerization of but-1-ene was performed in an all glass made grease and mercury free batch circulation reactor at 298 K using 20 Torr (1 Torr = 133.3 Nm^{-2}) of H_2 and 10 Torr of but-1-ene. The analysis was performed by a gas chromatograph Varian Aerograph series 1400 equipped with a Porapac-Q column which was operated at 313 K. The absence of any influence of diffusion effects under operating conditions was adequately checked. Prior to each catalytic test the catalysts were reduced in situ under hydrogen flow for 1 h at the desired temperature (298 or 623 K).

3. RESULTS AND DISCUSSION

In Table 1 the atomic ratios Cu/Pd from chemical analysis (CA) and XPS measurements, the Pd and Cu particle

TABLE 1

Cu/Pd Atomic Ratios from Chemical Analysis (CA) and XPS Analysis, Particle Sizes, *d*, Lattice Parameters, *a*, as Determined by XRD and Estimated Alloy Composition (27)

Catalyst		Cu/Pd_{CA}	Cu/Pd_{XPS}	d_{Pd} (Å)	a_{Pd} (±0.005 Å)	Alloy composition (Cu content at%)
1.5Pd	(298 K)			110	3.899	
	(623 K)			200	3.885	
0.6Pd	(298 K)			63	3.883	
	(623 K)			200	3.881	
0.025Cu–1.5Pd	(298 K)	0.03	nd[a]	80	3.901	
	(623 K)			316	3.886	
0.05Cu–1.5Pd	(298 K)	0.05	0.2	78	3.901	
	(623 K)		0.1	214	3.871	6
0.025Cu–0.6Pd	(298 K)	0.07	nd[a]	83	3.895	
	(623 K)			185	3.876	6
0.05Cu–0.6Pd	(298 K)	0.14	0.3	76	3.883	
	(623 K)		0.2	200	3.866	10

Note. Bulk values: $a_{Pd} = 3.890$ Å; $a_{Cu} = 3.615$ Å.

[a] Not determined due to the poor quality of the Cu 2*p* signal.

sizes, and the lattice parameters for the monometallic and bimetallic Cu–Pd catalysts are listed (27). Values relative to the samples reduced at 298 and 623 K are reported. The metal dispersion in the catalysts obtained from the particle dimensions range between 3 and 18%. Some H_2 adsorption experiment were also performed; however; the low concentration of the metals did not yield reliable results. As already mentioned, the addition of copper does not produce significant change in the Pd crystallite sizes, contrary to what is observed on silica-supported catalysts (18). All the bimetallic catalysts reduced at 298 K have a lattice parameter typical of the palladium metal lattice. After reduction at higher temperature the parameters changed significantly with increasing copper content, and copper particles were also visible in the X-ray pattern, although the quality of the Cu (111) reflection signal did not allow the attainment of the corresponding lattice parameter. It is worth noting that the surface atomic ratio of the bimetallic catalysts, as derived from the XPS measurements, are larger than the overall values determined by chemical analysis. Moreover, the increased reduction temperature decreases the Cu/Pd atomic surface ratio which has already been explained with an inward diffusion of copper concomitant with the formation of alloy (27). The last column of Table 1 reports the estimated alloy compositions obtained from the variation of the lattice parameter computed from the Pd-related diffraction peaks, following the results of Burch and Buss (32).

The XPS binding energies of the Pd $3d_{5/2}$ and Cu $2p_{3/2}$ of selected bimetallic and monometallic samples are presented in Table 2. As already reported (27), the samples reduced at 298 K contain most of the copper in the form of CuO with only a small amount of metallic Cu. H_2 treatment at 623 K achieves the complete reduction of copper. As far as Pd is concerned, it is in a metallic state; however, it is interesting to notice that in the samples containing CuO, the Pd $3d_{5/2}$ binding energy does not reflect the interaction with the support (24, 25), and the proper value for the Pd catalysts supported on pumice was found only after H_2 treatment at 623 K. No chemical shifts are observed between the monometallic and bimetallic catalysts.

