

Activity Enhancement by the Support in the Hydrogenation of C=C Bonds over Polymer-Supported Palladium Catalysts

Marco Zecca,^{*[a]} Roman Fišera,^[b] Giancarlo Palma,^[c] Silvano Lora,^[d]
Milan Hronec,^[b] and Milan Králik^[b]

Abstract: Four synthetic ion-exchange resins (AH, BH, CH, DH) of different hydrophilic/hydrophobic properties were used as supports for heterogeneous palladium catalysts (A, B, C, D). The resins contained styrene (STY) and 2-(methacryloxy)ethylsulfonic acid (MESA) as the comonomers. Either divinylbenzene (DVB: CH, DH resins) or *N,N'*-methylenebisacrylamide (MBAA: AH, BH resins) were used as the cross-linker. AH contained also *N,N*-dimethylacrylamide (DMAA) as

the third comonomer. The catalysts (Pd 0.25–0.45% *w/w*) were obtained by ion-exchanging the acidic forms of the resins with [Pd(OAc)₂] and reducing palladium(II) with excess sodium borohydride. The use of NaBH₄ also ensured the neutralization of the acidic sites of the supports. No effect of the hydrophilic/hydrophobic properties of the supports

was observed in the hydrogenation of cyclohexene and 2-cyclohexen-1-one in methanol, at 25 °C and 0.5, 1, and 1.5 MPa, respectively. However, catalysts A and B, containing amido groups provided by either DMAA or MBAA, proved to be more active than C and D. The observed activity enhancement was directly proportional to the nitrogen/palladium molar ratio in the catalysts. This finding suggests that amido groups promote palladium through a direct interaction with the metal surface.

Keywords: hydrogenations • ion-exchange resins • palladium catalysts

Introduction

Polymer-based catalysts have been under investigation for at least three decades. Academic research in this field has been mainly focused on the polymer-bound counterpart of homogeneous transition metal catalysts (hybrid catalysts),^[1–3] but no industrial accomplishment has been achieved yet. By contrast, functionalized cross-linked polymers are currently exploited as true heterogeneous catalysts in a number of industrial processes. In particular, ion-exchange resins based on sulfonated polystyrene are employed as acidic catalysts in the

synthesis of alkylmethyl ethers and of bisphenol A.^[4,5] Moreover, heterogeneous palladium catalysts supported onto ion-exchange resins are currently applied to the chemical removal of dioxygen from water, down to the ppb level,^[6] and to the one-pot synthesis of methylisobutylketone from acetone.^[5]

It is well known that the polymeric supports can affect the progress of the catalytic process in several ways. First, the local concentration of chemical species inside polymer-based catalysts can be different from the phase of reactants and products, as the consequence of kinetic, mass transport, and thermodynamic (partition between the catalyst and the reactants/products phases) effects. Thus, the affinity of the reagents and/or products towards the polymeric support plays an important role, not only in polymer-bound phase transfer catalysis,^[7] but also in other cases. For instance, in the partial hydrogenation of benzene over ruthenium catalysts supported onto both inorganic and polymeric carriers,^[8,9] the selectivity depends on the hydrophilic/hydrophobic properties of the supports. Of course, the affinity of reagents and/or products towards the catalytic support depends on the chemical structure of the latter and it must be emphasized that polymeric materials can be much more easily tailored than inorganic solids under this respect. Moreover, in the case of polymer-supported metal catalysts, the functional groups of polymeric support could also interact directly with the active

[a] Dr. M. Zecca
Dipartimento di Chimica Inorganica, Metallorganica e Analitica
Università di Padova, via Marzolo 1, 35131 Padova (Italy)
Fax: (+39)-049-8275223
E-mail: mzecca@chin.unipd.it

[b] Dr. R. Fišera, Prof. M. Hronec, Prof. M. Králik
Department of Organic Technology
Slovak University of Technology
Radlinského 9, 812 37 Bratislava (Slovakia)

[c] Prof. G. Palma
Dipartimento di Chimica Fisica, Università di Padova, via Loredan 2,
35131 Padova (Italy)

[d] Dr. S. Lora
Istituto di Fotochimica e Radiazioni di Alta Energia
C.N.R., via Romea 4, 35020 Legnaro (Padova) (Italy)

component and affect the intrinsic kinetics of the reaction. However, whereas the influence of the polymeric support on the catalytic activity has been studied in some detail for polymer-anchored metal complexes,^[10] relatively little attention has been paid to this issue in connection with polymer-supported metal catalysis.^[11]

For a few years we have been investigating polymer-supported metal catalysts.^[12–17] Our attention was mainly focused on the activity and stability of palladium nanoparticles dispersed inside gel-type resins. We studied the hydrogenation of cyclohexene,^[15] of benzene,^[9] and, in greater detail, the hydrogenation of aromatic nitrocompounds.^[16, 17] In this context, particular attention was paid to the deactivation of the catalyst. Investigation of the molecular mobility inside swollen polymeric catalytic supports and of their morphology at the nanometric scale provided a sound basis for the interpretation of the behavior of polymer-based catalysts.^[14, 15]

Then, our interest shifted to the interactions between the substrate, the support, and the catalytic sites. Due to our previous experience concerning the stability of polymer-based catalysts in the hydrogenation of cyclohexene, we decided to study this reaction with catalysts of different hydrophilic/hydrophobic properties. Moreover, we chose a second substrate of different hydrophilic/hydrophobic features, 2-cyclohexen-1-one, and also studied its hydrogenation on the same catalysts. The hydrogenation of a double carbon–carbon bond conjugated to a keto group is not only of academic interest, but has also a practical relevance: For instance, the hydrogenation of mesityl oxide (4-methyl-3-pentene-2-one) is the second step of the industrial one-pot synthesis of methylisobutylketone, which is carried out over polymer-supported bifunctional palladium catalysts.

