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Localization of Alkali Metal Ions in Sodium-Promoted Palladium Catalysts as Studied by Low Energy Ion Scattering and Transmission Electron Microscopy

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Three series of palladium-based catalysts have been studied by Low Energy Ion Scattering (LEIS) and Transmission Electron Microscopy (TEM). The first series is comprised of Na–Pd/SiO$_2$ catalysts, obtained by addition of palladium to a silica support and by further addition of sodium ions with a Na/Pd atomic ratio (R) equal to 0, 6.4, and 25.6. The second series consists of palladium catalysts supported on natural pumice, in which, due to a different loading of supported palladium, R', the (Na + K)/Pd atomic ratio, is equal to 17.0 and 39.4. The third series is represented by two palladium-based catalysts supported on "model pumices," synthetic silico-aluminates, obtained by sol-gel techniques, with a different amount of sodium, and R equal to 2.1 and 6.1, respectively. LEIS experiments and electron microscopy demonstrate a different location of alkali metal ions in the first two series: in the Na–Pd/SiO$_2$ catalysts sodium is distributed in a way which is not uniform on the support and on the palladium metal, which is partly decorated with Na ions, whereas in the Pd/natural-pumice series the palladium surface is sodium-free. The results on the third series of catalysts, Pd/model pumice, are not definitive on the basis of the LEIS and TEM analyses, but by FTIR study of CO and CO$_2$ adsorption, the decoration of palladium by sodium ions could be excluded. The results confirm the importance of the alkali metal ion location in alkali-promoted palladium catalysts and open new possibilities in the design of palladium-supported catalysts by a better control of promoter location. © 1996 Academic Press, Inc.

INTRODUCTION

Palladium-based catalysts are active and selective towards the partial hydrogenation of alkadienes and alkynes into alkenes (1). In this context, the catalytic behaviour of pumice-supported palladium catalysts (2) was tested in the selective hydrogenation of 1,3-cyclooctadiene in liquid phase (3). The results thus obtained were of special interest since these catalysts yield a constant turnover frequency (TOF) for Pd particles larger than 3–4 nm. Furthermore, the activity decrease at smaller Pd particle size is less marked than for other conventional palladium catalysts, pointing to specific properties of this support. This relative size-insensitivity has been confirmed for the selective hydrogenation of phenylacetylene to styrene (4). The high activity and selectivity observed at high metal dispersions could be of interest for industrial applications.

Pumice is a naturally occurring silico-aluminate containing typically 72 wt% of silica, 13 wt% of alumina, 4 wt% of water and also oxides of sodium and potassium (about 8 wt%). Traces of several other oxides are also present. After treatment with boiling 25% HNO$_3$ for 30 min and drying in a stream of nitrogen at 200°C for 2 days, these oxides are eliminated. This treatment leads also to a decrease of the content of water, alumina, sodium, and potassium. Longer treatment with nitric acid and successive drying do not change further the composition of pumice. To better understand the intricate interplay between the metal particles and the pumice support, "model pumices" containing different amount of sodium were prepared by sol-gel techniques and palladium was added to the new supports (5). Finally, it has been thought that it could be of interest to compare the properties of Pd/pumice catalysts with that of a more simple catalytic system, Na–Pd/SiO$_2$, prepared by successively adding palladium and sodium to the support.

As a first step we have tried to solve the problem of the localization of the alkali compound with respect to palladium and support using Energy Dispersive X-ray (EDX) spectroscopy, a technique which proved to be fruitful in the analysis of a similar catalytic system, K–Pd/SiO$_2$ (6), and Low Energy Ion Scattering (LEIS) which gives information on the outermost composition of the catalyst. This paper reports on the results thus obtained for the three series of catalysts, while in the preceding paper (7) a FTIR study of the chemisorption of CO and CO$_2$ shows what could be the role of alkali metal ions as a modifier of palladium properties.

