Model Pumices Supported Metal Catalysts

II. Liquid Phase Selective Hydrogenation of 1,3-Cyclooctadiene

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The catalyzed, selective hydrogenation, in liquid phase, of 1,3-cyclooctadiene was studied on a series of Pd catalysts supported on natural pumice, model pumices (with variable content of alkali metal ions), silica, and sodium-doped silica. At constant pressure of H_2 (1 atm.) the reaction follows a zero-order kinetic for all the Pd catalysts. At low metal dispersion ($D_x < 20\%$), Pd/pumice catalysts exhibit higher activity as compared to Pd/silica catalysts; the turnover frequency is maintained even at high metal dispersion in Pd/pumice but Pd/silica and Pd/model pumices without alkali ions show a decrease in activity. At increasing D_x, the binding energy shift of Pd $3d$ level is negative in Pd/pumice and positive in Pd/silica with respect to unsupported Pd metal. The different performances of the Pd/pumice catalysts are explained by the presence of alkali metal ions in the framework of the support. Addition of sodium ions to Pd/silica catalysts produces a negative shift of the binding energy, but the activity is not improved because the number of active sites diminished due to decoration of palladium particles by sodium ions. The Pd catalysts with alkali metal ions in the support are resistant to air oxidation. In Pd catalysts containing alkali metal ions the selectivity to cyclooctene is practically 100% and the constant rates ratio k_1/k_2 is more than 1000 with a maximum at dispersion 35–40%, whereas the selectivity in Pd catalysts without alkali metal ions decreases continuously at increasing dispersion.

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INTRODUCTION

Some recent results on pumice-supported metal catalysts (1–7) showed that electronic influences by the support can be important and can produce substantial improvement in the activity and selectivity of supported palladium catalysts (2–4, 6). It is now established that the alkali metal ions (Na^+ and K^+) present in the framework of natural pumice (8, 9) increase the electron density on the supported metal (10, 11) depending on metal dispersion (12). The alkali metal ions in the framework of pumice appear to decrease the adsorption of CO (13) but so far there have been no studies dealing with a definitive amount of alkali metal ions producing the best activity/selectivity performances in the

catalytic hydrogenation of a particular substrate. The recent application of the gel technique (14) to the synthesis of pumice-like materials with different alkali metal ions content allows one to obtain a series of Pd catalysts with a large range of alkali metal ions/palladium atomic ratios R aiming to find selective catalysts for particular reactions. Selectivity is indeed important for the purification of alkene feedstocks for the polymer manufactures from small amounts of alkadienes and alkynes at ppm levels (15–17). Although the addition of ionic salts (18) and traces of other metals (Si, Ge, Pb, Mn) (16, 19–21) to the Pd/Al_2O_3 catalyst, usually employed in industrial processes, improved the selectivity, at present carbon monoxide is most often used for such purpose (16, 21, 22). This reagent, besides being toxic, does not inhibit the formation of the so-called "green oil," an oligomer fraction which decreases the value of the monomer. The development of a selective catalyst which does not need the addition of carbon monoxide appears extremely important. The good results of selectivity so far obtained (6) with natural pumice as an alternative support for a palladium catalyst (1) might be improved by choosing a particular ratio of the alkali ions in the framework of the support (14) to the Pd atoms.

To test this possibility a series of palladium catalysts on synthetic pumice having a different content of Na^+, K^+, and ($Na^+ + K^+$) (14), and on silica, are here used in the catalytic hydrogenation of 1,3-cyclooctadiene (1,3-COD), in liquid phase. The choice of 1,3-COD as probe substrate, instead of other dienes, is justified by the absence of any isomerization process and by the possibility of immediate comparison with the performances of Pd/pumice (2) and Pd–Pt/pumice (23) already tested in our laboratory in the hydrogenation of this substrate.

EXPERIMENTAL

All experimental procedures were performed in standard Schlenk glassware under atmosphere of prepurified nitrogen. Anhydrous tetrahydrofuran (THF) was prepared

according to literature procedures (24) and distilled from potassium under nitrogen just before use.

1,3-Cyclooctadiene and cyclooctene (COE) (Aldrich) were purified by fractional distillation from potassium, passed over activated alumina and stored at $-5°C$, under nitrogen. Purity was tested by GC analysis. All other chemicals (Aldrich) were of reagent grade purity and were used without further purification.

