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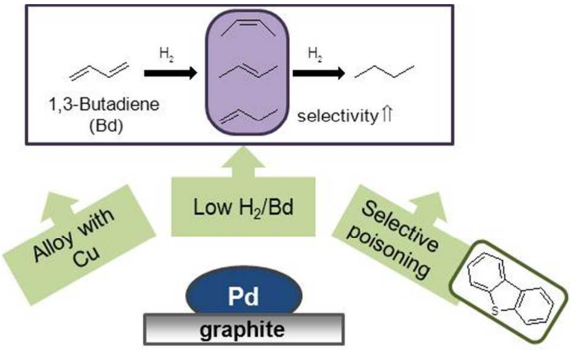

Control of selectivity in the hydrogenation of 1,3-butadiene is reached by tuning the graphite-supported Pd catalysts properties

Design of surface sites for the selective hydrogenation of 1,3-butadiene on Pd nanoparticles: Cu bimetallic formation and sulfur poisoning

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Abstract

Modifications to the selectivity during partial hydrogenation of butadiene over graphite supported Pd nanoparticles catalysts may be achieved by at least three methodologies: (1) changing the structure of the surface ensembles that constitute the active surface sites by the incorporation of another metallic component, such as Cu in the present case, (2) by a self-poisoning of the surfaces by strongly adsorbed carbonaceous intermediates, or carbon deposits, which are very sensitive to the presence of excess hydrogen in the feed during reaction, and (3) by anchoring a sulfur containing compound over the Pd surfaces. A detailed analysis of the selectivity variations, yielding 1-butene, cis- or trans-2-butene and undesired butanes is presented in these three cases, and the catalytic data are related with characterization data of these materials including transmission electron microscopy to determine the size of the nanoparticles and by X-ray photoelectron spectroscopy to obtain the surface analysis composition. The latter indicates that some electronic modifications on Pd take place.

Keywords: butadiene hydrogenation, Pd-Cu alloy, selective poisoning, sulfur

1. Introduction

Selective partial hydrogenation of conjugate double carbon-carbon bonds in diolefins, such as butadiene, or triple bonds in light hydrocarbons, such as acetylene, to yield monolefins, butenes and ethylene, respectively are reactions of great industrial interest. From a practical point of view, the production of olefins is a relevant process because these are the base compounds to produce polymers, while diolefins and alkynes act as poison of the polymerization catalysts. In addition to preventing the loss of valuable feedstock, over-hydrogenation leading to saturated hydrocarbons should be avoided [1]. On the other hand, from a scientific point of view, the catalyzed partial hydrogenation of butadiene is an interesting and challenging test, because the thermodynamics of the process indicate that the more favoured products are saturated hydrocarbons.

The major catalytic performances in terms of activity and selectivities are associated with Pd nanoparticles. Many studies have been performed applying Pd supported catalysts usually supported on oxidic supports [2-4] as well as in some cases carbon-based materials [5,6]. In many cases it has been well established that catalytic properties of Pd nanoparticles are size dependant [7] and that this group of reactions are structure sensitive. Therefore many studies have considered different structures of the Pd particles and possible surface atom arrangements to interpret the catalytic performances [8,9]. Additionally, to modify the Pd atoms surface structures many combinations of bimetallic catalysts have been studied and tested in reaction, resulting in a shift of selectivity. Thus, for the hydrogenation of acetylene over Pd-Au/SiO_2 catalysts the presence the Au decreases selectivity to ethane due to morphological changes of metallic particles [10], while for Pd-Ag/Al_2O_3 the presence of an adequate concentration of Ag improves the stability of this catalyst under reaction [11]. In both cases the deposition of carbon deposits during reaction seems to be a key parameter. For Pd-Cu/Al_2O_3 catalysts studied in the butadiene selective hydrogenation [12] the addition of Cu increases the selectivity towards n-butenes. A factor that must be considered under the conditions of operation is the presence and role of palladium hydride phases [13]. Formation of palladium β-hydride is favoured on large particles, and is often associated with unselective hydrogenation or total hydrogenation of alkynes [14]. Also, direct experimental evidence has been provided that the hydrogenation activity on Pd is strongly influenced by the presence of hydrogen species absorbed in the subsurface region of the metal catalyst and is governed by the permeability of the surface for hydrogen [15]. Solubility, diffusion and permeability of hydrogen in Pd bulk can be tuned by alloying with other elements such as Cu, Ag or Au [16]. Thus, any change in the stability of bulk palladium hydride and/or availability of surface and subsurface hydrogen species would have an effect on the selective hydrogenation of unsaturated hydrocarbons.

The key parameter of this type of partial hydrogenation processes is the control of the selectivity. In the case of butadiene, not only the formation of butenes is relevant, but also the selectivity to 1-butene versus 2-butenes, and among the latter, trans-2-butene *versus* cis-2-butene [17]. In order to adjust the selectivity, an additional component can be incorporated in the catalysts design. In this sense sulfur compounds can be adsorbed on the Pd surface sites, giving place to the so-called selective poisoning effect. This effect includes changes in the activity, for instance, reduction in the activity of the smallest metallic particles, because of the formation of surface coordinated compounds [18] or due to variations in the extent of coke formation [19] during reaction. Furthermore, modifications in the principal steps of the reaction mechanism can affect the selectivity, given that the inherent highly structure-sensitive character of these types of reaction when using Pd catalysts.

In the present contribution the development of catalytic Pd nanoparticles supported on a model carbon material, namely a high surface area graphite is reported. The study is focussed on the use of Pd nanoparticles as active sites for the hydrogenation of butadiene, studying their catalytic performances over a large range of reaction temperatures. It is attempted to understand how the selectivity can be modified when the surface ensembles that constitute the active surface sites are tailored by the incorporation of a second metallic component (Cu), by a self-poisoning of the surfaces by carbon deposits generated during the reaction, or by anchoring dibenzothiophene over the Pd surfaces. In all cases a detailed analysis of the modifications to selectivity is carried out based of the characterization results obtained for the original catalysts or for the spent materials, after use in reaction.

2. Experimental

2.1. Catalyst preparation

The selected support material for the catalyst preparation was a commercial high surface area graphite (G, HSAG 300 Timcal, S_{BET} = 300 m^2/g). For the preparation of the monometallic palladium catalyst, the support was stirred in aqueous solution and the pH of the suspension adjusted to 10 with a 2 M NaOH solution. Then, an aqueous solution of $Pd(NH_3)_4Cl_2 \cdot H_2O$ (Alfa Aesar, 39% Pd, 99.9% metals basis) was added to the support suspension. The mixture was stirred at room temperature for 2 h and then filtered, washed with a diluted NaOH solution mixture of water (100 ml) and 2 M NaOH (2 ml) and finally with distilled water. The catalyst was transferred to a drying oven (383 K) and left overnight. This catalyst will be referred to as PdG. The Pd loading corresponds to 1.8 %.