We report herein on our results on the hydrogenation of cyclohexene and 2-cyclohexen-1-one, which was found to be insensitive to the hydrophilic/hydrophobic properties of the supports. However, reaction rates appeared to be enhanced by the presence of amido groups in the polymeric carriers.

Abstract in Italian: *Quattro resine per scambio ionico (AH, BH, CH, DH), dotate di proprietà idrofiliche/fobiche differenti, furono utilizzate quali supporti per catalizzatori eterogenei di palladio (A, B, C, D). I catalizzatori furono ottenuti mediante immobilizzazione di palladio(II) per scambio ionico a partire da [Pd(OAc)₂] e sua successiva riduzione con NaBH₄ in eccesso. Fu quindi studiata la reazione di idrogenazione del doppio legame C=C nel cicloesene, nel cicloesanone e nel 2-cicloesen-1-one, a 25 °C e alla pressione di 0.5, 1.0, e 1.5 MPa, rispettivamente, in presenza dei catalizzatori A, B, C, D. Alcuni dei supporti polimerici contenevano gruppi ammidici e i catalizzatori basati su di essi risultarono più attivi degli altri, indipendentemente dalla pressione di idrogeno. Inoltre fu osservato che l'aumento di attività catalitica era direttamente proporzionale al rapporto molare fra azoto e palladio. Ciò suggerisce un effetto di promozione diretta del catalizzatore da parte dei gruppi ammidici eventualmente presenti nel supporto.*

Results and Discussion

Commercially available sulfonated polystyrene/divinylbenzene ion-exchange resins were employed in our previous work on the hydrogenation of 4-nitrotoluene.^[16] These materials are usually fully sulfonated and therefore are highly hydrophilic. At the start of this work we aimed at the preparation of polymer-based catalysts with controlled hydrophilic/hydrophobic properties, as we were interested in ascertaining whether cyclohexene and 2-cyclohexen-1-one showed different affinities towards the supports and how the reaction was eventually affected. Therefore, we prepared four copolymers (AH, BH, CH, DH) of 2-(methacryloxy)ethylsulfonic acid (MESA), which served as the source of both sulfonic groups for ion-exchange and hydrophilic monomeric units, with styrene (STY) which supplied the hydrophobic monomeric units. AH contained also a substantial proportion of a third, hydrophilic comonomer, *N,N*-dimethylacrylamide (DMAA). The resins were obtained in their acidic forms. Previous experience showed that i) cross-linked copolymers of MESA and STY synthesized in *N,N*-dimethylformamide (DMF) solution contain substantial amounts of both the solvent and water,^[14] and ii) whereas STY copolymerizes almost quantitatively, MESA does not. This also occurred in the synthesis of AH, BH, CH, and DH, as confirmed by their elemental analyses (C, H, N, S, Table 1). The elemental analyses, evaluated in a similar way as in ref. [13], revealed that the newly formed resins contained 3–10% (w/w) of DMF and 5–10% (w/w) of water. The relevant data are reported in Table 1 and Table 2 and the chemical structure of the resins is sketched in Scheme 1.

The solvent compatibility of the four resins, which depends on their hydrophilic/hydrophobic properties, was assessed from the bulk expanded volumes values in several solvents, which are reported in Figure 1. Comparable values of bulk expanded volumes were also obtained for the catalysts after

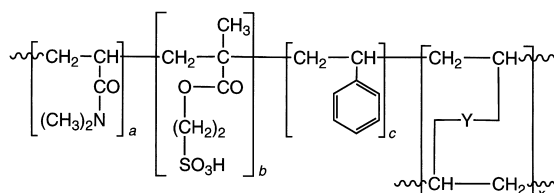
Table 1. Compositions (weight %)^[a] of resins AH, BH, CH, and DH.

	AH		BH		CH		DH	
	calcd	found	calcd	found	calcd	found	calcd	found
1 % C	54.37	54.87	69.29	68.68	57.41	56.97	72.02	72.83
2 % H	7.78	7.52	7.22	7.07	6.98	6.64	7.37	7.37
3 % N	5.46	5.43	1.61	1.51	0.53	0.51	0.58	0.58
4 % S	4.95	4.97	4.52	4.45	7.36	7.38	4.02	3.99
5 % water	10		4.8		9.8		6.0	
6 % DMF	10		4.8		3.2		3.6	

[a] The expected elemental weight percentages were calculated on the assumption that the resins contained water and DMF in the proportion reported in entries 5 and 6 and that polymerization yields were as reported in Table 2.