Supports and Palladium Catalysts

The preparation of the supports is reported in the previous paper (14). The preparations of the "model pumices" supported palladium catalysts were performed, adapting literature procedures used for Pd/silica catalysts, with two different precursors, $[Pd(NH_3)_4](NO_3)_2$, by ion exchange (25–27) or $[Pd(C_3H_5)_2]$ according to Yermakov (28). Structural characterization of the catalysts was performed with X-ray (29) and XPS (10–12) techniques as described previously (14). The catalysts used in this work and their microstructural characteristics are listed in Table 1.

Kinetic Studies

The hydrogenation reactions were performed in an apparatus described previously (2, 4), at $25 \pm 0.1°C$. The reactor was connected by stopcocks to a vacuum line and to a gas adsorption system operating at atmospheric pressure of hydrogen. A side arm closed by a silicone septum allowed withdrawal of the samples for GC analyses. All the reactions were performed at the constant stirring rate of 2.500 rpm. At this stirring rate there is no gas–liquid diffusion (2). The amorphicity and the low specific surface area of pumices guarantee also limited liquid–solid diffusive effects (30). Before starting the reaction the catalyst–THF system was stirred for half an hour with H_2. In the case of Pd catalysts without sodium ions in the support this time must be much longer to have reproducible results (see Results and Discussion).

In all the experiments the molar ratio substrate/Pd was $5.000:1$ and substrate concentration was 0.25 M, in THF. Kinetic analyses were performed by a GC DANI 3800 HR PTV, equipped with a Supelco capillary column SPB1701 and a DANI 68/10 FID detector. The system was associated to a Shimadzu C-RIB Chromatopac automatic integrator. Deviations in repeated experiments were less than 4%.

RESULTS AND DISCUSSION

The reaction mechanism for the catalyzed hydrogenation of 1,3-COD to COE was obtained, as previously described (2), following a procedure similar to that employed by Happel and Sellers (31), neglecting further hydrogenation of COE since cyclooctane (COA) is not detectable before complete consumption of 1,3-COD. The equation

TABLE 1

Structural Characteristics of Supported Palladium Catalysts

Catalyst[a]	Support[b]	Pd%	Atomic ratio Na/Pd	Atomic ratio K/Pd	Metal dispersion[c] D_x%	ΔE (Pd $3d_{5/2}$) (eV)
Si_2	SiO_2	1.0	0	0	32	—
Si_1	SiO_2	1.0	0	0	39	—
Si_0	SiO_2	1.0	0	0	47	—
Z_2	$Synt_0$	1.0	0	0	10	—
Z_1	$Synt_0$	1.0	0	0	17	—
Z_0	$Synt_0$	1.2	0	0	39	−0.1
Na_6	$Synt_{Na_1}$	0.3	6.4	0	18[d]	−0.6
Na_5	$Synt_{Na_4}$	0.28	68	0	25[d]	−0.5
Na_4	$Synt_{Na_1}$	0.95	2.1	0	27	−0.5
Na_3	$Synt_{Na_1}$	0.3	6.4	0	32[d]	—
Na_2	$Synt_{Na_1}$	0.95	2.1	0	32	—
Na_1	$Synt_{Na_2}$	1.4	3.5	0	39	−0.4
Na_0	$Synt_{Na_3}$	0.55	2.9	0	50	—
$Na\text{-}K_1$	$Synt_{Na\text{-}K_1}$	0.27	7.5	6.2	32[d]	—
$Na\text{-}K_0$	$Synt_{Na\text{-}K_2}$	0.3	20	16	39[d]	—
K_2	$Synt_K$	0.2	0	64	27[d]	+0.1
K_1	$Synt_K$	0.15	0	88	39[d]	—
K_0	$Synt_K$	0.55	0	20	56	−0.1
W_7	Pumice	1.0	6.4	7.0	14	−0.4
W_6	Pumice	0.37	18.3	20	22	−0.5
W_5	Pumice	0.86	7.9	8.6	28	−0.4
W_4	Pumice	0.61	11.1	12	32	−0.6
W_3	Pumice	0.39	17.4	19	32	−0.4
W_2	Pumice	0.1	62.8	68.5	39	−0.7
W_1	Pumice	0.2	33.9	37	51	−0.6
W_0	Pumice	0.05	136	148	62	−1.0
Pd/Na-synt	$Na\text{-}synt$	0.22	22.5	—	12[d]	[e]
(6.4) Na-Si	Na-doped SiO_2	1.5	6.4	—	52	−0.5
(1.6) Na-Si	Na-doped SiO_2	1.5	1.6	—	56	−0.6

[a] $Si_x = Pd/SiO_2$; $Na_x = Pd$/synthetic pumice with sodium; $K_x = Pd$/synthetic pumice with potassium; $Na\text{-}K_x = Pd$/synthetic pumice with sodium and potassium; $Z_x = Pd$/synthetic pumice without sodium and potassium; Pd/Na-synt = catalyst doped with sodium on the support surface. For the preparation and characterization of Pd/pumice catalysts (W series) see Ref. (29).