Bimetallic copper-palladium catalysts were prepared by impregnation of an aliquot of sample PdG with a solution of $Cu(NO_3)_2$•$3H_2O$ in a 1:1 H_2O:C_2H_5OH mixture, which contained an adequate amount of salt to give an atomic Cu:Pd ratio of 1:1. This sample was also dried in a drying oven (383 K) overnight. The catalyst will be referred to as PdCuG. Also a monometallic copper catalyst was prepared by wetness impregnation of support with a solution of $Cu(NO_3)_2$•$3H_2O$ (Alfa-Johnson Mathey) in a 1:1 H_2O:C_2H_5OH mixture to give a 1 wt. % Cu loading.

For the preparation of dibenzothiophene-poisoned catalysts, PdG-DBT and PdCuG-DBT, the fresh catalysts were previously reduced in a fixed bed reactor under a 30 ml/min H_2 flow at 423 K for 2 h. These reduced samples were then impregnated with a solution of dibenzothiophene (DBT, $C_{12}H_8S$, Merck) in toluene adjusted in concentration to give 2 molecules of DBT for each Pd atom. The catalysts were left to dry overnight at room temperature and then in an oven at 423 K for 6 h.

2.2. Catalyst characterisation

X-ray photoelectron spectra of the fresh and used samples were recorded with an Omicron spectrometer equipped with an EA-125 hemispherical electron multichannel analyser and X-ray source (Mg Kα) operated at 150 W, with a pass energy of 50 eV. Each sample was pressed into a small pellet of 15 mm diameter and placed in the sample holder and degassed in the chamber for 6-8 h to achieve a dynamic vacuum below 10^{-8} Pa before analysis. The spectral data for each sample was analysed using CASA XPS software. The relative concentrations and atomic ratios were determined from the integrated intensities of photoelectron lines corrected for the corresponding atomic sensitivity factor.

Transmission electron microscopy (TEM) images of the used catalysts were measured using a JEOL JEM-2100 field-emission gun electron microscope operated at 200 kV. The samples were ground and ultrasonically suspended in ethanol before deposition over a copper grid with carbon coated layers. From the obtained TEM images the mean diameter (*d*) of the Pd particle size (Table 1), was calculated based on a minimum of 100 particles, using the following equation where n_i is the number of particles with diameter d_i:

$$d = \frac{{}_{i} n_i d_i}{{}_{i} n_i}$$

2.3. Catalytic measurements: hydrogenation of 1,3-butadiene

The partial hydrogenation of 1,3-butadiene (Bd) reaction was carried out in a fixed bed glass reactor at atmospheric pressure. The Bd was fed into the reactor in a mixture of N_2, H_2 and Bd at a total flow rate of 70 ml/min (62.8 ml/min N_2, 6 ml/min H_2 and 1.2 ml/min Bd) giving a H_2:Bd ratio of 5. The reaction was carried out at 293 K, except for the S-poisoned samples that, due to their lower activities, the reaction temperature was set to vary in the range 293-473K. A second series of reaction conditions were tested for the non-poisoned catalysts in which the H_2:Bd ratio was 1.2 and the temperature was increased from 293 to 423 K. The reaction products were analysed by a Varian 3400 on-line gas chromatograph with thermal conductivity and flame ionisation detectors with a 20% BMEA Chromosorb P80/100 column.

The conversion of Bd was calculated as,

$$XBd\ \% \ = \frac{[Bd]_i - [Bd]_f}{[Bd_i]} \times 100$$

where $[Bd]_i$ represents the initial Bd molar flow rate (mmol/min) and $[Bd]_f$ the final Bd molar flow rate. The selectivity of each product was calculated as:

$$S_i\ \% \ = \frac{C_i}{\sum_i C_i} \times 100$$

where C_i represents the molar flow rate of the product whose selectivity is being calculated e.g. 1-butene, and ΣC_i represents the total molar flow rate of all the products e.g. 1-butene, cis-2-butene, trans-2-butene and butane.

Table 2 summarises the most important data obtained for the non-poisoned and S-poisoned samples.

3. Results and discussion

3.1 Consequences of presence of Cu

Figure 1A displays the evolution of conversion and of selectivity to butenes (1-butene +cis-2-butene+ trans-2-butene) with time of reaction in the hydrogenation of 1,3-butadiene (Bd) over the PdG and PdCuG catalysts, previously reduced at 423 or 523 K. It was observed that irrespective of the temperature of reduction the bimetallic catalyst gave higher conversions than the monometallic, and that it deactivated to a lesser extent. For both catalysts, an increase in conversion with reduction temperature was observed, which may be correlated with the level of reduction of the metal. Reduction of Pd^{2+} complexes by hydrogen can require temperatures above 473 K [20]. The deactivation observed was likely caused by accumulation of a carbonaceous overlayer on the surface of the Pd particles that, considering the low temperatures of reaction, might consist of different irreversibly adsorbed species [14]. The hydrocarbon balance confirmed the accumulation of deposits and indicated that the process gradually slowed down with time on reaction. This carbon deposition was lower for the bimetallic PdCuG catalyst. It has been reported that by purging the catalyst in a reducing stream free from hydrocarbons for several hours the activity could be recovered [12].

As far as the selectivities are concerned, the main product of reaction was butane, irrespective of the catalyst employed or temperature of reduction (Figure 1B and Table 1). Partial hydrogenation to butenes was higher for the bimetallic PdCuG catalyst. Furthermore, both catalysts demonstrated a decrease in the selectivity to butenes after 523 K reduction, from 17 to 5% for PdG and from 37% to 10% for PdCuG. On the other hand, selectivity to butenes increased as the conversion decreased with time on stream in all cases (Figure 1A), which could suggest some role of accumulated carbonaceous deposits. Further to this, 1-butene selectivity (1-b) with respect to the sum of 1- and 2-butene (c-2-b and t-2-b) was higher for the monometallic (41%) after reduction at 423 K, than for the bimetallic catalyst (28%) as can be seen in Table 1. After reduction at 523 K, both catalysts gave the same selectivity to 1-butene, *ca*. 25 %. The trans/cis ratio of 2-butenes (t/c in Table 1) for the monometallic catalyst was 5.1:1 when reduced at the lower temperature and 4:1 when reduced at 523 K. The addition of Cu to Pd catalyst seemed to reduce the trans/cis ratio to values around 3.4:1 for both temperatures of reduction. Opposing trends in terms of variations in the trans/cis ratio have been observed for Pd-Cu/Nb_2O_5 [21].