3.1. *Hydrogenation of Phenylacetylene*

During the activity measurements performed in excess of hydrogen, the concentration of the styrene produced changed linearly with time. The rate calculated was constant and denoted by *k*. The turnover frequencies (TOF) calculated from such a rate constant normalised by the number of

TABLE 2

Pd $3d_{5/2}$ and Cu $2p_{3/2}$ Binding Energies after Different Thermal Treatments

Catalyst	Treatment	Pd $3d_{5/2}$ (eV)	Cu $2p_{3/2}$ (eV)
0.05Cu–1.5Pd	H_2 (298 K)	335.7	931.7, 933.9
	H_2 (623 K)	334.8	931.9
0.05Cu–0.6Pd	H_2 (298 K)	335.7	931.7, 933.4
	H_2 (623 K)	334.8	931.7
1.5Pd	H_2 (298 K)	334.8	
	H_2 (623 K)	334.8	
0.5Cu	H_2 (298 K)		933.8, 932.4
	H_2 (623 K)		932.4

TABLE 3

Rate (k), Turnover Frequency (TOF), and Selectivity to Styrene (S_{sty}) Calculated at Total Conversion of 95%

Catalyst (298 K)	k ($mol_{styrene}\ s^{-1}\ g_{Pd}^{-1}$)	TOF (s^{-1})	S_{sty} (%)
0.6Pd	1.01×10^{-2}	6.0	80
0.025Cu–0.6Pd	8.93×10^{-3}	7.3	89
0.05Cu–0.6Pd	6.20×10^{-3}	4.7	88
1.5Pd	1.22×10^{-2}	7.7	81
0.025Cu–1.5Pd	9.87×10^{-3}	7.5	89
0.05Cu–1.5Pd	9.60×10^{-3}	7.3	90

TABLE 4

Rate (k), Turnover Frequency (TOF), and Selectivity to Styrene (S_{sty}) Calculated at Total Conversion of 95%

Catalyst (623 K)	k ($mol_{styrene}\ s^{-1}\ g_{Pd}^{-1}$)	TOF (s^{-1})	S_{sty} (%)
0.6Pd	3.57×10^{-3}	6.4	81
0.025Cu–0.6Pd	2.63×10^{-3}	4.7	92
0.05Cu–0.6Pd	3.76×10^{-4}	0.7	83
1.5Pd	4.32×10^{-3}	7.7	80
0.025–Cu1.5Pd	1.88×10^{-3}	5.0	89
0.05Cu–1.5Pd	1.50×10^{-3}	3.2	85

palladium sites and the selectivity to styrene, calculated as ratio of styrene concentration over styrene + ethylbenzene concentration at a total conversion of 95%, are reported in Table 3 for the catalyst reduced at 298 K.

Analogous data are reported in Table 4 for the series of catalysts reduced at 623 K. Since the calculation of the palladium sites was based on the dispersion obtained from the X-ray diffraction data, the derived TOF values may not take into account the real number of the active surface sites specially in bimetallic systems. For this reason both quantities, k and TOF, are considered. In Figs. 1 and 2 the selectivity to styrene versus the conversion percentage are plotted for the samples reduced at 298 K. As appears from Tables 3 and 4, it is remarkable to note that the presence of copper as CuO does not modify the catalytic activity, except for the 0.05Cu–0.6Pd sample for which a decrease is observed, whereas the selectivity towards styrene increases. Once the copper is totally reduced at 623 K, the rate and the turnover frequencies of the bimetallic decrease with increasing copper content while the selectivity trend remains essentially the same as observed for the samples reduced at 298 K. Previous catalytic study of the same reaction on pumice-supported palladium catalysts (22) detected formation of polymeric species at the initial stage of the reaction, producing a flattening effect on the catalytic activities and therefore making the reaction “structure insensitive” (17). As illustrated in Table 1, the XPS Pd 3d binding energy shifts of the bimetallic Cu–Pd catalysts reduced at 298 K with respect to the monometallic catalyst indicate that CuO decreases the electron density of palladium. However, according to the previous finding on the“structure insensitivity” of the considered reaction, the variation of the electron density of the palladium does not affect the hydrogenation of the alkyne (22). Consequently, the invariance in the rate as well as in the TOF observed in the presence of CuO suggests that the number of the active sites is not modified by CuO that is, therefore, located on the support rather than the palladium particles. The increase of the styrene selectivity at very large phenylacetylene conversion may indeed be due to a structure sensitivity of the subsequent hydrogenation of styrene to ethylbenzene, inhibited by more electron deficient palladium particles (21–25). After the H_2 treatment of the same bimetallic catalysts at 623 K, formation of the metallic copper and alloyed Cu–Pd particles determines

