Effect of sulfur or nitrogen poisoning on the activity and selectivity of Y-zeolite-supported Pt–Pd catalysts in the hydrogenation of tetralin

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The effects of dibenzothiophene or quinoline poisoning on the activity and selectivity of Y-zeolite-supported Pt–Pd catalysts, in the hydrogenation of tetralin at 523 K and 70 bar initial pressure, were studied in a high pressure batch reactor as a function of composition. It was found that both poisons influenced, in very similar ways, the patterns of tolerance to poisons and of *cis/trans* selectivity *vs.* catalyst composition.

KEY WORDS: aromatic hydrocarbons; tetralin; hydrogenation; *cis/trans* selectivity; platinum; palladium; bimetallic catalysts; zeolite support; dibenzothiophene; quinoline; sulfur; nitrogen; poisoning; thiotolerance

1. Introduction

Recently, much interest has arisen in zeolite-supported noble metal catalysts in connection with their application to the hydrogenation of aromatic hydrocarbons contained in petroleum distillates [1,2]. This is because these catalysts have been shown to maintain useful catalytic activity, even in the presence of relatively high amounts of sulfur compounds (up to several hundred ppm, sulfur basis [3,4]), which are always present in petroleum feeds. As a consequence, economically successful processes have evolved, based on this class of catalysts, aimed at reducing the aromatics content of middle-distillate fuels to the levels required by modern environmental legislation [5]. It is known that platinum–palladium bimetallic catalysts perform better than either of the monometallic catalysts in this type of application [6].

It is commonly believed that the large tolerance to sulfur displayed by these catalysts is due to the electron-deficiency of the metal particles when deposited in zeolite cages, caused by a combination of high metal dispersion and electron transfer to the acidic support [7,8]. It is thought that adsorption of sulfur on metal surfaces occurs with electron transfer from the metal to the non-metal, so that the metal–sulfur bond is weakened when the metal particles are electron deficient.

Besides sulfur, petroleum distillates also contain significant amounts of nitrogen compounds, which are also poisons for metal catalysts and are more difficult to remove than sulfur compounds by catalytic hydrotreating. However, very little is know in the detail about the poisoning of aromatics hydrogenation on metals by the nitrogen compounds normally present in petroleum feeds (mostly polyaromatic heterocycles, such as quinoline and indole), nor about the tolerance of noble metals to nitrogen.

In the present work, we compare the effects of nitrogen (as quinoline) and sulfur (as dibenzothiophene) on the activity of a series of Y-zeolite-supported platinum–palladium catalysts, in the hydrogenation of tetralin (1,2,3,4-tetrahydronaphthalene) at high pressure. A potassium-containing platinum/zeolite catalyst was also studied, in order to obtain information on the effect of the support acidity on the catalytic activity and tolerance to sulfur and nitrogen.

Special attention was given to the effects of the bimetallic composition and addition of poisons on the *cis/trans* selectivity of the decalins (decahydronaphthalenes) produced during the hydrogenation reaction. *Cis/trans* selectivity in the hydrogenation of cyclic hydrocarbons has recently been considered as a useful probe for electronic effects in catalysis on metals and metal sulfides [9,10].

2. Experimental

2.1. Preparation of the catalysts

With all catalysts, the same dealuminized zeolite (framework $SiO_2/Al_2O_3 = 22.6$) was used as the support. The support was first ion-exchanged with an ammonium chloride solution, in order to decrease its sodium content to the level of traces. After washing free of chloride and drying at 393 K, the support was ion-exchanged with an aqueous solution of palladium and/or platinum salts. The ion-exchange

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was carried out at room temperature for 24 h and the precursor salts were tetramminepalladium(II) chloride and tetrammineplatinum(II) nitrate, in the case of the bimetallic catalysts, or tetrammineplatinum(II) chloride, in the case of the monometallic platinum catalyst. In all preparations, a ratio of 20 cm^3 of solution per gram of support was used and the concentrations of the precursor salts were chosen so as to obtain a total metal content of 80 μmol metal per gram of catalyst, assuming a 100% yield in the ion-exchange, and the desired proportion between the metals.

After washing free of chloride, filtering and drying at 393 K, the catalysts were calcined under a 300 cm^3/min flow of dry synthetic-air at 723 K for 4 h and reduced at this same temperature under a 300 cm^3/min flow of hydrogen. The catalysts were then purged with a nitrogen current, cooled to room temperature and passivated by allowing air to slowly diffuse into the pre-treatment reactor.