[b] For the preparation and characterization of the synt supports see preceding paper (14).

[c] Determined from volume-weighted average Pd crystallite diameters obtained by LB analysis of the (111) XRD peak. See Ref. (29).

[d] Determined from SAXS measurements. See Ref. (29).

[e] The Pd $3d$ signal was too noisy to obtain a reliable shift.

used to fit the experimental data (t vs $C_{1,3\text{-COD}}$) was

$$t = [(1 - Q)(1 - C_{1,3\text{-COD}}) - Q \ln C_{1,3\text{-COD}}]/k, \quad [1]$$

where Q is the ratio of the adsorption constants on the catalyst surface $K_{COE}/K_{1,3\text{-COD}}$ and the concentration of COE in the liquid phase is $C_{COE} = 1\text{-}C_{1,3\text{-COD}}$; k is a constant that depends only on the pressure of H_2; and Q and k are nonlinear parameters. For a detailed description of Eq. [1] and its derivation see Ref. (2). Some selected experiments
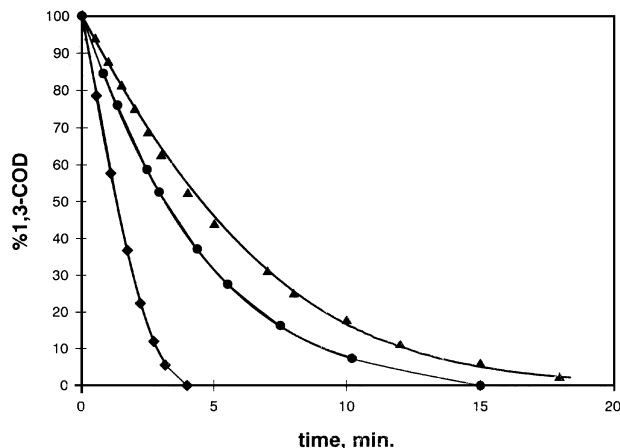
FIG. 1. Hydrogenation of 1,3-COD on Pd catalysts: W_2 (◆), Na_6 (●), K_2 (▲). Experimental points and fitting with Eq. [1].

using the fitting procedure of Eq. [1] are reported in Fig. 1, while data for all the catalysts are listed in Table 2.

The reactions follow a zero-order kinetic behavior up to high extents of conversion, in agreement with the experiments performed on the analogous reaction with Pd/natural pumice catalysts (2). As already established (2, 23), the rate determining step is the surface reaction

$$1,3\text{-}COD_* + 2H_* \overset{k_1}{\Rightarrow} COE_*, \qquad [2]$$

where X_* represents a surface adsorbed species.

The dependence of turnover frequencies (TOF_1) with dispersion D_x is shown in Fig. 2, where the results obtained with Pd/natural pumice (2) and Pd/SiO$_2$ catalysts are also reported. Figure 2a contains data relative to Pd catalysts with alkali metal ions in the framework of the support. Figure 2b contains data relative to Pd catalysts without or with alkali ions added to the catalyst surface. Although in all the series of Pd catalysts here examined (Table 2 and Fig. 2) the activity (TOF_1) is influenced by a combination of particle size and support effects, the latter appears more important. In order to facilitate the interpretation of the data in Fig. 2, the TOF_1 values corresponding to catalysts having similar or the same support have been connected. Along the same series of catalysts TOF_1 does not change significantly with D_x in the region of low metal dispersion. For D_x higher than 20–30% the decrease of metal particle size produces a general decrease in activity. Such a decrease is influenced by the presence of alkali metal ions in the framework of the support.