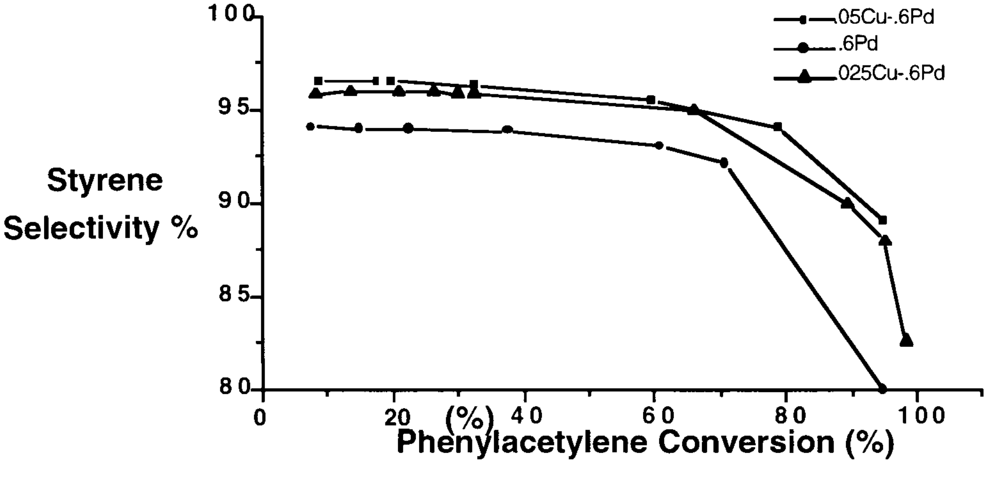

FIG. 1. Styrene selectivity versus phenylacetylene conversion on the copper-promoted 0.6Pd/pumice-supported samples prepared by organometallic route and reduced at 298 K.

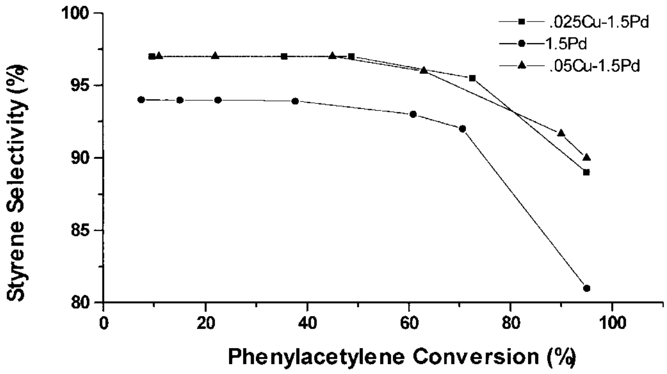

FIG. 2. Styrene selectivity versus phenylacetylene conversion of the copper-promoted 1.5Pd/pumice-supported samples prepared by organometallic route and reduced at 298 K.

the decrease in conversion rate likely due to the dilution of the palladium active sites by copper. The larger selectivity with respect to monometallic samples can be explained with the variation of the ensemble size rather than electronic effects. As already suggested (19), and also indicated here by the absence of chemical shifts between monometallic and bimetallic catalysts, the addition of metallic copper does not modify the electronic properties of palladium. Indeed, the decrease in the ensemble size needed for multiply adsorbed alkylidene species and formation of oligomers inhibits the further hydrogenation of styrene to ethylbenzene (5). According to these results, the preparation procedure from organometallic precursor, in which CuO is produced at low temperature reduction, yields catalysts as active as the corresponding monometallic samples, but more selective towards the production of styrene.

3.2. Hydrogenation of But-1-ene

The catalytic results of the hydrogenation of but-1-ene are summarised in Table 5. The rate of but-1-ene conversion and formation of the products were extrapolated to zero time, and the initial rates were calculated. The turnover frequencies of the hydrogenation and isomerization, TOF_{hyd} and TOF_{isom}, refer to the initial state. The corresponding selectivities listed in Table 4 have been calculated as the following ratio:

$$[TOF_{isom}/(TOF_{hyd} + TOF_{isom})] \times 100.$$

TABLE 5

Turnover Frequencies for But-1-ene Hydrogenation and Isomerization, TOF_{hyd} and TOF_{isom}, Respectively, and Selectivity, S%, to But-2-ene for the Catalysts Reduced at 298 K

Catalyst	TOF_{hyd} (s^{-1})	TOF_{isom} (s^{-1})	S% But-2-ene
0.6Pd	0.25	1.69	87
0.025Cu–0.6Pd	0.06	1.44	96
0.025Cu–0.6Pd (623 K)	0.31	5.63	95
0.05Cu–0.6Pd	0.02	0.37	95
1.5Pd	0.16	1.10	87
0.025Cu–1.5Pd	0.08	1.22	94
0.025Cu–1.5Pd (623 K)	0.25	1.86	88
0.05Cu–1.5Pd	0.02	0.26	93

Note. The values for two catalysts reduced at 623 K are also given.