Table 2. Polymerization yields (mol%) for each comonomer in the synthesis of resins AH–DH.

	AH	BH	CH	DH
STY	90	100	100	100
MESA	85	85	80	80
DVB	–	–	100	100
DMAA	100	–	–	–
MBAA	100	100	–	–



	a	b	c	x	Y
AH	0.33	0.26	0.37	0.04	-C(O)NHCH ₂ NHC(O)-
BH	0	0.28	0.78	0.04	-C(O)NHCH ₂ NHC(O)-
CH	0	0.37	0.58	0.05	-C ₆ H ₄ -
DH	0	0.17	0.78	0.05	-C ₆ H ₄ -

Scheme 1. Chemical structures of resins AH, BH, CH, DH.

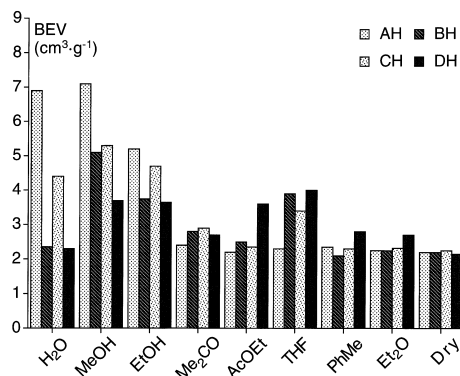
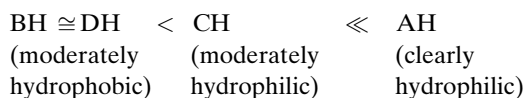


Figure 1. Bulk expanded volumes (BEVs) of resins AH, BH, CH, and DH.

reduction with NaBH₄. The data in Figure 1 indicate that hydrophilicity increases in the following order:



This sequence is in agreement with the expectation that the lower the proportion of STY in the resin, the higher its hydrophilicity.

After the synthesis, the resins were exchanged with palladium(II), which was subsequently reduced to the metal with excess NaBH₄ in ethanol. This reduction procedure ensures a homogeneous metal distribution throughout the volume of the catalyst beads and the removal of DMF adsorbed in the support.^[13]

In order to get insight about the relative affinities of cyclohexene and 2-cyclohexen-1-one, we measured the bulk expanded volumes (BEVs) of resins AH, BH, CH, and DH swollen with mixtures of methanol with cyclohexene and cyclohexanone, respectively, at different compositions. Cyclohexanone was taken as a mimic of the unsaturated cyclic ketone and used instead. The results are illustrated in Figure 2.

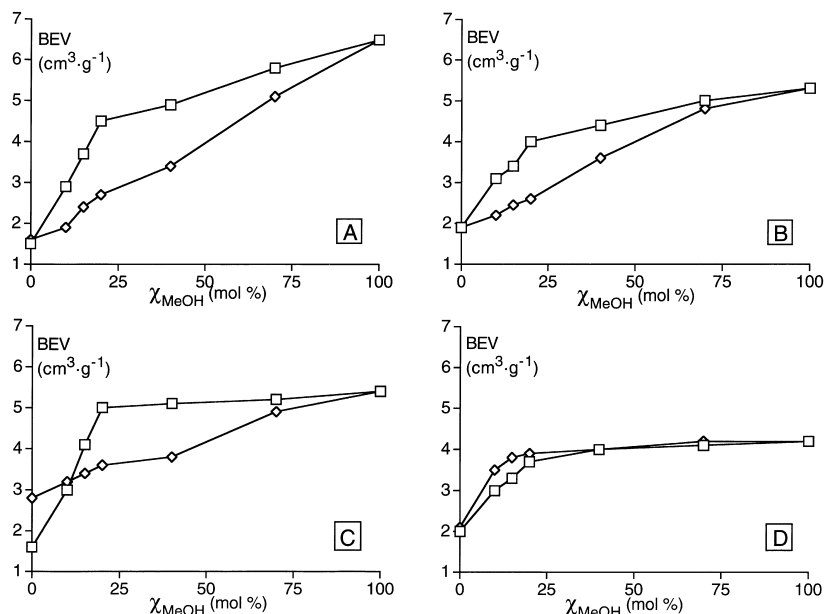


Figure 2. Bulk expanded volumes of catalysts A, B, C, and D in cyclohexene/methanol mixtures (squares) and 2-cyclohexanone/methanol mixtures (diamonds) versus mixtures' composition.

As shown in Figure 2, the BEV value of all investigated resins was much higher in pure methanol than in both pure cyclohexene and cyclohexanone, which gave generally negligible swelling of the polymer network, if any. This is probably due to the fact that whereas in methanol the -SO₃H groups are extensively dissociated, in cyclohexene or cyclohexanone ionic pairs are strongly held together. Thus, in methanol the electrostatic repulsion among the fixed negative ionic charges helps swelling. However, the BEV of BH in methanol was the highest for this resin, but it was practically negligible in water (Figure 1). This indicates that in general the electrostatic repulsion among fixed charges is not the only factor aiding swelling. Thus, methanol must also be able to interact considerably with the hydrophobic domains, different from water. This highlights the amphiphilic nature of methanol.