EXPERIMENTAL

Materials and Treatments

The main characteristics of the catalyts are given in Table 1. The methods of preparation are described

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TABLE 1

Characteristics of Pd-Supported Catalysts

Catalyst	Sample	Pd wt%	Na wt%	K wt%	$R = Na/Pd$ at. ratio	$R' = (Na + K)/P$ at. ratio	TEM (nm)[a]	SAXS (nm)	D_H (%)[d]
Pd/SiO_2	1	1.50	0.00	0.0	0.0	—	1.7[b]	n.d.	70
$Na–Pd/SiO_2$	2	1.50	2.08	0.0	6.4	—	2.0–6.0	n.d.	52
$Na–Pd/SiO_2$	3	1.50	8.32	0.0	25.6	—	n.d.	n.d.	49
Pd/pumice	4	0.37	1.49	2.79	—	39.4	2.0–20.0	n.d.	29
Pd/pumice	5	0.86	1.49	2.78	—	17.0	n.d	5.3[c]	28
$Pd/synt_2$	6	0.95	0.44	0.0	2.1	—	2.0–6.0	n.d.	50
$Pd/synt_3$	7	0.80	1.06	0.0	6.1	—	4.0–10.0	n.d.	47

[a] Lowest and highest diameters (Ref. 7).

[b] Average size diameter (Ref. 7).

[c] Ref. 2.

[d] Determined by chemisorption with H_2, according to the methods of Aben and Benson *et al.* (see Ref. 7).

elsewhere (2, 5–12). Pd/SiO_2 catalysts were prepared by ion exchange between silica (Aerosil from Degussa, 200 $m^2 g^{-1}$) and a solution of $[Pd(NH_3)_4](OH)_2$ (6, 8). The solid was calcined in an oxygen flux at 573 K. The precursor thus obtained was added to a solution containing the desired amount of sodium nitrate, then evacuated to dryness under reduced pressure in a rotary evaporator. The reduction was carried out in flowing hydrogen (4 l h^{-1}) by heating at 2 K/min from room temperature to 573 K for ca. 15 h. The silica consists of spherical particles having an average size of 13 nm; the BET surface area is found to be 200 $m^2 g^{-1}$ and the pore radius, as determined from the N_2 adsorption–desorption isotherm at 77 K, is 12 nm and corresponds approximately to the intraparticle distance. Addition of palladium and sodium does not alter dramatically the morphology: as an example, the BET surface areas of samples 1 and 2 reduced at 573 K are found to be 180 and 167 $m^2 g^{-1}$, respectively.

Pumice (9), which is an amorphous natural silicoaluminate of volcanic origin, was treated with a 25% nitric acid solution to eliminate most impurities. This treatment decreases the content of aluminium, sodium and potassium both in the surface (as shown by XPS analyses (13)) and in the bulk (determined by atomic absorption spectrophotometry, AAS). The samples were then dried at 473 K for 12 h. The XPS analyses showed that the surface concentration of sodium is slightly increased upon heating. The surface area (BET) is found to be 7 $m^2 g^{-1}$ and the surface composition (by XPS peak intensities) after purification is 85.5%, SiO_2; 6.8%, Al_2O_3; 2.0%, Na_2O; 3.2%, K_2O; and 2.5%, H_2O (values in wt%). This is close to that of zeolites, but in contrast to the latter the structure is amorphous.

Palladium was added to natural pumice according to Yermakov's procedure (12), consisting of reacting the –OH groups of pumice with a pentane solution of $[Pd(C_3H_5)_2]$ of known concentration (2) at low temperature, leading to two precursors of pumice-anchored Pd species which contain different amounts of metal (Table 1). Reduction of the pumice-anchored Pd species was accomplished by flowing hydrogen (4 l h^{-1}) at 258 K for 0.5 h, then at 273 K for 1 h, and at 298 K for 0.5 h. This low temperature procedure minimizes sintering of metal crystallites and is sufficient to ensure complete reduction of palladium. The catalysts were vacuum-dried and stored at room temperature in nitrogen containing traces of oxygen (2). The catalysts passivated were then examined by TEM. Model pumices were obtained from sol-gel techniques (5, 10, 11). The chemical composition (determined by atomic absorption spectrophotometry) is similar to that of natural pumice (SiO_2, Al_2O_3 at ca. 84 and 14 wt%, respectively), (Table 2). Two samples were studied, denoted $synt_2$ and $synt_3$, both amorphous ($synt_3$ shows some crystallinity), differing in BET surface areas (43 and 12 $m^2 g^{-1}$, respectively), in pore size distribution and in alkali content (0.6 and 1.44 wt% for Na_2O; 0% K_2O). Palladium was added to model pumices according to the procedure used for Pd/silica catalysts (6–8).

The palladium precursor on model pumice samples was reduced in flowing hydrogen (4 l h^{-1}) by heating at 2 K min^{-1} from room temperature to 573 K for ca. 15 h.