In the series of catalysts without alkali metal ions in the support (Si_x and Z_x) the trend (Fig. 2b) is similar to that found for the selective hydrogenation of butadiene on Pd/Al$_2$O$_3$ (32), Pd/SiO$_2$ (33), and Pd/C (33), i.e. a drastic decrease in activity at dispersion higher than 20%. Pd catalysts with only potassium (K series) (Fig. 2a) do not show a remarkable increase of activity with respect to the Si_x and

Z_x series, at similar metal dispersion, and the amount of the potassium ion does not influence greatly the activity. In all the other Pd/pumice series the activity is high and practically constant up to $D_x \sim 30\%$, then decreases with increasing dispersion. However, at similar dispersion, catalysts containing sodium in the framework of the support are always more active than those of the Si_x and Z_x series. The different behavior can be attributed to electronic effects played by the supports. Indeed the positive shift of Pd $3d$ binding energy in Pd/silica at high dispersion was associated (33–36) to a decreased electron density on the supported palladium which caused the drastic decrease of activity in the hydrogenation of the electron-rich highly unsaturated hydrocarbons (alkadienes and alkynes) because of a strong interaction between the metal and the substrate (17, 36–39). Accordingly, on addition of a strong σ-donor ligand such

TABLE 2

Kinetic Data of the Catalyzed Hydrogenation of 1,3-Cyclooctadiene

Catalyst[a]	Metal dispersion[b] $D_x\%$	TOF_1 (s^{-1})	$TOF_2 \times 10^3$ (s^{-1})	k_1/k_2	$Q = K_E/K_{1.3}$
Si_2	32	42	75	560	0.24
Si_1	39	34	76	450	0.22
Si_0	47	32	76	420	0.20
Z_2	10	79	75	1050	0.34
Z_1	17	78	74	1030	0.31
Z_0	39	35	75	470	0.21
Na_6	18[c]	93	119	780	0.67
Na_5	25[c]	88	94	870	0.49
Na_4	27	82	84	940	0.24
Na_3	32[c]	79	71	1030	0.47
Na_2	32	68	78	960	0.48
Na_1	39	47	65	730	0.86
Na_0	50	34	48	710	0.41
Na-K_1	32[c]	88	81	1070	0.43
Na-K_0	39[c]	75	77	1000	0.85
K_2	27[c]	52	62	840	0.51
K_1	39[c]	37	69	540	0.48
K_0	56	25	73	350	0.44
W_7	14	89	110	810	0.44
W_6	22	91	80	1150	0.34
W_5	28	91	77	1200	0.26
W_4	32	89	73	1230	0.21
W_3	32	88	70	1250	0.20
W_2	39	85	62	1400	0.18
W_1	51	62	42	1480	0.17
W_0	62	32	39	830	0.16
Pd/Na-synt	12[c]	40	43	940	0.15
(6.4) Na-Si	52	16	12	1360	0.14
(1.6) Na-Si	56	12	11	1090	0.11

[a] Si_x = Pd/SiO$_2$; Na_x = Pd/synthetic pumice with sodium; K_x = Pd/synthetic pumice with potassium; Na-K_x = Pd/synthetic pumice with sodium and potassium; Z_x = Pd/synthetic pumice without sodium and potassium; Pd/Na-synt = catalyst doped with sodium on the support surface. For Pd/pumice catalysts (W series) see Ref. (29).
[b] Determined from volume weighted average Pd crystallite diameters obtained by LB analysis of the (111) XRD peak. See Ref. (29).
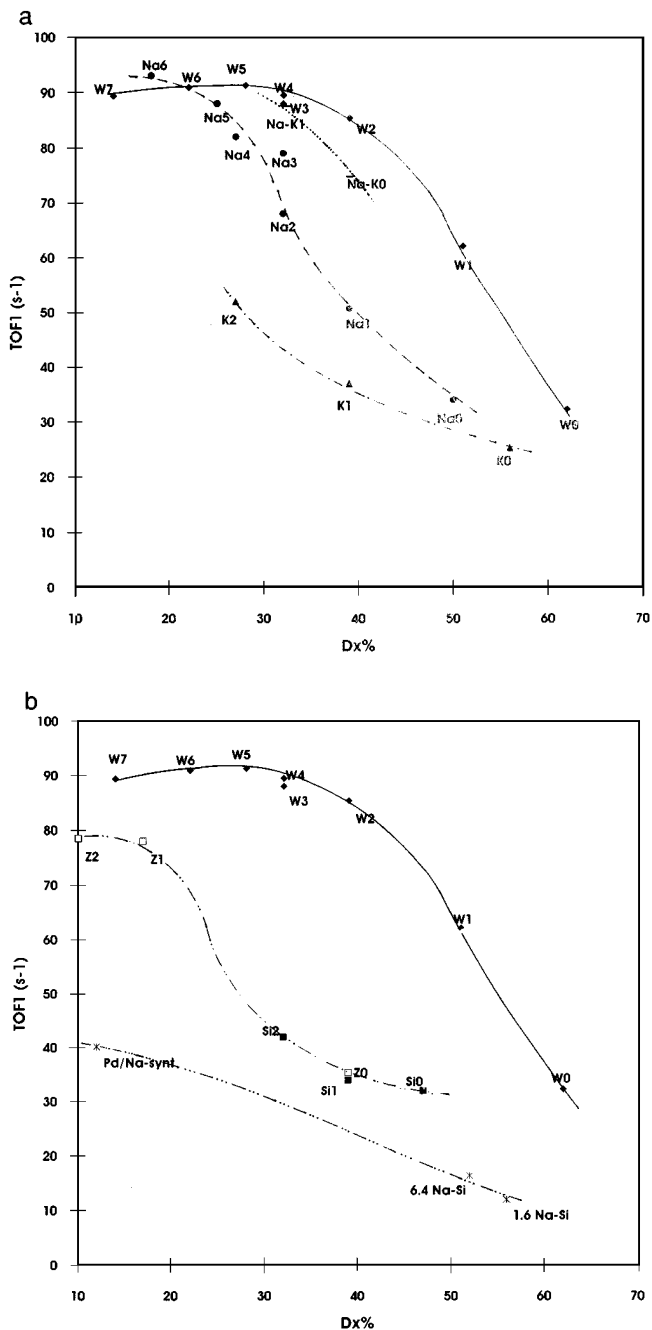[c] Determined from SAXS measurements. See Ref. (29).