Resin DH showed the same behavior upon swelling in methanol/cyclohexene and methanol/cyclohexanone mixtures of different compositions. In fact, the changes of BEV as a function of the molar fraction of methanol (χ_{OH}) were practically the same in both cases. The BEV of DH in pure methanol was the lowest among the investigated resins and, moreover, it was very poorly swollen by both pure cyclohexene and cyclohexanone. This highlights the hydrophobic nature of DH and the generally poor swelling power of cyclohexene and cyclohexanone. When χ_{OH} was increased from 0 up to about 0.25, the BEV reached practically the same value as in pure methanol. Further increase of χ_{OH} did not further change the BEV value. This suggests that for DH the interaction of methanol, cyclohexene, and cyclohexanone are relatively weak hence the resin always takes up selectively the better swelling agent available, that is methanol.

The behavior of CH swollen with methanol/cyclohexene mixtures was qualitatively the same. However, as BEV in pure methanol is higher than for DH, the initial increase was steeper for CH and furthermore the BEV increased almost linearly. These findings point to the same direction as before: Due to very weak interaction of cyclohexene with the resin,

methanol was absorbed preferentially to allow the largest possible swelling of the polymer network.

By contrast, the behavior of CH swollen with methanol/cyclohexanone mixtures was totally different. When χ_{OH} was progressively increased, a practically linear steady growth of the BEV value was observed in the whole composition range ($\chi_{\text{OH}} = 0-1$). This indicates that some specific interaction occurs between CH and cyclohexanone. Moreover, the BEV in pure cyclohexanone ($\chi_{\text{OH}} = 0$) was considerably higher than in pure cyclohexene, which also suggests that the cyclic ketone has actually a higher affinity towards CH than the cyclic alkene.

When resins AH and BH were swollen with methanol/cyclohexene mixtures, their behavior resembled that of CH and DH. However, the BEV did not reach the value observed in pure methanol at χ_{OH} as low as 0.25–0.30. After that point a further linear, albeit smoother, increase of the BEV values was recorded up to $\chi_{\text{OH}} = 1$. This suggests that the cyclohexene interaction with AH and BH could be slightly stronger than with CH and DH.

On the other hand, when resins AH and BH were swollen with methanol/cyclohexanone mixtures, their behavior was qualitatively the same as that of CH. Also in this case the data indicate that cyclohexanone has a higher affinity than cyclohexene towards AH and BH, respectively.

Further information concerning methanol–support substrate affinity was obtained from the comparison of solute concentrations, before and after swelling, in methanol/cyclohexene and methanol/cyclohexanone mixtures used to swell the catalysts. As described in the experimental, they were actually swollen in a known amount of “solvent” and, after equilibration, a known amount of “solute” was added to the suspension (in the following discussion “solvent” and “solute” are the most and the least abundant component, respectively, of the swelling mixture, see also Experimental Section). The molar fraction of the “solute” before swelling was not measured directly, but it was calculated as described in the Experimental Section. On the other hand, molar fractions after swelling were directly measured in the liquid phase in equilibrium with the swollen polymer.

We carried out two sets of experiments, where methanol played the role of either the “solute” (Table 3) or the “solvent” (Table 4).

When methanol was used as the “solute”, it was added to the resins previously swollen in cyclohexene, cyclohexanone, or 2-cyclohexen-1-one. Its addition generally brought about an appreciable increase of the BEV of the support, as it was expected from the BEV measurements. The molar fraction of methanol (χ_{OH}) in the free liquid phase was always found significantly lower after swelling than before, that is the partition coefficient of methanol is always much greater than one, although it was not possible to calculate its value from our data.^[18] This clearly indicates that, in general, methanol was preferentially driven into the polymer network, probably as the consequence of stronger methanol–support interaction with respect to the “solvent”–support interaction. This finding is completely coherent with BEV values found for the resins in methanol, cyclohexene, and cyclohexanone.

As for the relative affinity of cyclohexene and cyclohexanone for the various materials, the data of Table 3 show that

Table 3. Mole fractions (% , χ) of methanol, before^[a] and after^[b] swelling of catalysts A, B, C, and D with a 1M methanol solution in a) cyclohexene, b) cyclohexanone, and c) 2-cyclohexen-1-one.

	mass of catalyst (dry, mg)	mass of methanol (mg)	χ after	
			before	after
a) cyclohexene				
A	107.6	34.6	9.7	3.3
B	100.0	32.1	9.4	3.3
C	98.3	37.8	10.9	2.8
D	102.4	35.0	10.1	2.1
b) cyclohexanone				
A	118.9	31.2	9.1	6.3
B	109.1	36.0	10.7	7.2
C	103.0	31.2	9.5	6.9
D	96.2	40.8	12.1	0.7
c) 2-cyclohexen-1-one				
A	101.4	32.3	12.2	3.7
B	105.6	37.0	12.3	3.2
C	103.7	33.0	10.2	3.1
D	101.2	41.1	13.1	0.9

[a] Theoretically calculated from the employed amounts of methanol and solvent; [b] measured in the liquid phase by GC (see also Experimental Section).

for catalyst D the decrease in χ_{OH} for the cyclohexanone solution was not very different from those observed for the cyclohexene and 2-cyclohexen-1-one solutions. This indicates that the relative affinities of cyclohexene and cyclohexanone (and 2-cyclohexen-1-one) towards the support of catalyst D are similar, in agreement with the BEV data discussed above. Moreover, for each kind of solution the decrease in χ_{OH} for catalyst D was always larger than for the other materials. These facts are also consistent with the hypothesis that the partition process is mainly driven by swelling in the absence of strong interactions of methanol, cyclohexene, cyclohexanone, and 2-cyclohexen-1-one with the support.