A potassium-containing platinum catalyst was prepared by ion-exchanging the reduced and passivated platinum catalyst with a 12 g/dm^3 potassium chloride solution. The catalyst was then again submitted to the same calcination and reduction procedures described above.

2.2. Characterization

The palladium, platinum and potassium contents of the catalysts were determined by mass-spectroscopy with an inductively coupled plasma source (ICP-MS).

The crystallinity (percentage crystalline material) and the unit cell parameter, a_0, of the zeolite in the catalyst samples were determined by X-ray diffraction.

The micropore surface areas of the catalysts were determined by nitrogen gas adsorption at its boiling point (77 K), using the t-plot method [11]. Before the analyses, the samples were treated at 723 K under static air in an oven and evacuated *in situ* at 573 K for 1 h.

The carbon monoxide chemisorption capacity of the catalysts was measured using a volumetric method. The samples were first treated under a helium flow at 373 K for 1 h, then reduced in flowing hydrogen for 1 h and evacuated at this same temperature before the analysis. The adsorption isotherms were measured at 373 K. For each sample, two isotherms were measured in the equilibrium pressure region of 90–210 Torr, with an intermediate evacuation at the temperature of the experiment. Parallel straight lines were fitted to each of the two sets of data points and the difference between these lines was taken to represent the amount of irreversibly chemisorbed CO.

Both the potassium-containing and the pure monometallic platinum catalysts were characterized by temperature-programmed desorption of ammonia. The experiments were performed in a conventional flow-type apparatus, with thermal conductivity detection. The samples were pre-treated *in situ* under a helium flow at 773 K for 1 h. After cooling to 448 K, pulses of ammonia were injected until saturation of the samples was attained. The desorption was carried out under a 50 cm^3/min helium flow, in the temperature range of 448–773 K, using a linear heating rate of 10 K/min. The amount of chemisorbed ammonia was estimated from comparison of the area of the desorption peak with the area of injected ammonia pulses of known volume.

2.3. Catalytic measurements

In the catalytic measurements, the hydrogenation of 1,2,3,4-tetrahydronaphthalene (tetralin) was used as a model reaction. The experiments were carried out in a high pressure 250 cm^3 batch reactor manufactured by Parr, equipped with a pressure transducer. The feed consisted of 30 cm^3 of tetralin and 70 cm^3 of n-hexadecane. In the poisoning experiments, either quinoline, in an amount corresponding to 400 ppmw nitrogen, or dibenzothiophene, in an amount corresponding to 100 ppmw sulfur, were added to the feed. The experiments were performed at a constant temperature of 523 K and initial pressure of 70 bar.

The catalyst amounts were 100, 300 and 500 mg, respectively, in the experiments with the pure feed, the nitrogen poisoning experiments and the sulfur poisoning experiments. This means that the ratio of poison molecules to total metal atoms in the reactor was in the range of 130–210 in the experiments with nitrogen poisoning and 8–14 in the sulfur poisoning experiments.

The catalysts, sieved to the 74–88 μm range, were placed in the reactor and reduced, under a 200 cm^3/min flow of hydrogen (STP), at 573 K and 14 bar pressure, for 2 h. After cooling to 523 K, the solvent was added and kept under stirring at 523 K and 70 bar pressure for 1 h, which allowed ample time for the temperature in the reactor to stabilize. Next, the tetralin was added and the pressure drop in the reactor due to the hydrogenation reaction began to be monitored as a function of time. In the poisoning experiments, the poisons were introduced with the solvent.

After a fixed pressure drop of *ca.* 14 bar, a sample from the liquid phase was drawn from the reactor and analyzed by gas chromatography, in order to assess catalyst selectivity, and the experiment was interrupted.

By means of a PETROBRAS standard proprietary program for liquid–vapor equilibrium calculations in hydrogen/hydrocarbon mixtures, the pressure drop values were converted to hydrogen uptake and, by assuming that the only reaction in the system was the conversion of tetralin to decalins, tetralin conversion values were calculated as a function of time. The equilibrium calculations were necessary in order to correct the observed pressure drop values for changing solubility of the hydrogen in the liquid as a function of pressure, for partial vaporization of the hydrocarbons, for non-ideality of the gas phase and for changes in the volume occupied by the liquid as the reaction proceeds. The good agreement between the conversion values obtained from the pressure drop measurements and those obtained from the chromatographic analysis demonstrated that the simplifying assumptions caused negligible error in the results.