TABLE 2

Chemical Composition and Morphology of the Different Supports

Type	SiO_2 (%)	Al_2O_3 (%)	Na_2O (%)	K_2O (%)	H_2O (%)	B.E.T (m^2/g)	Morphology (WAXS)
SiO_2	100	—	—	—	—	200	crystalline
$synt_2$	83.55	14.35	0.6	—	1.50	43	amorphous
$synt_3$	83.37	14.24	1.44	—	0.95	12	amorphous[a]
pumice[b]	85.5	6.8	2.0	3.2	2.5	7	amorphous

[a] Some crystallinity is present.

[b] Surface composition (by XPS), after HNO_3 treatment.

Low Energy Ion Scattering (LEIS) Spectroscopy

This technique consists of directing a beam of monoenergetic ions towards a surface. Due to the conservation of momentum and of energy of the ions during the scattering by the surface atoms, the energy of the backscattered ions depends on the mass of the surface atoms (14) according to the formula:

$$E_1 = E_0 \left(\frac{\cos\theta + \sqrt{\gamma^2 - \sin^2\theta}}{1+\gamma} \right)^2,$$

where E_1 is the energy of the scattered ion after an elastic collision with an atom and E_0 the kinetic energy of the incident ion, θ is the scattering angle, and γ is the mass ratio of the surface atom and incident ion ($\gamma = M_{\text{at}}/M_{\text{ion}}$).

The energy spectrum of the scattered ions is equivalent to a mass spectrum of the surface atoms; peaks related to atoms with different masses are well separated (Pd, O, Si, Na, K) in contrast to the situation arising from surface atoms with comparable masses such as Si and Al. When inert gas ions such as He^+ are used, it has been shown that the scattering results exclusively from the outermost atomic layer of the solid (14, 15). This technique is fruitful for the analysis of catalysts, as shown in recent reviews (15, 17). The LEIS experiments were performed with 2 keV $4He^+$ ions in an ESCALAB 200R system (Fison Instruments). The pressure after bakeout was lower than 5×10^{-10} mbar in the UHV chamber when the primary ion beam was turned on. The intensity of the primary beam was fixed at 50 nA on an impact spot of around 0.5 mm^2. The current density was selected to minimize the damages caused to the surface, and for these conditions a few minutes were necessary to eliminate a monolayer. The scattering angle was 142° and the ions scattered from the target were energy-analyzed with a hemispherical analyzer. Surface charging during analysis was eliminated by flooding the sample with low-energy electrons (4–6 eV). Samples (30 mg) were pressed into the sample holder which consisted of a stainless streel grid (1×1cm). Samples were reduced according to the procedure defined previously, then transferred into the preparation chamber of the spectrometer without contact with air, in hydrogen atmosphere, outgassed at the reduction temperature to maintain a certain hydrogen coverage aimed at preventing surface pollution. Finally the samples were transferred into the measurement chamber. The residual pressure was 10^{-9} mbar.

Trasmission Electron Microscopy (TEM)

Energy dispersive X-ray analyses were carried out in a JEOL JEM 2010 electron microscope working in a high resolution configuration (the point-to-point resolution was 0.196 nm). With this microscope, fitted with a Link Pentafet diode and Isis EDX analyser, it is possible to perform EDX analysis with an electron probe as small as 1 nm ("nanoprobe mode"). In practice 5–25 nm nanoprobes were used in this study. Sample powders were ultrasonically dispersed in a non-polar solvent (acetone) to avoid possible dissolution of sodium compounds. A drop of the suspension thus obtained was deposited on a carbon film supported on a 200 mesh copper grid.

RESULTS AND DISCUSSION

Unpromoted and Sodium-Promoted Pd/SiO$_2$

Typical LEIS spectra obtained as a function of time are shown in Fig. 1 (sample 3). For unpromoted Pd/SiO_2 catalysts (sample 1) reduced at 573 K or at 773 K, palladium is not detected at short analysis time; only the peak of O and Si atoms can be observed at 810 and 1200 eV, respectively. At longer analysis time (ca. 6 min), the peak related to palladium atoms emerges (at 1750 eV) and then remains almost unchanged (Fig. 2). This phenomenon is probably related to the sputter etching effect resulting from ion bombardment (the palladium surface of the outermost layer of the catalyst is initially covered with H atoms).