For all the other catalysts (A, B, C) the decrease in χ_{OH} for the cyclohexanone solution was always smaller than in the cyclohexene solution. This finding indicates that cyclohexanone competes “for the polymer” with methanol better than cyclohexene, which is also fully coherent with the hypothesis that cyclohexanone has a higher affinity than cyclohexene towards the polymeric supports of catalysts A–C. The decrease in χ_{OH} values observed for the methanol solution in 2-cyclohexen-1-one were comparable with those found for solutions of methanol in cyclohexene, thus indicating a relatively poor affinity of 2-cyclohexen-1-one towards the investigated materials. Incidentally, this finding shows that cyclohexanone is not an appropriate mimic of 2-cyclohexen-1-one.

The data of Table 4 were obtained when methanol was used as the “solvent”. In this case, the molar fractions of the “solute” (cyclohexene, cyclohexanone, and 2-cyclohexen-1-one) in the free liquid phase in equilibrium with the swollen resins were practically the same as before swelling. This is again in agreement with the hypothesis that methanol interacts much more strongly with the supports than the cyclic alkene and ketones. In the presence of a large excess of the alcohol, BEVs were very close or equal to those observed in pure methanol. This was apparently the case when the

concentration of cyclohexene was 1M ($\chi = \text{ca. } 4 \times 10^{-2}$; Figure 2), the same as in the catalytic tests discussed below. This indicates that under these conditions the polymer chains are fully solvated by methanol molecules. This prevents the interaction of the "solute" with the polymeric support, independently of its nature. Hence, it can almost freely flow from the liquid phase to the swollen polymer and its partition coefficient approaches unity.

An appreciable decrease, albeit not large, of the molar fraction of both cyclohexanone and 2-cyclohexen-1-one was observed for catalyst C (Table 4), which is based on the

Table 4. Mole fractions (% , χ) of a) cyclohexene, b) cyclohexanone, and c) 2-cyclohexen-1-one before^[a] and after^[b] swelling of resin-based catalysts A, B, C, D with a 1M solution in methanol.

mass of catalyst (dry, mg)	mass of a), b), or c), respectively (mg)	χ		
		before	after	
a) cyclohexene				
A	98.4	130	5.6	5.6
B	104.2	155	6.4	6.3
C	104.0	142	5.1	5.1
D	98.0	157	4.5	4.6
b) cyclohexanone				
A	99.4	137	5.4	5.2
B	104.3	135	4.9	5.0
C	102.0	152	5.8	5.1
D	83.6	145	5.3	5.4
c) 2-cyclohexen-1-one				
A	102.2	149	5.6	5.5
B	101.6	157	5.7	5.6
C	101.8	152	5.3	4.9
D	97.0	145	5.2	5.1

[a] Theoretically calculated from the employed amounts of methanol and solvent; [b] measured in the liquid phase by GC (see also Experimental Section).

support with the highest content of sulfonic groups. This finding suggests that the main interaction of cyclohexanone and 2-cyclohexen-1-one with supports generally involves the ionic sites of the latter, with effects appearing only at relatively high content of the sulfonic groups. The particular affinity of cyclohexanone towards resin CH, highlighted by the relatively high BEV value of this material in the pure ketone, also supports this idea.

The catalytic tests were carried out under kinetic regime, as checked with catalysts particles of different sizes (0.1–0.14 mm and 0.14–0.18 mm). Hence, mass transport phenomena are not rate determining in the tests described herein. Therefore, the effects of swelling, on which diffusion in polymeric materials dramatically depends, can be neglected. Under kinetic control, the concentration of the involved species (reactants, products) is homogenous throughout the catalyst and depends only on the respective affinities, which depend in turn on the hydrophilic/hydrophobic properties of the supports. Accordingly, they could be expected to affect the concentration of reactants and products thermodynamically rather than kinetically. In fact, if two substrates are adsorbed to different extents, rather than at different rates, onto a supported catalyst, different rates of the catalytic process could be eventually observed because of their different concentration at the active sites, even assuming that the catalyst is equally active for both.

Our data on the partition of cyclohexene and 2-cyclohexen-1-one demonstrate that both has similar affinities towards each of the employed catalysts and therefore we need not worry about this possibility. Moreover, the results described above show that at a 1M concentration in methanol, even substrates of different affinity are distributed to the same extent between the liquid and swollen polymeric phase, due to the levelling effect of very strong methanol–support interactions. As for metal leaching, we did not observe loss of the metal in any case investigated.

The initial relative hydrogenation rates at 0.5, 1.0, and 1.5 MPa for both substrates are reported in Table 5 (the values

Table 5. Initial reaction rates ($\text{mols}^{-1}\text{kg}_{\text{Pd}}^{-1}$) and relative initial reaction rates (in brackets) with respect to the rate over the catalysts C, for cyclohexene (ene) and 2-cyclohexen-1-one (one).