Catalytic activities were calculated from the initial slopes of tetralin conversion *vs.* reaction time and converted to turnover frequencies (TOF) based on the CO chemisorption capacity of the catalysts, assuming a 1 : 1 ratio of chemisorbed CO to metals [2,12,13].

3. Results

3.1. Characterization results

Table 1 shows the chemical compositions of the catalysts as determined by ICP-MS.

The results for the structural parameters of the zeolite in the different catalysts (unit cell parameter, a_0, and percentage of cystalline material), micropore surface area and CO/metals ratio, determined by chemisorption, are reported in table 2. No significant differences were found, neither in the structural parameters of the zeolite, nor in the micropore surface areas, between the pure support and the end catalysts, showing that no disruption of the zeolite structure nor any major pore blockage occurred during the preparation and pre-treatment of the catalysts, including the potassium-containing sample, Pt–K/Y. The crystallinity values reported in table 2 are generally above 100%. This simply means that the catalysts were more crystalline than the zeolite sample taken as a crystallinity standard and confirms that the zeolite structure was preserved during catalyst preparation.

The dispersions of the supported metals, as estimated from the CO/metals ratio, assuming a 1 : 1 stoichiometry, varied significantly from catalyst to catalyst, but was especially small with the Pt–K/Y sample. This cannot have been due to pore blockage by potassium and was probably caused by poisoning of the platinum surface by this element. The possibility of platinum loss from the catalyst due to exchange with potassium may be excluded from the fact that no decrease in platinum content was observed by ICP-MS after potassium incorporation (*cf.* table 1), as might have been expected from the fact that the exchange with potassium chloride was carried out after reduction of the platinum catalyst, *i.e.*, with the platinum in the metallic rather than in an ionic state. However, the present results do not allow us to exclude that the decrease in dispersion was due to sintering of the metal particles induced by the potassium and/or by the calcination and reduction treatments that followed its incorporation.

Table 1
Chemical composition of the catalysts determined by ICP-MS.

Catalyst	Pd (wt%)[a]	Pt (wt%)[a]	K (wt%)[a]	Pd (mol%)[b]
Pt/Y	–	1.2	–	–
Pt–K/Y	–	1.2	0.9	–
31Pd–Pt/Y	0.19	0.77	–	31
54Pd–Pt/Y	0.41	0.64	–	54
72Pd–Pt/Y	0.30	0.21	–	72
Pd/Y	0.40	<0.01	–	100

[a] Relative to catalyst weight.
[b] Relative to metals.

Table 2
Structural and textural parameters of the catalysts.

Catalyst	a_0[a] (nm)	% crystallinity[b]	MSA[c] ($m^2\,g^{-1}$)	CO/metals[d]
Pt/Y	2.432	99	778	0.50
Pt–K/Y	2.434	113	750	0.15
31Pd–Pt/Y	2.433	119	762	0.29
54Pd–Pt/Y	2.434	122	759	0.28
72Pd–Pt/Y	2.433	123	778	0.45
Pd/Y	2.434	121	772	0.27
Support	2.434	n.a.	761	–

[a] Unit cell parameter.
[b] Percentage of crystalline material in the samples as compared to a standard sample taken to be 100% crystalline.
[c] Micropore surface area measured by the t-plot method.
[d] Measured by CO chemisorption.

Table 3 shows the results for the TPD of ammonia from the platinum/zeolite catalysts. It is clear that, as expected from the basic nature of potassium ions, addition of this element caused a marked decrease, both in the amount of ammonia desorbed and in the temperature of the TPD peak maximum. Therefore, both the number and strength of the acidic sites present in the Pt/Y catalyst were decreased by potassium addition. We assume that the change in acidity is associated with the support, since the acidity of metal/zeolite catalysts originates from the zeolite rather than from the metal.

3.2. Effect of sulfur and nitrogen poisoning on the product distribution during tetralin hydrogenation

In all experiments, the isomeric decalins were by far the main reaction products, along with minor amounts of other substances, identified by GC-MS mainly as normal and methyl-branched alkanes. Except for the decalins and traces of naphthalene, no other products which could be attributed to tetralin conversion were observed in significant amounts. Therefore, the by-products observed arise mostly from decomposition of the n-hexadecane solvent, as confirmed in catalytic experiments with the pure solvent.