Therefore, addition of copper to Pd supported on graphite reduced the deactivation and slightly improved the catalytic selectivity for partial hydrogenation of 1,3-butadiene. Furthermore, the lower selectivity to 1-butene and the lower trans/cis ratio obtained over PdCuG seem to indicate that the addition of Cu to Pd catalyst altered the mechanism of Bd hydrogenation. Generally, thermal hydrogenation of Bd occurs *via* 1,4-addition to trans-2-butene as the main product [22]. Over palladium, the main product is usually 1-butene, with selectivities of up to 60 %, and the trans/cis ratios of

2-butenes are greater than 10. These facts are explained based on the mechanism established from deuterium tracer studies [23-25] where two processes can take place: 1) 1,2-addition to the σ-bonded half-hydrogenated states giving 1-butene and 2) 1,2- and 1,4-addition to the two π-allylic states of adsorbed butadiene giving 1-butene and cis- and trans-2-butenes. The trans/cis ratio is governed by the ratio of the anti- and syn-conformations of butadiene, ratio 10:1 to 20:1 (anti:syn) in gas phase, and of the butenyl half-hydrogenated intermediate states. These conformations are non-interconvertible on Pd, which explains the high trans/cis ratio obtained with this metal [24]. On PdG the trans/cis ratio was higher than the predicted thermodynamic equilibrium composition of 2-butenes, trans/cis ratio at 293 K which is 3.5, but lower than that observed for other Pd catalysts [23]. The higher production of cis isomer could be explained by a limited interconversion between syn- and anti- forms of 1,3-butadiene allowing change in conformation of adsorbed Bd. Taking all this into consideration, it could be concluded that the addition of copper to the palladium catalysts altered the reaction mechanism leading the hydrogenation product distribution to be governed by the conformation of the butenyl half-hydrogenated intermediated states. As the trans/cis ratio did not show any notable variation with increasing reduction temperature, it can be suggested that partial reduction of Pd surface sites did not alter the route of hydrogenation. Formation of butane due to consecutive hydrogenation of C_4H_9 adsorbed species was less favoured for the bimetallic catalyst.

It has been suggested that the improved selectivity towards n-butenes is related to subtle changes in the relative concentrations of surface species, which would imply the decreased stability of the adsorbed intermediate alkenes, i.e the n-butenes. Then, desorption of the alkene would be promoted limiting further hydrogenation [26]. A possible geometric effect due to dilution and/or decoration of Pd surface atoms by Cu lead to a more selective catalyst for the partial hydrogenation. The reduction in the size of the Pd ensembles would weaken adsorption of 1,3-butadiene or butenes. Furthermore, as shown above, Cu seemed to prevent the formation of the carbonaceous adlayer, which could block selective sites. These assumptions agree with those previously proposed in the hydrogenation of ethyne with Pd catalysts promoted with Group 11 metals. The increase in selectivity to ethene has been related to prevention of inactivation of small groups of Pd atoms, termed Type A sites, by coverage of carbonaceous species, and to reduction of the large palladium ensembles responsible for ethene hydrogenation, termed Type E sites [27].

However, even bearing in mind that the geometric effect usually predominates, an electronic effect cannot be disregarded. Therefore, the electronic properties of Pd and the surface composition on the various catalysts were investigated by XPS. The binding energy (BE) of Pd $3d_{5/2}$ and the ratios between the atomic concentrations of elements are summarized in Table 2. The XPS spectra for Pd 3d of all the catalysts are shown in Figure 2. Freshly prepared PdG sample exhibited a doublet corresponding to Pd $3d_{5/2}$ (BE= 338.3 eV) and $3d_{3/2}$ (BE = 343.3 eV) peaks. These BE values were in good agreement with those reported in the literature for palladium catalysts prepared with the same palladium precursor $Pd(NH_3)_4Cl_2$ [28], highlighting that surface complex containing Pd and Cl remained on the surface after the stages of impregnation and drying. The presence of carboxylic groups on the surface and the π-system of the support may be responsible for stabilization of the precursor complex [29]. Sample reduced at 423 K, PdG-423, showed two contributions at 337.7 and 335.7 eV for Pd $3d_{5/2}$. The higher energy of the peak at 335.7 eV compared to that for metallic Pd (Pd0, 335.3 eV) was characteristic of highly dispersed palladium nanoparticles in the oxidation state Pd^+, likely arising from electron transfer from palladium to carbon as previously suggested [19]. It is also well known that the core level BE of palladium significantly depend on the Pd-particle size of supported catalysts. In highly dispersed Pd/C catalysts [5], the shift of the binding energy of the core level was 1.0–1.3 eV. The complex stabilisation by the carbon surface contributed to the fact that metal particles stayed small after reduction. The peak at 337.7 eV was close to that for freshly prepared PdG sample, and allows an assignment to Pd (II) species due to residual precursor but more probably to re-oxidized species during air contact before XPS study, since the samples were not *in situ* reduced. On the other hand, for the freshly prepared bimetallic PdCuG catalyst, the Pd $3d_{5/2}$ signal was detected at a lower BE, 337.8 eV. The Cu $2p_{3/2}$ core level XPS spectrum (Figure S1) showed a peak centered at 932.0 eV which added to the occurrence of satellites at higher binding energy was indicative of the presence of a small amount of Cu(II) species. However, the main peak could be deconvoluted in two components at 931.6 and 933.2 eV with a majority contribution arising from the low BE component. Cu mainly existed in the partially reduced form (probably Cu^+) suggesting that its reduction takes place during the preparation process or is facilitated under vacuum [30]. After reduction at 423 K, PdCuG-423 sample, the Pd $3d_{5/2}$ peak could be deconvoluted in the two contributions observed for monometallic sample at 335.7 and 337.7 eV. The analysis of the XP spectra for samples after reaction, PdG-423-r and PdCuG-423-r, gave also the two contributions at around 337.7 and 335.8 eV. The lower intensity of the peak of palladium in samples after reaction (Figure 2) as compared with reduced catalysts, PdG-423 and PdCuG-423, suggested some carbon deposition on the Pd particles during reaction. This reduction in Pd surface composition took place to a greater extent for the monometallic sample (see Pd/C ratio in Table 2), which was consistent with the higher deactivation observed for PdG sample (Figure 1). Then the selectivity variations could be interpreted in terms of electron density of the catalytic sites. Electron-rich sites generated upon Cu addition would lead to a more selective catalyst for the partial hydrogenation due to a weaker adsorption of 1,3-butadiene. Electron-deficient sites would have the opposite effect, the diene or the intermediate butenes would be more strongly adsorbed favouring butane formation.

Finally, it has been postulated that hydrogenation is closely connected to the adsorption state of hydrogen atoms on the Pd metal and, after promotion or alloying with Cu, geometric and/or electronic effects can influence the availability of surface and subsurface hydrogen for reaction. In fact, it is known that Cu decreases both the surface adsorption and the bulk absorption (hydride formation) of hydrogen compared to Pd crystallites [12]. Hydrogen diffusion and permeation behaviour in Pd-Cu membranes also depends heavily on the composition and nano-scale structure of the alloy phase [31]. In addition, the presence of Cu decreased the carbon coverage that has a vital role in the performance of the catalysts as will be seen in next section.