Catalyst	Substrate					
	ene			one		
	0.5 MPa	1 MPa	1.5 MPa	0.5 MPa	1 MPa	1.5 MPa
A	80 (2.1)	102 (2.2)	114 (2.3)	84 (2.1)	104 (2.1)	117 (2.6)
B	52 (1.4)	68 (1.5)	76 (1.5)	54 (1.4)	64 (1.3)	72 (1.4)
C	38 (1)	46 (1)	55 (1)	40 (1)	49 (1)	54 (1)
D	44 (1.2)	52 (1.1)	58 (1.2)	46 (1.2)	53 (1.1)	57 (1.2)

were calculated from the first derivative of the quadratic polynomial fitting of points from 0 up to 70% of the conversion). The data show that the hydrogenation rates of both substrates change to a very similar extent from a catalyst to another.

In addition, if the ratios of the initial hydrogenation rates of 2-cyclohexen-1-one and cyclohexene (Table 6) are compared for each catalyst at different pressures, it appears that the substrate which is hydrogenated faster depends on the pressure of hydrogen. All these data confirm that the hydrophilic/hydrophobic properties of the support do not play an important role.

Table 6. Initial rate over catalysts A, B, C, and D of 2-cyclohexen-1-one hydrogenation relative to cyclohexene.

Cat	0.5 MPa	1 MPa	1.5 MPa
A	1.05	1.02	1.03
B	1.04	0.94	0.95
C	1.05	1.07	0.98
D	1.05	1.02	0.98

Catalyst B appears to be generally a little more active than D. The most important difference between them is the nature of the cross-linker: Whereas D contains divinylbenzene, B contains methylene-bis-acrylamide. Moreover, catalyst A, which incorporates a substantial amount of *N,N*-dimethylacrylamide, is by far the most active one, hence we can argue that increasing the amount of nitrogen in the resins enhances the catalyst activity.

In fact, the rate enhancement can be quantitatively correlated to the molar ratio between nitrogen and palladium in the catalysts. The true nitrogen content, that is without the contribution of DMF, which is removed during the reduction of palladium(II), can be obtained from the elemental analyses

data of Table 1. If the initial hydrogenation rates of cyclohexene and 2-cyclohexen-1-one over catalysts A, B, and C (the latter assumed as a typical unpromoted catalyst) are plotted as a function of the respective nitrogen/palladium molar ratios, the curves depicted in Figure 3 are obtained.

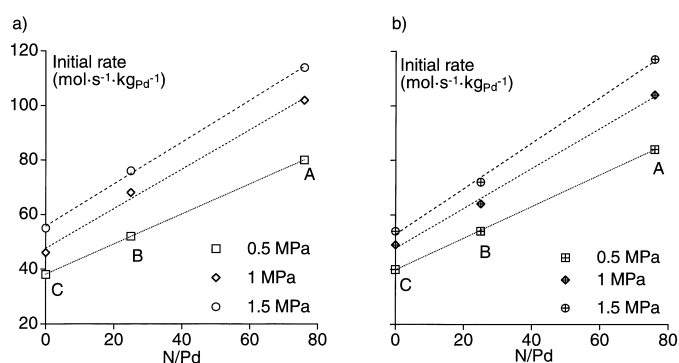


Figure 3. Initial hydrogenation rate of cyclohexene a) and 2-cyclohexen-1-one b) over catalysts A, B and C versus nitrogen/palladium (N/Pd) molar ratio in the catalysts.

Although some care is necessary in drawing conclusions (each curve contains only three points), the results are apparently the same at all of the investigated pressure values: Hydrogenation rates are linearly dependent on the N/Pd ratio in the catalysts for both substrates. The direct proportionality of the reaction rates to N/Pd ratios indicates that nitrogen from the amido groups of DMAA and MBAA directly promotes the palladium catalyst. Moreover, amido groups from DMAA and from MBAA are comparably effective in promoting the catalysts, in that the only source of amido groups in catalyst B is the cross-linker.

Since mechanistic details of the reaction are not known yet, we cannot decide whether the effects of this interaction are mainly electronic or steric. However, according to the theory of catalysis over metals and alloys,^[19] electronic effects seem to be dominant. We have already argued that the promoting effect depends on a direct interaction of amido groups with the palladium crystallites. We can further speculate that a donor–acceptor interaction between the nitrogen atoms, which possess free electron pairs, and palladium atoms of the surface likely occurs. A similar “coordinative” interaction between the surface atoms of a polymer-protected platinum colloid and the nitrogen atoms of amido groups from the protecting poly(*N*-isopropylacrylamide) matrix has been recently proposed.^[11b] This could build up electron density on the metal, thus making a process like the dissociative adsorption of dihydrogen easier (Figure 4).

Conclusion

The differences in hydrophilic/hydrophobic properties of the resins in the investigated resin-supported palladium catalysts did not affect the hydrogenation rate of cyclohexene and

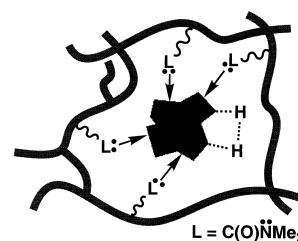


Figure 4. Schematic representation of the interaction of the surface of a palladium crystallite with the amido groups from the polymeric support.