Table 4 shows the total percentage areas of these by-products, with respect to the total chromatographic area, for the different experiments. Since a flame ionization detector was used in the gas chromatography, these percentage areas are closely related to percentage weights.

Although the effect of catalyst composition on by-product formation is not easy to rationalize from the results,

Table 3
Results for TPD of ammonia with the platinum/zeolite catalysts.

Catalyst	Desorbed NH_3[a] ($\mu mol\,g^{-1}$)	TPM[b] (K)
Pt/Y	751	650
Pt–K/Y	438	628

[a] Ammonia desorbed in the TPD experiments between 448 and 773 K.
[b] Temperature of the TPD peak maximum.

Table 4
Percentage of total peak area in the gas chromatograms due to by-product formation in tetralin hydrogenation (523 K; 70 bar; solvent *n*-hexadecane).

Catalyst	% area		
	Pure feed	Nitrogen poisoning	Sulfur poisoning
Pt/Y	0.01	0.07	3.8
Pt–K/Y	0.02	0.007	0.3
31Pd–Pt/Y	0.8	0.06	4.7
54Pd–Pt/Y	0.5	0.01	2.1
72Pd–Pt/Y	0.1	0.04	4.6
Pd/Y	0.2	0	n.a.

some clear generalizations may be drawn from the poisoning experiments. Thus, it is apparent that poisoning with quinoline (QUIN) strongly inhibited by-product formation. This indicates that, not surprisingly, these products are principally formed by cracking of the *n*-hexadecane solvent on the acidic sites present on the zeolitic support. On the other hand, poisoning with dibenzothiophene (DBT) strongly enhanced the formation of by-products. This is probably the result of an increase in the Brønsted acidity of the zeolite due to dissociation of the H_2S formed from DBT hydrogenolysis [14].

As might have been expected, the potassium in catalyst Pt–K/Y strongly inhibited the effect of DBT on by-product formation. The reasons for this may be twofold: neutralization of the acidic sites formed by H_2S dissociation and inhibition of the DBT decomposition due to poisoning of the platinum by potassium.

3.3. *Effect of bimetallic composition on catalytic activity, selectivity and tolerance to poisons*

Figure 1 shows the catalytic activity for tetralin conversion, in terms of the turnover frequency (TOF), based on the CO chemisorption capacity of the catalysts after hydrogen reduction, as a function of the composition of the metallic phase, both in the presence and in the absence of the added poisons. Both poisons caused a considerable decrease in the catalytic activity, but the effect of the sulfur compound was much more pronounced, since a smaller concentration of DBT, by a factor of four, caused a three to four times larger effect on activity, as compared to QUIN. With the pure feed, the activities of the bimetallic catalysts were generally smaller than those of the monometallic ones but, in the presence of the poisons, maximum activity was found in the composition range of 50–70% palladium, in agreement with literature data, as far as sulfur poisoning is concerned [2].

The tolerances of the catalysts to sulfur and nitrogen compounds may be measured by the ratio of the rate of reaction in the presence to that in the absence of the poisons. These results are shown in figure 2 and demonstrate that the tolerance patterns are very similar in both cases. This suggests that their modes of action are also similar, which is surprising, since sulfur is usually considered an electron-withdrawing adsorbate, whereas nitrogen is expected to be an electron-donating one, due to the basic character of QUIN and its hydrogenation and hydrogenolysis products, including ammonia.

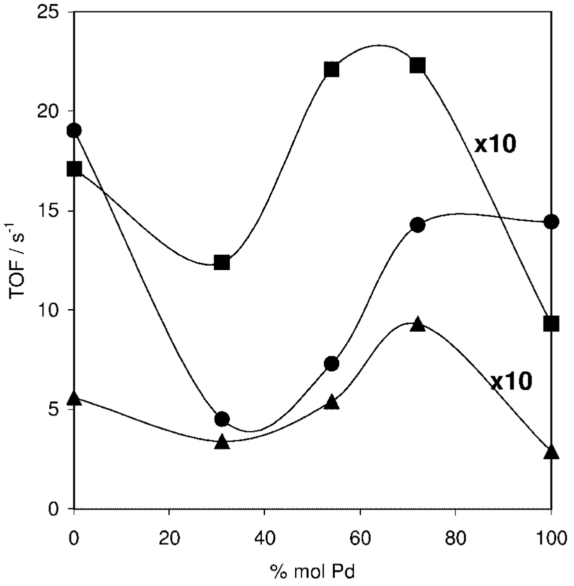


Figure 1. Effect of bimetallic composition and poisoning on the turnover frequency for tetralin hydrogenation on Pd–Pt/zeolite catalysts at 523 K and 70 bar. Values for the poisoning experiments are multiplied by 10. (●) Pure feed, (■) nitrogen poisoning and (▲) sulfur poisoning.