3.2 Influence of the H_2/Bd ratio

Some experiments were carried out over both samples reduced at 423 K with a H_2/Bd ratio of 1.2 rather than 5 as used before, and varying the reaction temperature in the range 293-423 K. Figure 3 shows the evolution of conversion, selectivity to 1-butene compared to butenes and of the trans/cis ratio. At low temperatures, both catalysts seemed to deactivate as occurred in the isothermal experiments under conditions of excess of H_2. Once the catalysts become equilibrated, the hydrogenation reaction continued to consume almost all of the hydrogen in the feed at higher temperatures. The selectivities changed considerably when comparing with data obtained with the H_2/Bd ratio of 5, although both catalysts followed similar trends. Selectivities to butenes were greater than 95% at all temperatures. Additionally, the selectivity of 1-butene among butenes started at 57% and decreased to 38 % as the temperature increased. The evolution of the products indicated that 1-butene was converted to cis-2-butene and butane. The trans/cis ratio was higher for the monometallic than for the bimetallic catalyst, (5.0 and 3.2, respectively) at 313 K, as occurred under excess of H_2. However, the values obtained for PdCuG at RT were higher (4.8 vs 3.2) for the low H_2/Bd ratio than for reaction under excess of hydrogen. Also, this ratio decreased with reaction temperature approaching the thermodynamic value. The thermodynamic equilibrium composition of butenes at 423 K has been calculated as 10.3, 60.3 and 29.4% for 1-butene, trans-2-butene, and cis-2-butene, respectively, which gives a trans/cis ratio of 2.06 [32].

With increased hydrogen partial pressure in the feed mixture in which the H_2/Bd molar ratio was increased from 1.2 to 5, the monometallic catalyst completely lost selectivity toward partial hydrogenation. As a consequence of the excess hydrogen, the coverage of butadiene was probably less, and the number of H atoms available on the surface per mol of Bd greater than in the case of H_2/Bd=1.2, thereby favouring over hydrogenation and isomerisation of butene isomers. This seemed to suggest that, at a critical H_2/hydrocarbon molar ratio, a change in the surface behaviour for the hydrogenation reaction occured. Similar effects of the influence of the H_2/hydrocarbon molar ratios had been observed in previous studies [6,10,14]. It is proposed that a β-PdH phase formation is favored at high H_2 to hydrocarbon ratio and on larger particles. The role of this β-hydride phase on the selectivity has been widely confirmed [14,33]. Despite this, it is more generally accepted that this sudden change in catalytic behaviour was caused by a drastic reduction in the extent of carbonaceous deposits that limits the coke coverage left on the catalyst surface at high H_2/Bd molar ratios [10]. However, there are different opinions about the role of this carbonaceous overlayer. It could take part in the partial hydrogenation *via* a hydrogen transfer mechanism [34], whose involvement increases with an increase of hydrogen/hydrocarbon ratio and temperature. On the other hand, it could only decrease the size of the working ensembles, creating small sites at which selective semi-hydrogenation occurs and, causing a reduction in the abundance of large palladium ensembles that are responsible for the undesired over-hydrogenation reaction [14]. Recent studies are more in the line that the decisive role of the carbon deposition is to influence the adsorption state of hydrogen atoms. Subsurface carbon decreases the surface H coverage that is responsible for total hydrogenation by reducing the stability of adsorbed H [35]. On the other hand, it has been revealed that carbonaceous deposits facilitate hydrogen diffusion from the surface into the bulk of the Pd particles for the replenishment of the weakly bound volume-absorbed H atoms required for alkene hydrogenation [36]. The change of the selectivity patterns with time of reaction at RT for the 5:1 ratio also pointed to an effect of the carbonaceous deposits. Finally, it seems that the effect observed in the bimetallic catalyst due to Cu addition was blurred for the low H_2/Bd ratio. Therefore, the carbonaceous deposits formed during hydrogenation play a fundamental role controlling the hydrogen availability and predominating over the effect produced by Cu promotion.

3.3. Selective poisoning

The addition of DBT to PdG and PdCuG clearly lowered its activity compared to that of the non-modified catalyst and since there was very little conversion of Bd at 293 K the reaction data were collected at increasing temperatures. Figure 4 displays the evolution of conversion, selectivity to 1-butene compared to butenes and of the trans/cis ratio with reaction temperature. While for PdG-DBT sample higher conversions were obtained after reducing at 523 K, for PdCuG-DBT catalyst the conversion values were lower. All the dibenzothiophene-poisoned catalysts gave selectivities to butane below 4 % irrespective of the reduction temperature (Table 1). Also, there was very little change in the distribution of products, with trans-2-butene being the main product, probably due to the higher reaction temperatures compared with the experiments carried out over the non-modified samples (293 K). The selectivity to 1-butene started around 30 % for all samples (Figure 4B), and decreased with reaction temperature and conversion following different tendencies. Although S(1b/1b+2b) was lower than for PdG-423, it was still slightly higher than the thermodynamic equilibrium composition of butenes, which as indicated above, for 323 K was calculated as 10, 60 and 29 % for 1-butene, trans-2-butene, and cis-2-butene, respectively. As occurred for the non-modified samples, lower t/c ratios were observed for the bimetallic catalyst in comparison with the monometallic counterpart. However, the trans/cis ratios were still higher than for the corresponding non-modified catalyst. As the temperature of reaction increased, the ratios tended towards values near the thermodynamic equilibrium, trans/cis ratio of 2.06 at 423 K. At reaction temperatures above 423 K, the initial tendency observed for both selectivity and trans/cis ratio was inverted, and PdCuG-DBT-423 and -523 showed higher values than PdG-DBT-523.

The possible interaction between sulfur and Pd atoms was studied by XPS. The Pd 3d spectra for the catalysts modified with DBT (Figure 2B) showed an asymmetric broadening suggesting that Pd existed in various oxidation states. Therefore, the spectra for Pd $3d_{5/2}$ were curve-fitted in two individual components or states of Pd with binding energies at 337.8 and 335.7 eV for as prepared PdG-DBT and PdCuG-DBT. The low BE component coincided with the component observed for reduced PdG-423 sample (Figure 2A b) and its presence was consistent with the fact that samples were subjected to a reduction pretreatment prior to exposure to DBT. As commented above, the peak at

BE of 337.8 eV could be attributed to Pd (II) species and could be due to residual precursor or to re-oxidation before the XPS study. However, it may also be ascribed to Pd interacting with sulfur ligand molecules covering a part of the metallic surface. Similar ranges of binding energies have been reported for Pd^{2+}-S compounds [37]. As occurred for the non-modified sample, Cu peak could also be deconvoluted into two species: one oxidized and one reduced (Figure S1). Therefore, it was not completely reduced during the H_2 pretreatment at 423 K before deposition of DBT. The binding energy of the S 2p line at 164.0 eV corresponded to non-S-bound DBT, as it has been measured for a number of S-containing carbonaceous materials [38]. The S/Pd ratio showed that the amount of DBT deposited was similar for both samples.