2-cyclohexen-1-one at 0.5, 1.0, and 1.5 MPa in methanol at 25 °C. On the one hand, it was observed that when the catalysts were added to the reaction mixtures (1M solutions of the substrates), only methanol interacted with the polymeric chain of the resins and this quenched any substrate–support interaction. On the other hand, we get some evidence that anyway the substrates have similar affinities towards the catalyst resins.

We have serendipitously found that the presence of amido groups in the polymeric supports enhances the rate of the chemical reaction. Under the employed conditions the rate enhancement is proportional to the molar ratio between nitrogen in the support and the active metal. This result indicates that it is possible to “play” with the functional groups of polymeric carriers of polymer-supported metal catalysts not only to match their physico-chemical properties to the nature of solvent, reagents, and products, but also to change directly the intrinsic reactivity of the active metal.

Experimental Section

Materials and methods: Cyclohexene, methanol (MeOH), ethanol (EtOH), toluene (tol), acetone (Me₂CO), tetrahydrofuran (THF), diethyl ether (Et₂O), and ethyl acetate (AcOEt) were supplied from Lachema, Brno, Czech Republic. MBAA, DMAA, and DMF were obtained from Aldrich. Reagent-grade MESA, STY, and DVB were supplied by Strem, Newburyport (MA), USA. 2-Cyclohexen-1-one, sodium borohydride, and palladium(II)acetate were purchased from Fluka. All the products were employed as received, with the exception of cyclohexene and 2-cyclohexen-1-one, which were purified prior to use by distillation. Atomic absorption measurements for Pd determination were performed on a Carl Zeiss Jena AAS 3 atomic absorption spectrometer.

Synthesis of polymers AH, BH, CH, DH: The polymers were prepared by γ -ray irradiation of DMF solutions of the monomers at room temperature, as described in ref. [13]. The compositions of the polymerization mixtures are given in Table 7.

Solvent compatibility of AH, BH, CH, DH: The solvent compatibility of the resins was evaluated from their bulk expanded volumes (BEVs) in different solvents as described in ref. [13].

Table 7. Composition of the monomer mixtures for the synthesis of resins AH, BH, CH, and DH.

Resins	Monomer ^[a]				
	ST	MESA	DMAA	MBAA	DVB
AH	38.0	27.8	30.3	3.9	–
BH	74.4	21.7	–	3.9	–
CH	53.3	41.9	–	–	4.8
DH	74.7	20.2	–	–	5.1

[a] mol%.

Preparation of catalyst A, B, C, D: The palladium catalysts supported on polymers were prepared starting from the acid form of the parent resins by exchanging them with the appropriate amount of palladium(II) acetate in 1:1 acetone/methanol. Each product was washed with methanol and reduced prior to use with 0.066 M sodium borohydride in ethanol (10 equiv) for 1 h, then washed with methanol, and activated with hydrogen in methanol at 25 °C and 0.5 MPa for 10 min in the hydrogenation reactor. After the activation, the catalyst was washed three times with methanol and immediately used for the catalytic tests. The analysis for palladium was carried out as described previously,^[17] and yielded the following metal content (w/w, %): A: 0.460, B: 0.266, C: 0.362, D: 0.371

Partition measurements: Catalysts A, B, C, D were swollen with mixtures of methanol with cyclohexene, cyclohexanone, and 2-cyclohexen-1-one, respectively. After equilibration, the molar fraction of the most dilute species were measured in the liquid phase. Two sets of experiments were carried out for each catalyst, which had been swollen with:

i) solutions of methanol ("solute") in cyclohexene, cyclohexanone, and 2-cyclohexen-1-one ("solvent"), respectively;

ii) solutions of cyclohexene, cyclohexanone, and 2-cyclohexen-1-one ("solute"), respectively, in methanol ("solvent").

The dry catalyst (ca. 100 mg) was put into a weighed stoppered flask. After weighing the flask with the solid within, a defined volume of "solvent" (see above) was poured into the flask, which was stoppered and weighed again. The amount of added "solvent" was slightly higher than the minimum required for complete swelling. Thus, after deposition of the swollen material only a little proportion of "solvent" was present as free liquid. The catalysts were let to swell for 12 h. Then, the "solute" was added and the flask was weighed again. The amount of "solute" was such to set its concentration, with respect to the overall volume of the "solvent", to about 1 M. The exact amounts of the catalyst, "solvent", and "solute" were measured as the difference between consecutively measured weights. After 6 h of occasional stirring, the swollen catalyst was let to settle. Then, samples of the liquid were taken for GC analysis after which the mole fraction of the "solute" was determined (molar fraction after swelling). In view of the experimental procedure, it was not possible to measure the molar fraction of the "solute" before swelling. This was calculated from the masses of "solvent" and "solute".