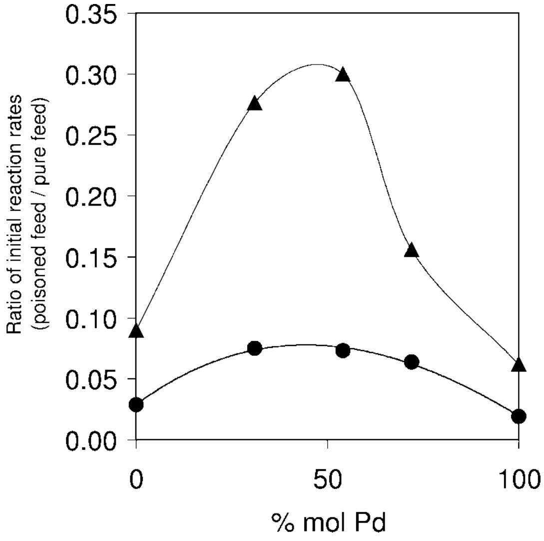


Figure 2. Effect of bimetallic composition on the tolerances to nitrogen (▲) or sulfur (●) of Pd–Pt/zeolite catalysts in the hydrogenation of tetralin at 523 K and 70 bar.

Figure 3 shows the *cis/trans* decalin ratio as a function of composition, for the experiments with the pure feed and with the added poisons. Despite the fact that *trans*-decalin is the thermodynamically favored isomer (equilibrium *cis/trans* ratio *ca.* 0.16 at 523 K [15]), under the present conditions the observed *cis/trans* ratios were much larger than one, in the experiments with the pure feed. Both QUIN and DBT caused a marked decrease in selectivity for the *cis* isomer, approximately by the same factor. It should be stressed that the selectivity values were taken at very closely the same decalin conversion, so the comparison is valid.

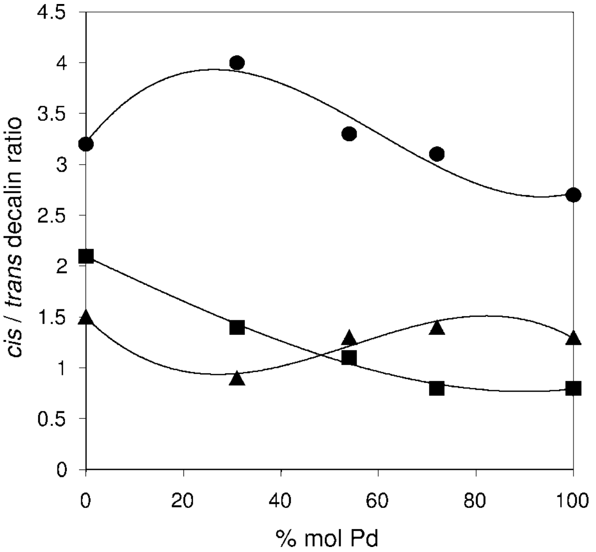


Figure 3. Effect of bimetallic composition and poisoning on the *cis*- to *trans*-decalin ratio in the hydrogenation of tetralin at 523 K and 70 bar on Pd–Pt/zeolite catalysts. (●) Pure feed, (■) nitrogen poisoning and (▲) sulfur poisoning.

Table 5
Catalytic activity results in tetralin hydrogenation with the Pt/zeolite samples (523 K; 70 bar; solvent n-hexadecane).

Catalyst	Initial rate (μmol g^{-1} s^{-1})	TOF (s^{-1})	S tolerance[a]	N tolerance[a]
Pt/Y	590	19.0	0.03	0.09
Pt–K/Y	98	10.7	0.05	0.07

[a] Ratio of the rate in the presence to that in the absence of the added poison.