As far as the samples after reaction are concerned, the most obvious feature in the Pd 3d region (Figure 2 B) was the shifting of the maxima to lower BE and the asymmetry at the higher BE side. The temperature of post-reduction did not seem to affect significantly the XP spectra and the peaks showed two contributions at 338.2 and 335.7 eV for both the monometallic and bimetallic catalysts. Furthermore, the proportion of the two species changed compared to that for the freshly modified catalysts, the component at lower BE, i.e. reduced Pd metal, being clearly of greater intensity. This could be due to desorption/decomposition of the DBT molecules during the reduction and/or reaction treatment and seemed to indicate that reduced states are stabilized by the addition of DBT. The reaction also brought about changes in the Cu 2p spectra. The satellites associated with the Cu peak disappeared and the main peak shifted to lower binding energy 931.3 eV (Figure S1). This value was lower than that for Cu(0) or Cu(+1) and could be associated to the formation of alloyed Pd-Cu particles. It has been reported that the richer the alloy in Pd, the lower is the observed binding energy for the Cu $2p_{3/2}$ peak [30]. Also, the decrease of the Cu/Pd ratio as the temperature of reduction increased for used samples (Table 2), PdCuG-DBT-423-r and -523-r, agreed with a surface enrichment in Pd. Contrary to what was observed for the non-modified samples, the amount of surface Pd (see Pd/C ratio in Table 2) barely changed after reaction. The particle diameter *d* obtained by TEM for PdG-DBT and PdCuG-DBT samples (Table 2) indicated that the presence of DBT avoided the agglomeration of the nanoparticles and then, the slight reduction in the surface Pd observed by XPS was probably due to metal covered with DBT molecules or retained sulfur. Furthermore, after reaction, the signal for S 2p disappeared for all samples except for PdG-DBT-423-r. The binding energy for the peak was 164.0 eV which corresponds again to the non-S-bound form of DBT.

Therefore, exposure of Pd catalysts to DBT clearly had a pronounced effect on the catalytic behaviour; it led to a great reduction of the Bd hydrogenation capability and to the improvement in the selectivity to butenes. Examples in the literature where catalysts have been selectively poisoned with sulfur-containing compounds such as thiophene have displayed similar findings [17,39,40]. It has been suggested that sulfur deactivates not only the metal site where it is adsorbed but also the neighbouring sites [41]. This poisoning is known to be governed by electronic and geometric factors. XPS analyses showed that DBT was molecularly adsorbed on the freshly prepared catalysts and that some residual amounts remained adsorbed on the monometallic catalyst after reduction at 423 K and subsequent reaction. The latter could justify the low conversions observed for PdG-DBT-423. The DBT molecules could be blocking the catalytic active sites and only a residual activity would remain. It has been observed that molecular desorption of DBT from a sample obtained following DBT adsorption on Ag/TiO_2 takes place in the 448-598 K range [38]. After reduction of our catalysts at 523 K, decomposition and/or hydrogenolysis of DBT could take place, as occurred for thiophene [42], and catalytic activity was partly recovered for PdG-DBT-523. Regeneration of S-poisoned Pd catalysts has been observed after *ex-situ* treatments at 393-513 K with H_2 [43] for catalysts used in selective hydrogenation of styrene to ethylbenzene. However, it has been observed for surfaces examined for the hydrogenation of butadiene that regeneration seems to be more efficient in the presence of the hydrocarbon, probably due to a competitive adsorption of butadiene and H_2S for the surface sites and this effect slightly increases with temperature in the range 373-508 K [39]. On the other hand, after DBT decomposition, sulfur seemed to be retained on the surface as adsorbed S or other decomposition products [4,44]. The presence of these sulfur species could lead to lower hydrogen and/or butadiene adsorption and therefore inhibit the hydrogenation of butadiene. Although no peak could be detected for this irreversible adsorbed sulfur species (notice that detection limits of the XPS technique is around 0.5%), the observed component of Pd 3d 5/2 peak at the high BE side (338.2 eV) was shifted to higher BE compared with the component for the fresh modified sample (337.7 eV). This could imply that palladium became more electron-deficient, due to an electron transfer from the metal to the sulfur [45]. In the bimetallic catalysts, DBT decomposition or hydrogenolysis seemed to occur even at 423 K (no S 2p peak in XPS). Furthermore, due to the incorporation of Cu, the palladium atoms had a higher electron-donor character and therefore the bimetallic catalyst was less thio-resistant. This contrasts with results found for Pd-Pt bimetallic catalyst where the interaction between the metals gives rise to enhanced sulfur tolerance for the isomerisation of n-hexane [46]. It is known that copper-based catalysts are more sensitive to sulfur poisoning than palladium catalysts [47,48]. Additionally, sulfur tolerance of Pd-Cu alloy membranes is affected by the alloy composition and phase structure, face-centered cubic (fcc) or body-centered cubic (bcc), including possible Pd or Cu segregation

[49,50]. These facts could explain the different behaviour of conversion at the two reduction temperatures for the mono and bimetallic catalysts.

The DBT or the irreversibly adsorbed S derived from DBT decomposition also affected the distribution of products during Bd hydrogenation. The sulfur appeared to poison the 1,2-addition process to the σ-bonded half hydrogenated states which leads to 1-butene then lowering the 1-butene yield and increasing the trans/cis ratio [17]. It generated electron-deficient sites, as detected by XPS, that progressively enhances the extent of allyl character in the chemisorbed states involved in the 1,4-addition process. Therefore, these electron transfers can modify the relative rates of competitive surface reactions, thus modifying the selectivity [43]. This has been clearly established for Pt catalysts by using electron-donating and accepting compounds, which modulate the activity, the thermodynamic selectivity and even the mechanistic selectivity [51].

All these phenomena are not the result of pure electronic effects but rather the occurrence of geometric actions has to be considered. So, similar inferences as to those obtained for the role of carbonaceous ad-layer can also be achieved. In this sense, and as proposed for acetylene hydrogenation [44], DBT or the retained sulfur species would create a template on the surface, which would expose Pd ensembles that might accommodate Bd but not 1-butene, consequently improving the selectivity in the hydrogenation of the former. A scenario, where the sulfur species would reduce the accessibility and concentration of the subsurface hydrogen species that promote non-selective hydrogenation, cannot be disregarded. Different effects of H_2S on hydrogen transport and permeability in Pd-Cu alloy membranes have been reported [50].

Conclusions

The results presented in this work can be summarized into the following points:

i) Addition of copper to Pd nanoparticles supported on graphite increases the selectivity to partial hydrogenation of 1,3-butadiene and reduces the rate of deactivation during reaction, probably due to diminishing the extent of carbon deposit formation. Furthermore, the selectivity to 1-butene (among butenes) and the trans/cis ratio diminished for PdCuG catalyst when compared with PdG. These reasons indicate that the addition of Cu to Pd catalyst modifies the availability of surface and subsurface hydrogen species either due to an electronic or geometric effect or a combination of both.

ii) By varying the hydrogen to butadiene ratio, the extent of carbon deposition on the Pd active sites can be modified. In this way we have observed that selectivity values change considerably as a consequence of these carbon deposits. These observations have been clarified by assuming modifications in the structures of the surface ensembles that constitute the active catalytic sites. In the case of the bimetallic Pd-Cu catalyst, the carbonaceous deposits formed during hydrogenation with butadiene rich reactant mixture play a fundamental role, which is predominant over the effect produced by Cu promotion by tuning the catalytic selectivities.

iii) Exposure of Pd catalysts to dibenzothiophene has a remarkable effect on the catalytic behaviour, suppressing the activities at low temperatures and improving the selectivity to butenes. Reversible adsorbed species containing sulfur affect significantly the distribution of products obtained during butadiene hydrogenation. Even after partial elimination of these chemisorbed species, by decomposition-desorption at 523 K, the retained sulfur was still capable of providing enhanced selectivity to butenes due to suppressed butadiene hydrogenation activity. Thus, sulfur species seems to poison efficiently some intermediate steps in the reaction mechanism. Based on the XPS results it is postulated that these chemisorbed species generate electron-deficient sites, again altering the possible surface intermediates produced during butadiene hydrogenation. Finally all the data obtained over model supported Pd based catalysts, lead to the conclusion that by rational design-modification of the surface composition, tuning of the produced olefins can improve the yield for a given product.