Figure 3a reports the evolution of sodium and palladium peak intensities for sample 2 ($Na–Pd/SiO_2$, $R = 6.4$); as the former increases the latter decreases, suggesting that the sodium compound decorates the palladium surface at the beginning of the experiment and that, due to ion etching, the sodium decoration is removed, uncovering the palladium surface. The sharp decrease of the sodium LEIS signal suggests that the sodium ions are present as a very thin layer. This picture accords well with the data from infrared spectroscopy of adsorbed CO (7): as the sodium promoter is added to the Pd/SiO_2 catalyst, the intensity of the CO bands related to the free metal surface decreases (this decrease cannot be accounted for by metal sintering) and goes to zero at high R values. Similar results are obtained for Pd/SiO_2 catalysts promoted by larger amounts of sodium

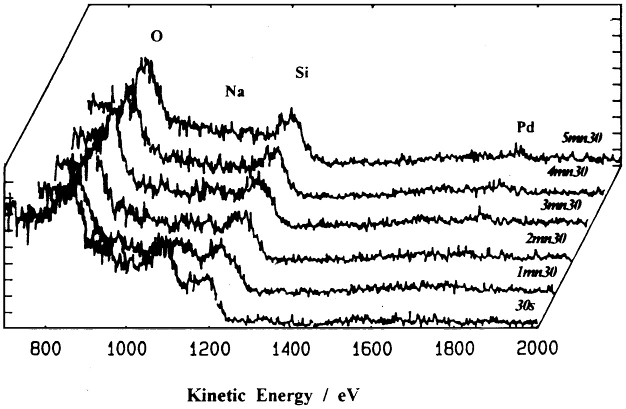

FIG. 1. Typical LEIS spectra obtained on sample 3, $Na–Pd/SiO_2$, $R = 25.6$ at different analysis times.

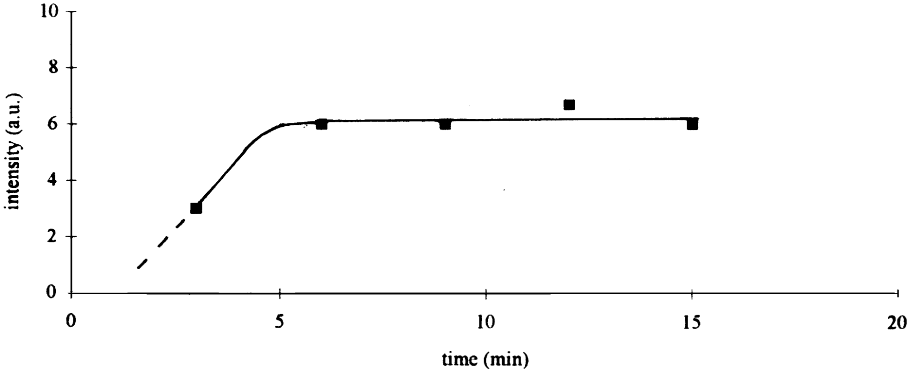

FIG. 2. Evolution of the LEIS peak intensity of palladium with analysis time for unpromoted Pd/SiO_2 catalysts reduced at 773 K (arbitrary units). Very similar results were obtained when the reduction was carried out at 573 K.

additive (sample 3, $R = 25.6$); the peak area of palladium first increases with time, then remains constant after ca. 3.5 min while that of sodium first decreases steeply and after 1.5 min decreases more slowly; it is reduced to zero after 4.5 min (Fig. 3b). This shows that at time between 3.5 and 4.5 min, the sodium atoms which are detected are deposited on the silica support, the surface of palladium being free from sodium.

Finally, it can be remarked that the Na peak intensity ratio observed by LEIS for samples 2 and 3 is nearly equal to that of their chemical content. Furthermore, it has been observed that, for samples 1–3, the oxygen peak intensity does not vary significantly with time, while that of silicon increases continuously.

EDX analysis of sample 2 shows that sodium ions are not uniformly distributed on the catalyst. The surface consists of areas where the alkali additive is associated with both silica and palladium, while a fraction of the surface, $SiO_2 + Pd$, is deprived of it. It is difficult to be precise on the relative abundance of both areas.