FIG. 2. Change of TOF_1 with metal dispersion. Comparison of Pd/pumice catalysts (W series (◆)). (a) Pd catalysts containing alkali metal ions in the support framework: Na (●), K (▲), Na-K (—). (b) Pd catalysts without alkali metal ions (Si (■) and Z (□)) or with alkali metal ions on the catalyst surface (∗).

as piperidine, reducing the electron deficiency of the supported palladium enhanced the activity of the catalysts (38).

Recently the positive binding energy (B.E.) shift in XPS measurements of Pd/Al_2O_3 catalysts (40, 41) was attributed to metal particle morphology rather than to metal dispersion. Even if morphology of the metal particles could also be important in other Pd catalysts, the above interpretation

does not change the consideration that a positive B.E. shift in Pd/Al_2O_3 catalysts is related to a decrease of the activity in the hydrogenation of unsaturated hydrocarbons on comparison with Pd/Al_2O_3 catalysts which do not show the positive B.E. shift (41).

On the contrary, the negative shift of B.E. in Pd/pumice (10, 11) is related to an electron density increase on the supported palladium, as shown by the trend of the Auger parameter shift (10). Such a parameter, given by the combination of the B.E. shift and Auger shift, has the advantage of being independent from possible charging and energy reference problems (42); it allows one to estimate the charge distribution on the palladium atoms. The electron density on the metal in the Pd/pumice series increases with metal dispersion (10) and with the atomic ratio $R = (Na)/(Pd)$ (43) and the trend of TOF_1 appears directly related to the factors which increase the electron density on the metal. In the Pd/pumice series the alkali metal ions, in addition to having a general positive effect on the activity, enlarge the range of utilization of the Pd catalysts toward higher metal dispersion since the decline of activity with increasing metal dispersion is gradual and much smaller than in other Pd catalysts on traditional supports (alumina (32), silica (33), carbon (32, 44)).

In Fig. 3, TOF_1 is reported as a function of R for metal dispersions $D_x = 35 \pm 5\%$. TOF_1 increases with R up to a constant maximum value. The data show that the effect of sodium is more relevant at high dispersion and that the Pd catalysts supported on silica or on model pumice not containing alkali metal ions have low activity. The potassium effect is practically absent, as seen by the position of K_1 in Fig. 3. Such behavior is in accord with the XPS results
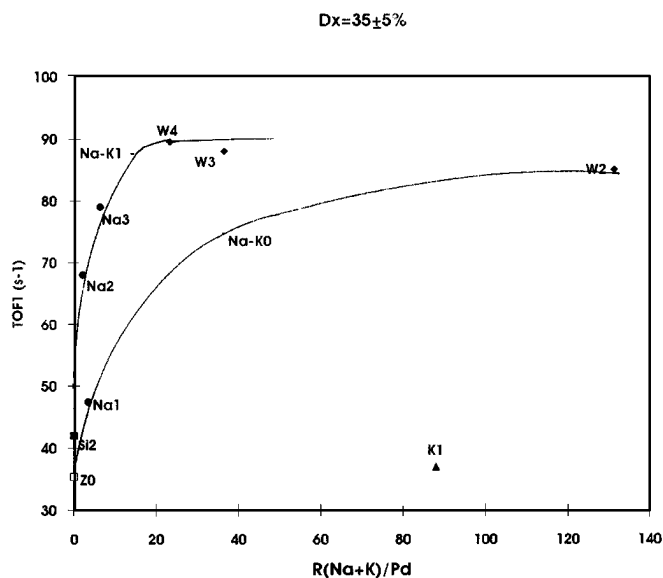