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Table 1. Results of PdG and PdCuG catalysts in the hydrogenation of 1,3-butadiene.

Catalyst		Conv. (%)	Butene composition (%)			t/c	Butane selectivity (%)
			1-b	t-2-b	c-2-b		
PdG	-423	50	41	49	10	5.1	83
	-523	95	26	61	13	4.0	95
PdG -DBT	-423	25[a]	24[a]	63[a]	13[a]	4.7[a]	1[a]
	-523	55[a]	18[a]	62[a]	21[a]	3.0[a]	4[a]
PdCuG	-423	82	28	56	16	3.2	63
	-523	98	23	60	17	3.6	90
PdCuG -DBT	-423	39[a]	21[a]	60[a]	19[a]	3.1[a]	4[a]
	-523	8[a]	26[a]	61[a]	14[a]	4.5[a]	2[a]

Reaction conditions as indicated in the Experimental section, H_2/Bd= 5, T= 293 K after 180 min

[a] Data obtained at a reaction temperature of 423 K.

Table 2. XPS data for PdG and PdCuG samples.

Sample		d^a (nm)	Pd/C	Cu/Pd	S/Pd
PdG	freshly prepared		0.0024		
	-423		0.0018		
	-423-r	4.0	0.0010		
PdG-DBT	freshly prepared		0.0022		2.43
	-423-r	1.7	0.0014		2.23
	-523-r	1.8	0.0018		-
PdCuG	freshly prepared		0.0022	0.38	
	-423		0.0020	0.28	
	-423-r	2.6	0.0020		
PdCuG-DBT	freshly prepared		0.0023	0.35	2.39
	-423-r	1.8	0.0020	0.33	-
	-523-r	2.0	0.0019	0.28	-

[a] TEM determinations over catalysts used in reaction.

Figure Captions

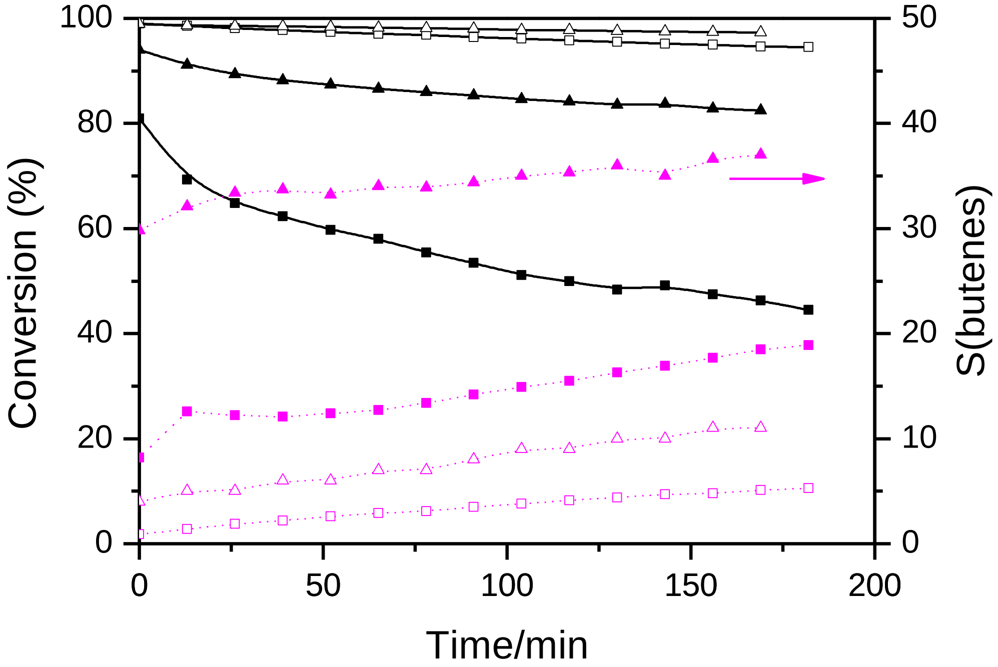
Figure 1. Top: Evolution of conversion (solid line) and selectivity to butanes (dash lines) in the hydrogenation of 1,3-butadiene at 293 K with a H_2/Bd= 5 ratio for PdG-423 (■), PdG-523 (□), PdCuG-423 (▲) and PdCuG-523 (△). Bottom: Selectivity distribution at 293 K, butane (grey), 1-butene (black), trans-2-butene (white), cis-2-butene (dark grey)

Figure 2. XPS spectra of the Pd 3d core level of A) non-modified samples, PdG freshly- prepared (a), PdG-423 (b), PdG-423-r (c), PdCuG freshly prepared (d), PdCuG-423 (e), PdCuG-423-r (f), and of B) modified samples, PdG-DBT freshly prepared (a), PdG-DBT-423-r (b), PdG-DBT-523-r (c), PdCuG-DBT freshly prepared (d), PdCuG-DBT-423-r (e), PdCuG-DBT-523-r (f).

Figure 3. Evolution of A) conversion, B) selectivity to 1-butene among butenes, and C) trans/cis ratio in the hydrogenation of 1,3-butadiene under a H_2/Bd= 1.2 ratio for non-modified PdG (■) and PdCuG (●) samples. Stars represent the values obtained for the same samples reduced at 423 K and under reaction conditions of H_2/Bd= 5 and T=293 K.

Figure 4. Evolution of A) conversion, B) selectivity to 1-butene among butenes, and C) trans/cis ratio for PdG-DBT-423 (■), PdG-DBT-523 (□), PdCuG-DBT-423 (●) and PdCuG-DBT-523 (○) samples in the hydrogenation of 1,3-butadiene with a H_2/Bd= 5 ratio. Stars represent the values obtained for the non-modified samples reduced at 423 K, PdG-423 and PdCuG-423, and under reaction conditions of H_2/Bd= 5 and T=293 K.