3.4. Effect of potassium addition on catalytic activity, selectivity and tolerance to poisons

Table 5 summarizes the results obtained with the platinum/zeolite catalysts, in terms of activity per gram of catalyst with the pure feed, the corresponding TOF values and the tolerances to sulfur and nitrogen, measured in the same way as in figure 2. Although the catalytic activity on a weight basis decreased by a factor of about six as a consequence of potassium addition, the TOF value decreased by a factor of only two, due to the simultaneous decrease in the chemisorption capacity of the metal, while the tolerances to sulfur and to nitrogen were practically the same. This is again surprising since, according to the electron-deficiency theory, a decrease in support acidity should cause a simultaneous decrease in the catalyst tolerance to sulfur, due to decreased electron transfer from the metal to the support. Therefore, potassium seems mainly to limit the access of reactant molecules to the platinum surface, rather than changing the properties of the catalytic sites.

The results for the *cis/trans* decalin ratio with the platinum/zeolite catalysts are shown in table 6. With the pure feed, the *cis/trans* decalin ratio did not change with potassium addition, which conforms to the idea that, despite strongly decreasing the acidity of the support, potassium has little influence on the catalytic properties of the platinum sites. Interestingly, however, contrary to what was found with the potassium-free catalysts, poisoning with QUIN or DBT did not cause any changes in the *cis/trans* selectivity.

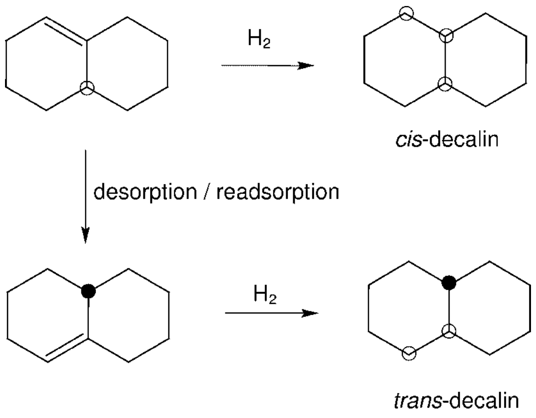
Table 6
Cis/trans selectivity in tetralin hydrogenation with the Pt/zeolite samples (523 K; 70 bar; solvent n-hexadecane).

Catalyst	*Cis/trans* decalin ratio		
	Pure feed	Nitrogen poisoning	Sulfur poisoning
Pt/Y	3.2	2.1	1.5
Pt–K/Y	3.2	2.8	3.1

4. Discussion

The hydrogenation of carbon–carbon double bonds on metals is intrinsically *cis* in character, as both hydrogen atoms must initially attack the adsorbed molecule on the side facing the surface. This has been neatly demonstrated by hydrogenation, deuteration and isotopic exchange experiments with a number of well chosen cyclic molecules [16,17].

According to Weitkamp [16], *trans*-decalin production depends on the formation of $\Delta^{1,9}$-octahydronaphthalene, which is originally formed with the hydrogen atom in position 10 oriented towards the surface, by *cis*-hydrogenation of the remaining double-bonds in the molecule. *Trans*-decalin may then be produced when this intermediate desorbs and is subsequently readsorbed, so that the hydrogen atom in the 10 position becomes oriented away from the surface, as shown in the scheme below:



It is then expected that factors that reduce the strength of interaction of the olefinic intermediate with the surface will also favor selectivity for the *trans* isomer. Schmitz *et al.* have already proposed a similar interpretation to explain the large *cis* selectivity of tetralin hydrogenation on Pt/HY catalysts [10].

Our results concerning the effect of QUIN poisoning on the *cis/trans* selectivity are in line with this expectation: donation of electrons by the basic molecule to the metal surface should reduce its electrophilicity and, therefore, reduce the strength of adsorption of the olefin. The surprising result is that poisoning with DBT caused such a similar effect to that of QUIN on the *cis/trans* selectivity, as well as on the pattern of catalyst activity *vs.* composition. According to Barbier *et al.* [1], co-adsorption of sulfur with olefins should result in an increase in the strength of adsorption of the hydrocarbon.

An explanation for this discrepancy could be that different adsorbed species would predominate on the surface, depending on the poison, operating conditions and catalyst properties. Thus, if conditions are such that the molecules of the poison are completely decomposed to leave only adsorbed sulfur atoms on the surface, then it may be expected that some electron transfer from the metal to the non-metal occurs, due to the difference in electronegativity between the elements. If, on the other hand, the dibenzothiophene is, at least partly, associatively adsorbed, the electron-rich character of the aromatic sulfur compound could predominate and the electron transfer would occur in the opposite direction.