FIG. 3. Influence of $R(Na + K)/Pd$ on TOF_1 ($D_x = 35 \pm 5\%$). Upper line ($D_x = 32\%$) and lower line ($D_x = 39\%$) connect catalysts with the same experimental D_x.

of Table 1, where the B.E. shifts of the potassium containing catalysts are not significant (35), differently from the sodium containing catalysts. A possible explanation of the much higher influence of sodium than that of potassium is that the electrostatic field is much higher for the sodium than for the potassium ion, because of the ratio Z/r (Z, ionic charge; r, ionic radius).

Therefore, the progressive decrease of activity in Pd/pumice catalysts, which is more evident at high metal dispersion (10), is attributed to a lower interaction between the electron-rich 1,3-COD and the electron density enriched supported palladium, i.e., to a reason which is the opposite of that responsible for the decrease in activity of palladium catalysts on silica or alumina (17, 36–39). Related to this different trend in the B.E. shift is the easy oxidation in air of the palladium catalysts not containing alkali metal ions (Z or Si series), specially when highly dispersed, so that treatment with hydrogen for long time is required before adding the diene to avoid very low activity. This treatment is not necessary for the pumice-supported palladium catalysts (W, Na, Na-K series), left for months in open atmosphere.

In order to find the Pd catalyst with the best activity/selectivity performances a detailed study of the second semi-hydrogenation was also performed. The rate determining step is again a surface reaction, namely,

$$COE_* + 2H_* \overset{k_2}{\Rightarrow} COA_*.$$ [3]

When alkali metal ions are present in the supports of Pd catalysts, the rate constant k_2 relative to reaction (3) is the same in both the direct hydrogenation of the pure COE and in the hydrogenation of the COE obtained from 1,3-COD; TOF_2 decreases with metal dispersion (Fig. 4). On
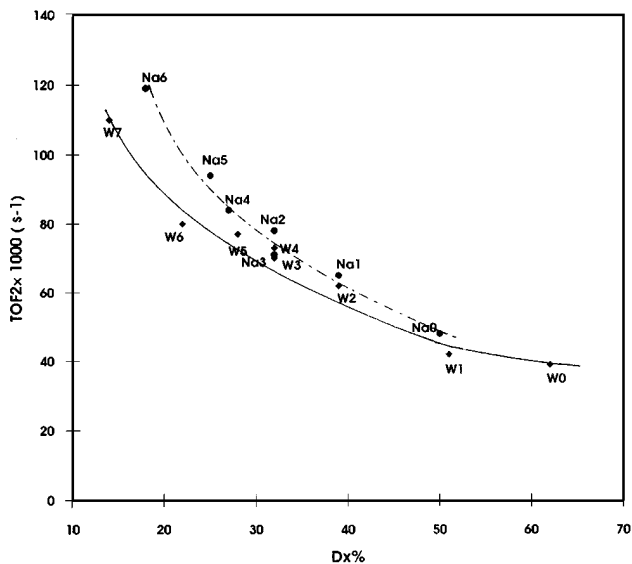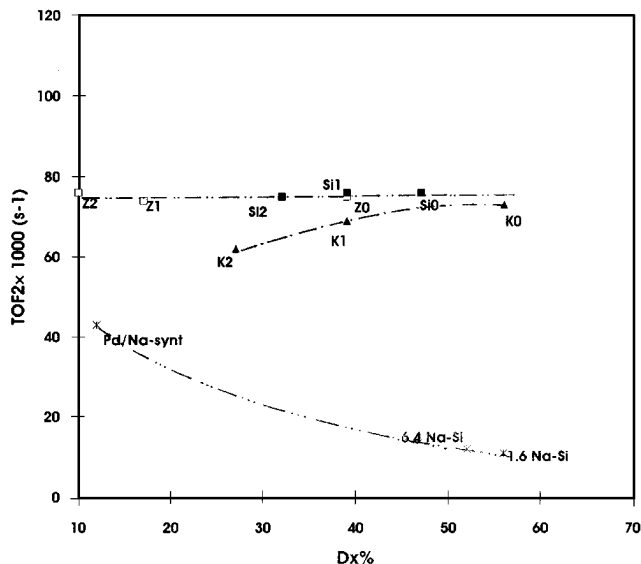