Catalytic tests: The catalytic tests were performed in a 25 cm³ glass-lined stainless steel reactor connected with a flexible metal capillary to an apparatus for measuring the hydrogen consumption at constant pressure similar to that described in ref. [13]. Typically, 6 cm³ of a 1 M solution cyclohexene or 2-cyclohexen-1-one in methanol were employed, with the amount of catalyst required to get an analytical concentration of palladium equal to 0.125 (1.5 MPa) or 0.25 (0.5 and 1 MPa) mol m⁻³. The reactor was loaded with the freshly activated catalyst, followed by the reactants, and hydrogen, put in a thermostated oil bath and vigorously shaken at about 12 Hz. The end of hydrogen take-up was considered as the end point of the reaction. The reaction products in the final reaction mixture were also analyzed by GC to confirm the total conversion of the substrate.

Acknowledgements

This work was supported by funds of the project SK-95/195/205: Ecologically clean technologies for refinery, chemical and petrochemical industry.

- [1] G. Parshall, *Homogeneous Catalysis*, 1st ed., Wiley, New York, **1980**, p. 227.
- [2] F. R. Hartley, *Supported Metal Complexes*, Reidel, Dordrecht, **1985**.
- [3] H. Hirai, N. Toshima in *Tailored Metal Catalysts* (Ed.: Y. Iwasawa), Reidel, Dordrecht, **1986**, p. 87.
- [4] P. M. Lange, F. Martinola, S. Oeckl, *Hydrocarbon Process* **1985**, 51.
- [5] H. Widdecke in *Synthesis and separations using functional polymers* (Eds.: D. C. Sherrington, P. Hodge), Wiley, Chichester, **1988**, pp. 149–179.
- [6] R. Wagner, P. M. Lange, *Erdöl, Erdgas, Kohle* **1989**, 105, 414.
- [7] M. Tomoi, W. T. Ford in *Synthesis and separations using functional polymers* (Eds.: D. C. Sherrington, P. Hodge), Wiley, Chichester, **1988**, p. 181.
- [8] a) J. Struijk, M. d'Angremond, W. J. M. Lucas-de Regt, J. J. F. Scholten, *Appl. Catal. A.: General* **1992**, 83, 263; b) J. Struijk, R. Moene, T. van der Kamp, J. J. F. Scholten, *Appl. Catal. A.: General* **1992**, 89, 77.
- [9] M. Hronec, Z. Cvengrošova, M. Králík, G. Palma, B. Corain, *J. Mol. Catal.* **1996**, 105, 25.
- [10] P. Hodge in *Synthesis and separations using functional polymers* (Eds.: D. C. Sherrington, P. Hodge), Wiley, Chichester, **1988**, p. 43.
- [11] a) P. E. Garrou, B. C. Gates in *Synthesis and separations using functional polymers* (Eds.: D. C. Sherrington, P. Hodge), Wiley, Chichester, **1988**, p. 123; b) C.-W. Chen, M.-Q. Chen, T. Serozawa, M. Akashi, *Chem. Commun.* **1998**, 831.
- [12] M. Králík, M. Hronec, S. Lora, G. Palma, M. Zecca, A. Biffis, B. Corain, *J. Mol. Catal.: A Chem.* **1995**, 97, 145–155.
- [13] M. Králík, M. Hronec, V. Jorík, S. Lora, G. Palma, M. Zecca, A. Biffis, B. Corain, *J. Mol. Catal.: A Chem.* **1995**, 101, 143–152.
- [14] M. Zecca, M. Králík, M. Boaro, G. Palma, S. Lora, M. Zancato, B. Corain, *J. Mol. Catal.: A Chem.* **1998**, 129, 27–34.
- [15] M. Králík, M. Zecca, P. Bianchin, A. D'Archivio, L. Galantini, B. Corain, *J. Mol. Catal.: A Chem.* **1998**, 130, 85–93.
- [16] R. Fišera, M. Králík, J. Annus, V. Krátky, M. Zecca, M. Hronec, *Collect. Czech. Chem. Commun.* **1997**, 62, 1763–1775.
- [17] M. Králík, R. Fišera, M. Zecca, A. A. D'Archivio, L. Galantini, K. Jeřábek, B. Corain, *Collect. Czech. Chem. Commun.* **1998**, 63, 1074–1088.
- [18] Some intrinsic problems arise when the partition of a species occurs between a liquid and a polymer which swells in contact with the liquid itself. First, not only the overall volume of the polymer phase changes upon swelling, but it also depends on the compositions of the liquid phase, sometimes dramatically, as it is shown also in this paper. This makes difficult to assess the volume of the polymer phase, in which concentrations must be determined. In fact, BEV is not suitable, because it also includes the interparticle volume, which does not belong to the swollen polymer phase. Moreover, it is matter of debate whether the concentration of solutes in the swollen polymer phase must be calculated with respect to its overall volume or to the fraction which is not occupied by the polymer chains, that is in the volume available to solvent molecules. Also in this case, the assessment of this volume in swellable polymers is not an easy task. It has not a fixed value, like in rigid porous solids, but it depends on the swelling properties of the polymer network. The volume fraction occupied by the polymer chains is a (decreasing) function the swelling volume: The larger the latter, the smaller the former.
- [19] V. Ponec, G. C. Bond, *Catalysis by Metals and Alloys*, Elsevier, Amsterdam, **1995**.

Received: October 7, 1999 [F2069]