Figure 1


Conversion (%)
S(butenes)
Time/min
0
20
40
60
80
100
0
10
20
30
40
50
0
50
100
150
200

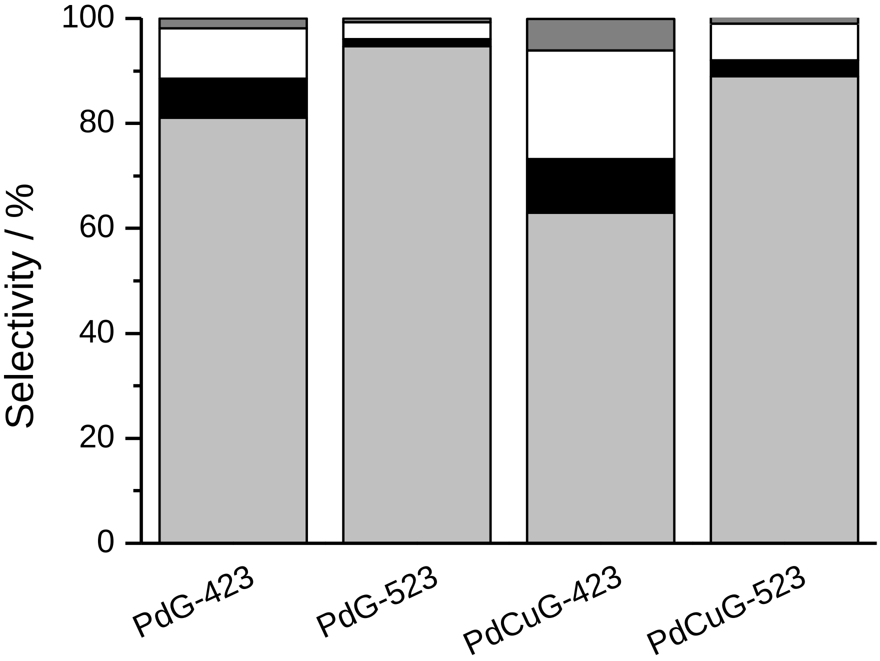

Selectivity / %
0
20
40
60
80
100
PdG-423
PdG-523
PdCuG-423
PdCuG-523

Figure 2

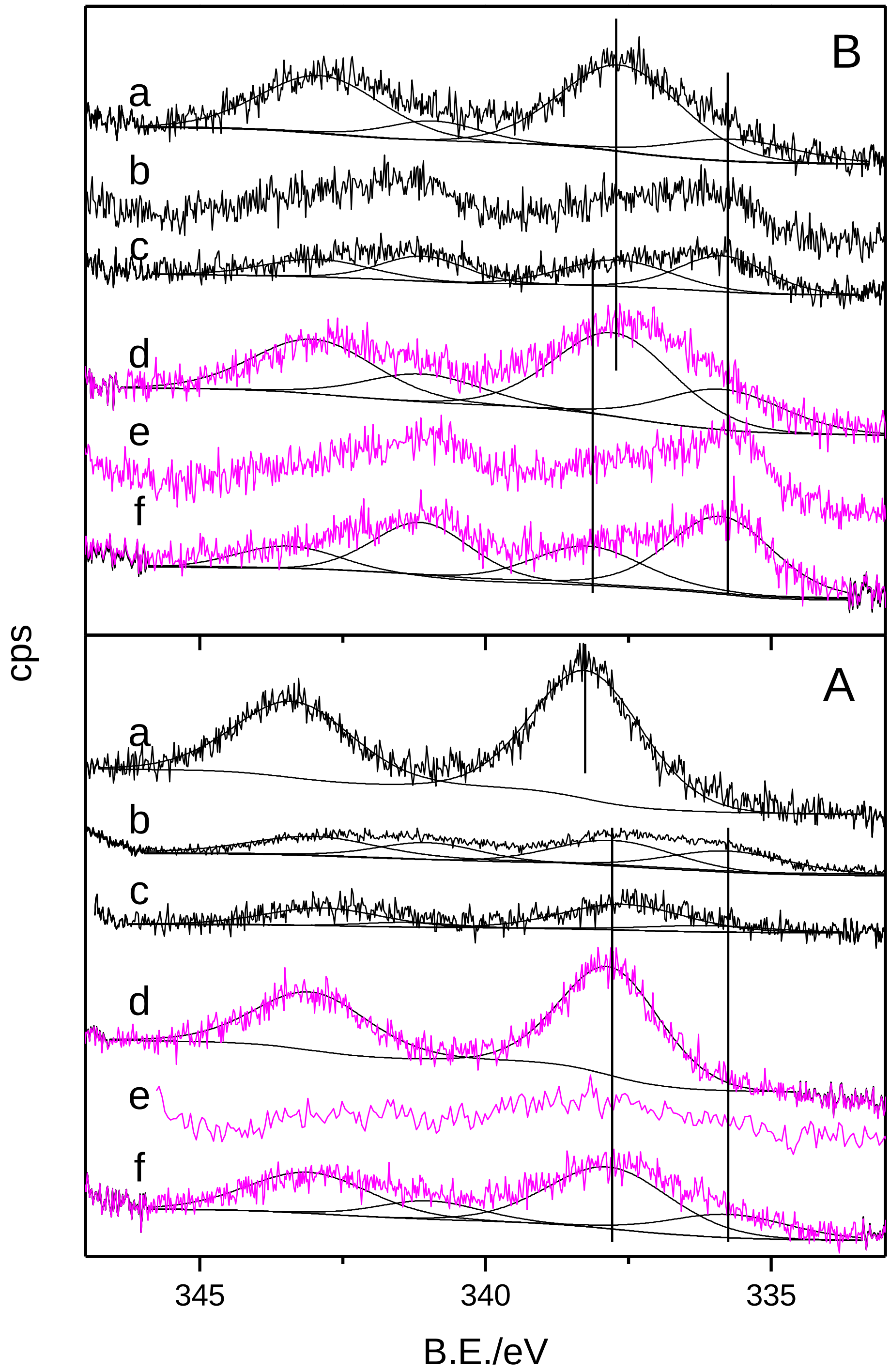


Figure 3

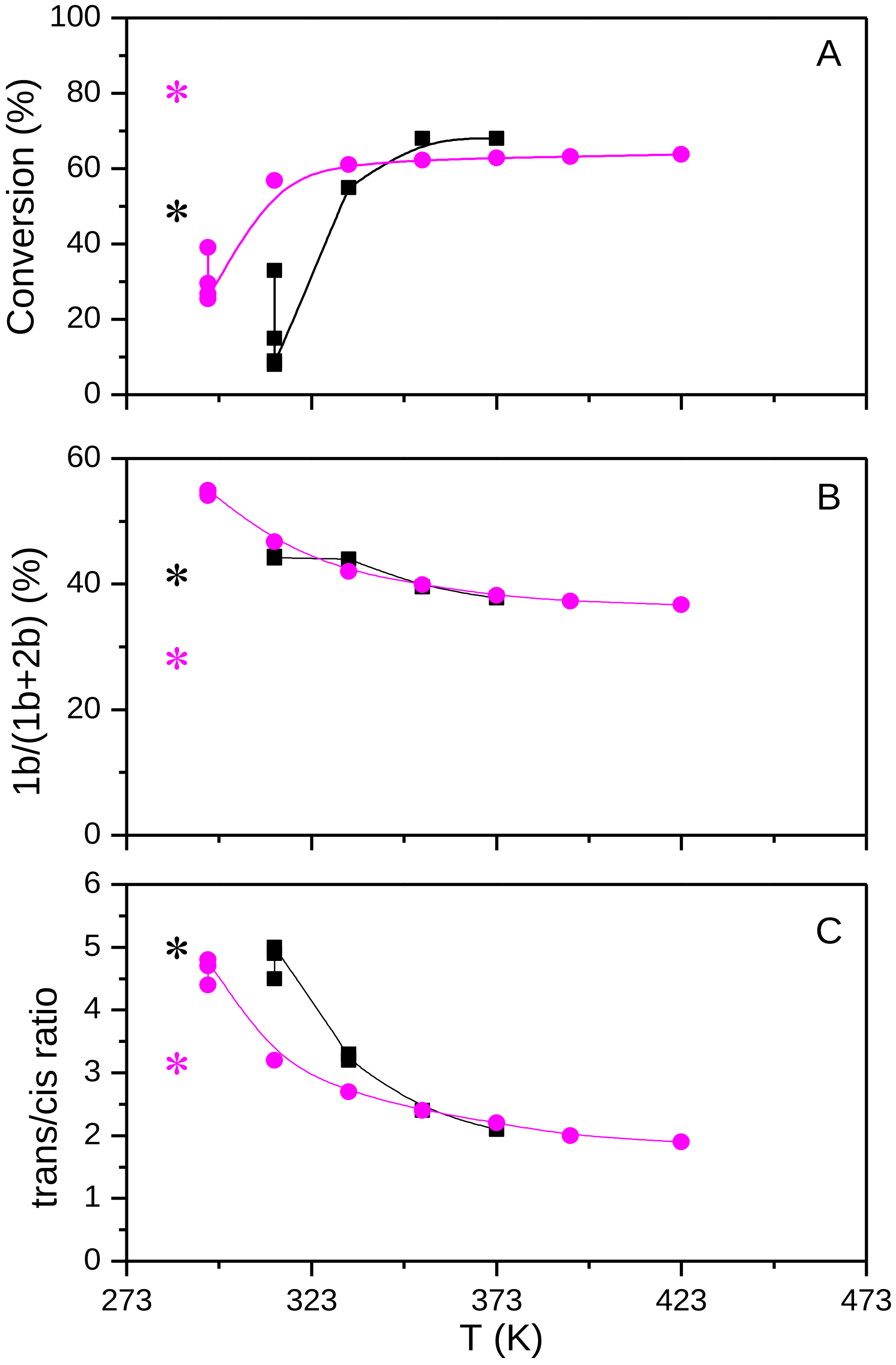