FIG. 5. Change of TOF_2 with metal dispersion: Pd catalysts without sodium (K (▲), Si (■), and Z (□)) or with sodium on the catalyst surface (∗).

the contrary, providing that sufficient stirring with H_2 was performed before starting the kinetics, no change in TOF_2 was found with Pd catalysts without sodium ions in the framework (Fig. 5). Similar results were already reported by Boitiaux *et al.* (37) in the liquid phase hydrogenation of 1-butene with Pd/Al$_2$O$_3$, while Hub *et al.* (39) found an increase of TOF_2 in the gas phase hydrogenation of 1-butene. Again potassium alone in the support structure does not show a relevant effect on the catalytic performance. Although with Pd/pumice catalysts k_1 is about three orders of magnitude higher than k_2 and the selectivity can be considered fairly good, it is interesting to follow the changes of k_1/k_2 with metal dispersion. A volcano curve of k_1/k_2 versus metal dispersion is found (Fig. 6) in the sodium-containing Pd catalysts, in accord with previous results on Pd/pumice catalysts (2). On the contrary (Fig. 7), a continuous decrease of k_1/k_2 is found for all the other catalysts (*Si*, *Z*, and *K* series).

The high selectivity of palladium catalysts was attributed to stronger adsorption of the diene as compared to the monoene (45). These results were obtained in a competitive gas phase hydrogenation of butadiene and 1-butene (which have similar hydrogenation constant rates) on Pd/SiO$_2$ catalysts at 60% metal dispersion and under high hydrogen pressure. As shown by several authors (34, 35, 39), the large positive B.E. shift of the Pd 3d level found at such high metal dispersion is indicative of a loss of metallic character which determines an increase of the interaction between the electron-rich substrate and the electron-deficient metal centers, with an expected larger effect on the diene as compared to the monoene. In our Pd catalyst without sodium ions in the structure of the supports (*Z*, *K*, and *Si* series)
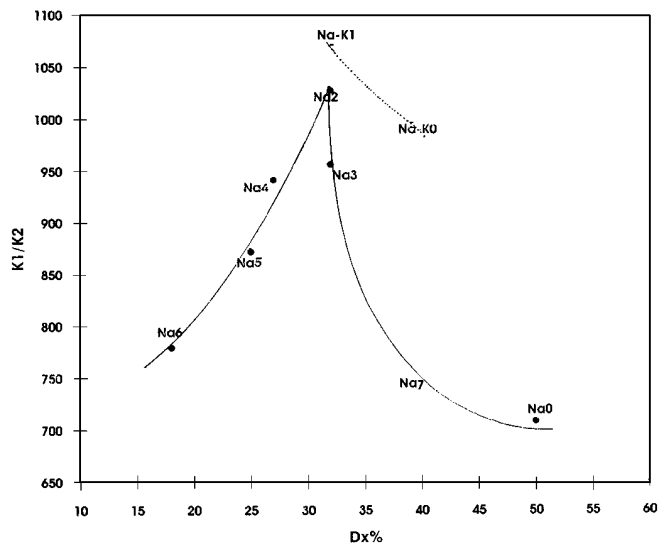

FIG. 4. Change of TOF_2 with metal dispersion: Pd/pumice catalysts (W (◆) series and Na (●) series).

FIG. 6. Volcano trend of k_1/k_2 ratio of Pd catalysts (Na (●) and Na-K (—) series) versus metal dispersion (D_x).

TOF_2 is practically constant on increasing metal dispersion in accord with the decrease of selectivity (Fig. 7). The continuous decrease of TOF_2 with metal dispersion in the Pd catalysts of the series *W*, *Na*, and *Na-K* indicates that the adsorption of the monoene on the metal becomes progressively lower as the electron density on the metal increases.