Nevertheless, the pattern of sulfur tolerance *vs.* bimetallic composition found in the present work is similar to the one reported in the literature [2], and therefore electron-deficiency of the metal particles may not be the predominant factor behind it.

From the characterization of mono- and bimetallic Pt and Pd catalysts supported on amorphous silica–alumina, Reinhoudt *et al*. [18] have recently concluded that one important effect of addition of palladium to platinum is to prevent the agglomeration of small metal particles under the influence of H_2S. This would favor the sulfur tolerance of the bimetallic catalysts as compared to the platinum catalyst, due to a larger steady-state active surface area. Since particle agglomeration under an H_2S atmosphere is thought to result from a decreased metal–support interaction [19], it is possible that the same phenomenon happens in the presence of nitrogen compounds. This possibility is currently under investigation in our laboratory.

Another surprising result was the lack of any sizeable effect of potassium addition, and therefore of modification of support acidity, on the sulfur and nitrogen tolerances of the platinum catalyst. Also the effects of poisoning on the *cis/trans* selectivity point to a lack of sensitivity of the catalytic properties of the metal particles to support acidity: the results relating to by-product formation show that DBT addition resulted in an increase, while QUIN addition resulted in a decrease in support acidity, yet both poisons caused essentially the same effect on the *cis/trans* decalin ratio in the Pt–Pd series. The reason for this may be the rather low dispersion of the metals, as estimated from CO chemisorption, pointing to average particle diameters in the region of 2.5–4 nm, whereas Anderson's calculations indicate that only particles smaller than *ca.* 1 nm can be significantly influenced by the support [20].

It is also interesting that, with the Pt–K/Y catalyst, no effect of nitrogen or sulfur poisoning on *cis/trans* selectivity was observed. One possibility to explain this result would be that the poisons do not adsorb on the platinum surface in the presence of potassium, to the same extent as in its absence, and therefore have little influence on the catalytic properties of the metal. However, this cannot be the case here, since one would then expect larger sulfur and nitrogen tolerances for Pt–K/Y than for Pt/Y, which was not observed.

Using Weitkamp's explanation for *cis/trans* selectivity in tetralin hydrogenation, a better interpretation could be that somehow potassium inhibits the turnover of the adsorbed $\Delta^{1,9}$-octalin responsible for *trans*-decalin formation. This cannot be attributed to an electronic effect, since potassium is an electron-donating element and an effect similar to that of QUIN on the *cis/trans* ratio would be expected. If it is assumed that, apart from the desorption–readsorption mechanism proposed by Weitkamp, the turnover of the intermediate olefin involves some sort of rollover mechanism without complete desorption, as proposed long ago to explain the propagation of isotopic exchange with deuterium to both sides of a cyclic molecule [16,17], then it is conceivable that the deposition of potassium on the surface could geometrically block this mechanism and therefore inhibit the production of the *trans* isomer, even if the energetics of the surface–adsorbate interaction is made more favorable by co-adsorption of the poison molecules.

5. Conclusion

Our results have shown that poisoning with quinoline of Y-zeolite-supported platinum and/or palladium catalysts has a considerably smaller effect on the catalytic activity for tetralin hydrogenation than poisoning with dibenzothiophene. However, the patterns of catalytic activity in the presence of the poisons and of tolerance to poisoning as a function of bimetallic composition were very similar in both cases and similar to literature findings relating to the thiotolerance of Pt–Pd catalysts. Since quinoline is clearly an electron-donating molecule, the standard interpretation that electron-deficiency of the metal particles improves the thiotolerance cannot be used to explain the improvement promoted by the Pt–Pd association.

Both poisons influenced the *cis/trans* selectivity of tetralin hydrogenation in very similar ways, which suggests that their mode of action on the catalysts is also similar. Therefore, the conclusion that sulfur poisoning involves electron transfer from the metal to the adsorbate may not be universally valid but may depend on reaction conditions and detailed properties of the catalyst.

No effect of support acidity, as modified by the addition of potassium to the catalysts, could be found on their tolerances to sulfur and to nitrogen. In the present case, this was probably due to the rather large average size of the metal particles, which would render them insensitive to electronic support effects.

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