In Figs. 3a and 3b the plots of selectivity of the reaction versus time measured on the 0.025Cu–0.6Pd/pumice catalyst reduced at 298 and 623 K, respectively, are reported. As previously observed on $Pd/\alpha\text{-}Al_2O_3$, the catalyst exhibits high isomerization activity (28), producing more *trans*-but-2-ene than *cis*-but-2-ene (16). As reported in Table 5, a decrease of the hydrogenation activity over the bimetallic catalysts reduced at 298 K and an increase of the selectivity to but-2-enes with respect to the corresponding monometallic Pd catalyst are observed. Reduction at 623 K restores the catalyst hydrogenation activity with a slight decrease in but-2-ene selectivity. The different catalytic behaviours exhibited by the various samples may be rationalised in terms of the catalyst structure. The catalysts reduced at low temperature contain CuO, which affects the Pd $3d_{5/2}$ binding energy, shifting it by 0.9 eV with respect to palladium on pumice. This corresponds to a substantial decrease in the palladium electron density (24, 27). The diminished hydrogenation rate with respect to the monometallic catalyst reflects the structure sensitivity of this type of reaction in accord with a recent study (28). The presence of CuO produced the same electronic effect attributed to a decrease in the Pd particle size. In addition, a decrease in the amount of hydrogen dissociated on Pd results in lower hydrogenation activity. The combination of the two effects will favour the isomerization for which no external hydrogen is needed, with a consequent increase of the selectivity to but-2-ene.

The complete reduction of CuO to metallic copper achieved at 623 K determines a change of the electronic properties of the palladium as revealed by the shift of the Pd 3*d* binding energy towards the value typical of palladium on pumice. The increased electron density on the palladium atoms (21, 26), along with a possible enhanced hydrogen availability, will favour the hydrogenation as compared to the isomerization, explaining the decreased but-2-ene selectivity with respect to the same catalysts reduced at 298 K. Ensemble size variation resulting in a decrease of contiguous sites may be the reason for the increased isomerization selectivity measured on the bimetallic catalysts reduced at high temperature with respect to the monometallic sample (28). The competition between the hydrogenation and isomerization may be explained in terms of the different number of adjacent surface atoms of the active metal required for forming the respective chemisorption complexes (33). The reaction involving the largest ensemble of these