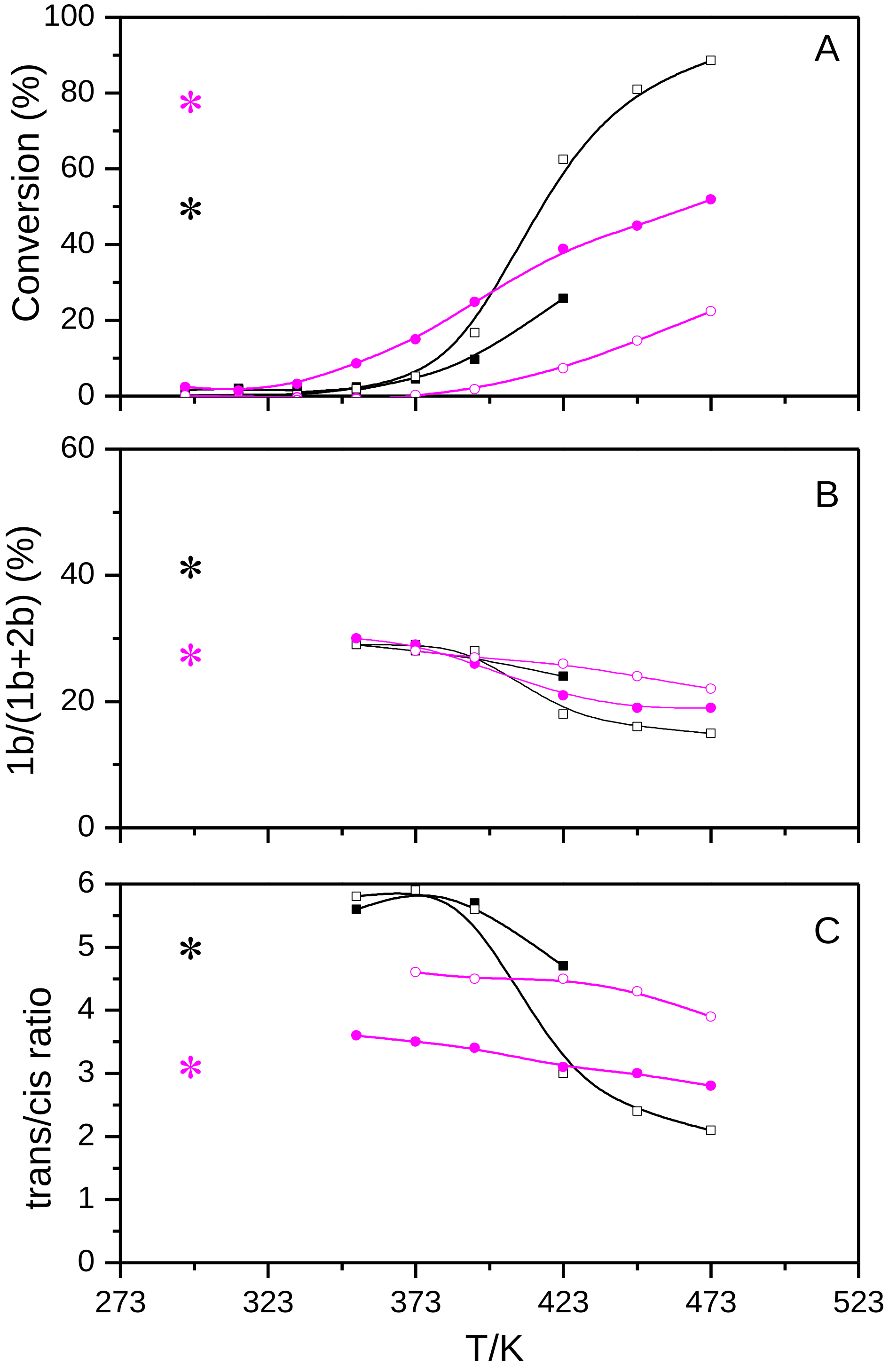

Conversion (%)
100
80
60
40
20
0
A
1b/(1b+2b) (%)
60
40
20
0
B
trans/cis ratio
6
5
4
3
2
1
0
C
*
*
273
323
373
423
473
T (K)

Figure 4


A
Conversion (%)
0
20
40
60
80
100
B
1b/(1b+2b) (%)
0
20
40
60
C
trans/cis ratio
0
1
2
3
4
5
6
273
323
373
423
473
523
T/K