Finally we consider the effect of the location of alkali metal ions when they are not in the support framework. Three catalysts, namely Pd/*Na-synt*, 6.4 *Na-Si*, and 1.6 *Na-Si*, (Table 2), were prepared, the first one by supporting palladium on *Na-synt* obtained by addition of NaOCH$_3$
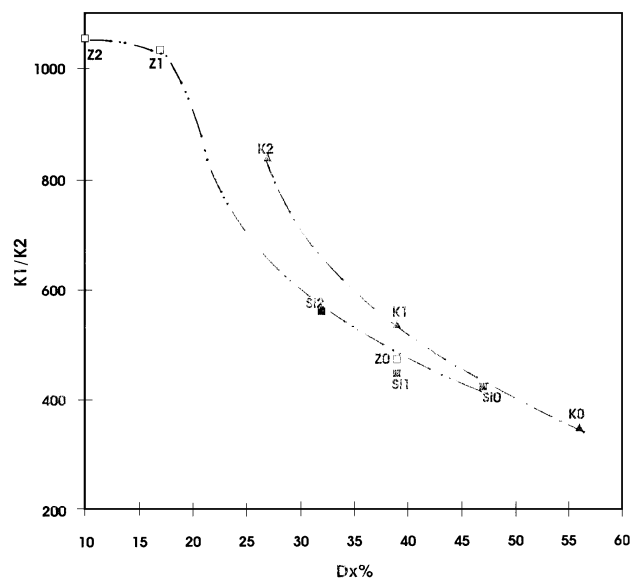

FIG. 7. The decrease of k_1/k_2 ratio with metal dispersion in Pd catalysts without sodium ions in the support framework: (Si (■), Z (□), and K (▲) series).

to *synt*$_0$ (14), and the other two by addition of NaNO$_3$ to *Si*$_1$ (13). As already reported for similar Na–Pd/SiO$_2$ catalysts (46) and as shown in Table 1, the B.E. shift in the three catalysts is negative as for all the Pd/pumice catalysts previously described. The TOF_1, however, is quite different from that found in those Pd/pumice catalysts with similar *R* values, due to the different location of the alkali metal ions. When the sodium ions are added to Pd/silica they distributed on the surface of the catalysts decorating part of the supported palladium, as shown by a LEIS (low energy ion scattering) study (47). In these cases, a decrease of the active sites occurs which counterbalances the increase of activity expected for the augmented electron density on the supported metal. Therefore it is not surprising that addition of sodium ions lowers the TOF_1 values (Fig. 2b) with respect to sodium free Pd catalysts of the same dispersion.

Although the hydrogenation of 1,3-COD is just a probe reaction, the results might be easily extended to substrates of industrial interest. Knowing the electron donor capacity of the substrate to be hydrogenated, the electron density on the Pd/pumice catalysts could be modulated by acting properly on metal dispersion and/or on alkali metal ions/palladium atomic ratio in order to achieve the best activity/selectivity performances in the selected reaction.

CONCLUSION

The experimental results of this article give a clear picture of the influence of alkali metal ions on the performances of supported palladium catalysts and of the importance of their location. The alkali metal ions in the framework of the support increase the electron density of the supported metal, decreasing the interaction of the supported palladium with the electron rich substrate to be hydrogenated. This effect produces a general increase of activity (TOF) compared with Pd catalysts on conventional supports (alumina, silica, carbon). The latter show indeed a decreasing activity at metal dispersion higher than 20–25%, because of a too strong interaction of the electron rich substrates with the electron-deficient supported metal. On the contrary the gradual decrease of activity of the Pd/pumice catalysts at increasing D_x is due to an insufficient activation of the electron rich substrate because of its repulsion towards the supported metal which becomes progressively electron richer. These arguments are supported by a progressive negative shift of B.E. of Pd 3d orbital in the Pd/pumice catalysts compared to the B.E. of the unsupported Pd metal (12, 43). A similar electronic effect of sodium ions added to Pd/SiO$_2$ catalysts is documented by XPS (43, 46). However, the influence of the increased electron density of these Pd catalysts on the activity of 1,3-COD hydrogenation is limited by the contemporary decrease of active sites due to decoration of Na$^+$ ions of the supported palladium as demonstrated by a LEIS study (47).

The influence of alkali metal ions in the framework produces a progressive decrease of TOF_2 with dispersion. Since TOF_1 starts to decrease at metal dispersion higher than 30–35%, the rate constants ratio k_1/k_2 has a volcano trend with a maximum of selectivity for the title reaction at about 35% metal dispersion.

ACKNOWLEDGMENTS

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