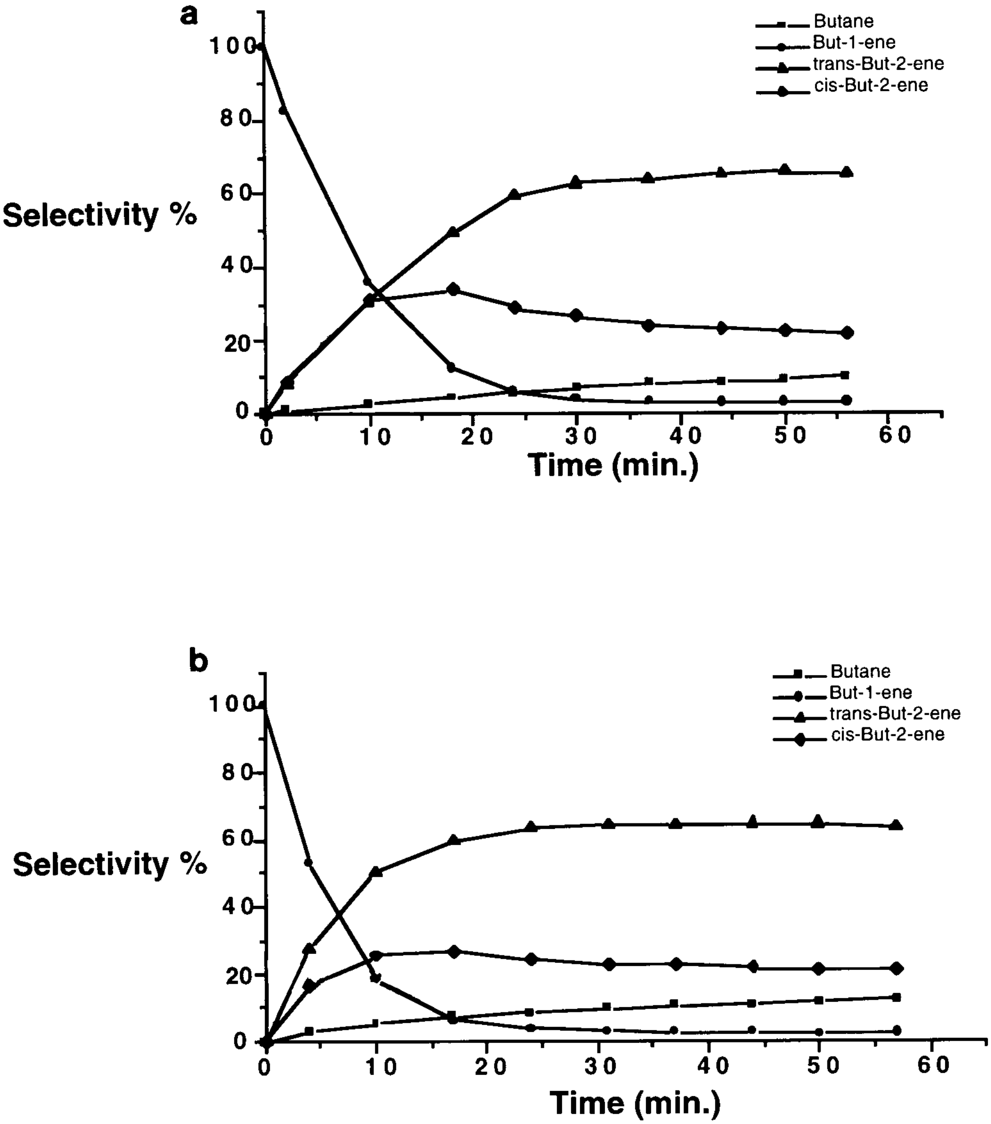

FIG. 3. Selectivity plot for the but-1-ene hydrogenation and isomerization over the 0.025Cu–0.6Pd reduced (a) at 298 K and (b) at 623 K.

atoms will be the most sensitive to alloying with a second metal unable to form such chemisorption bonds. While the hydrogenation of an olefin generally requires adsorption on multiple centres according to the Horiuti–Polanyi (HP) mechanism (28), the isomerization of an olefin may need only one metal centre according to the intramolecular shift mechanism (IM) (28). This would explain the increased but-2-ene selectivity of the bimetallic catalysts reduced at 623 K as compared to the monometallic one. The so-called "ligand effect" due to the electronic interaction of the Pd with the Cu following alloying is not considered important in the comparison of the monometallic with the bimetallic catalysts, since as shown by XPS, the binding energy of the Pd $3d_{5/2}$ is not modified by the addition of copper.

4. CONCLUSION

The chemical state of copper added to palladium catalysts supported on pumice has an important role in controlling the catalytic behaviour of palladium in the liquid phase hydrogenation of phenylacetylene and in the gas phase hydrogenation of but-1-ene.

For the first reaction, the presence of CuO leaves the conversion rate unchanged but increases the selectivity to styrene. On the other hand, the presence of metallic Cu decreases the conversion rate while still increasing the selectivity. This behaviour is explained by the variation of the electronic properties of palladium induced by the CuO, which would affect the hydrogenation of styrene to ethylbenzene, but not the hydrogenation of phenylacetylene to styrene. In the case of Cu metal, dilution of the palladium surface atoms is claimed to be responsible for the decreased activity and the ensemble size variation determines the increased selectivity to styrene with respect to the monometallic catalyst.

During the hydrogenation and isomerization of but-1-ene, addition of copper as oxide produces a consistent lowering of the hydrogenation activity and an increase in isomerization selectivity, whereas metallic copper, free and in an alloyed state with Pd, restores the hydrogenation activity and still maintains the higher selectivity with respect to a monometallic catalyst. Electronic effects determined by the CuO and ensemble size variations are considered responsible for the two behaviours.

ACKNOWLEDGMENTS

The authors acknowledge CNR (Consiglio Nazionale delle Ricerche) and MTA (Hungarian Academy of Science) for the bilateral program grant. The CNR is also acknowledged for the funds provided by the "Progetto Finalizzato M.S.T. A.-II."

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