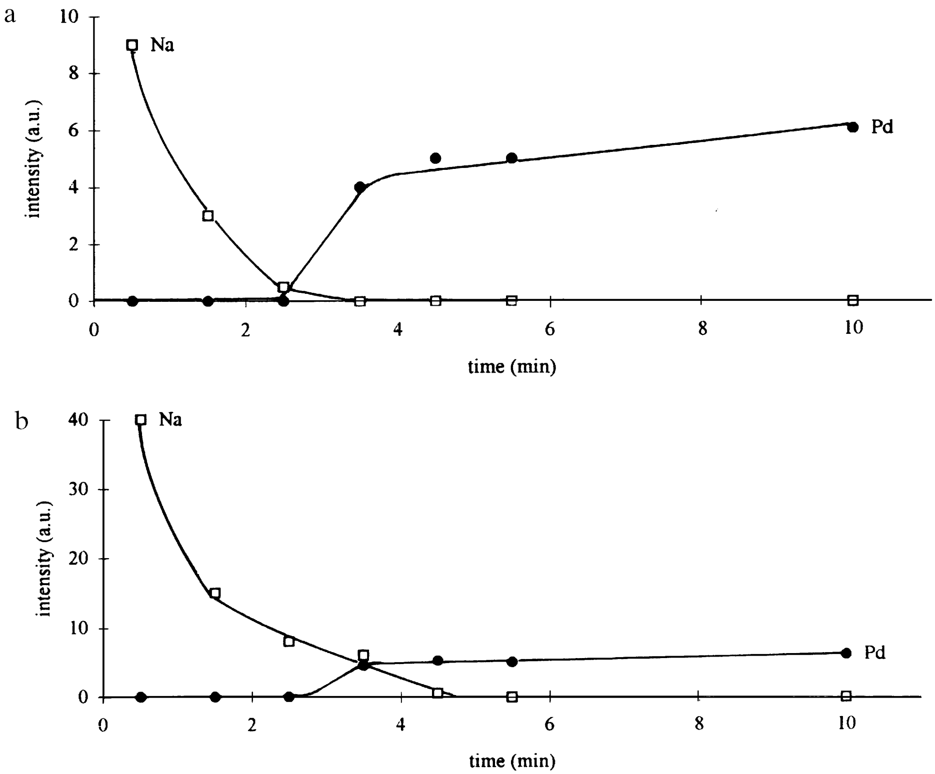

FIG. 3. Evolution of the LEIS peak intensities of sodium and palladium in catalysts Na–Pd/SiO_2 ($R = 6.4$) (a) and Na–Pd/SiO_2 ($R = 25.6$) (b) as a function of analysis time.

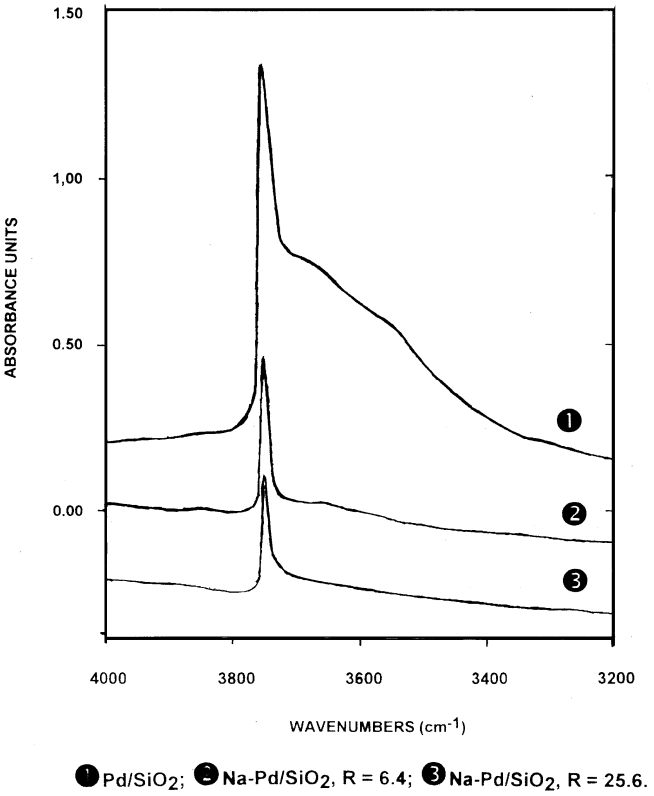

FIG. 4. Integrated absorbance of hydroxyl groups of the silica support of Na–Pd/SiO$_2$ per catalyst weight unit as a function of the amount of sodium additive. (1) Pd/SiO$_2$; (2) Na–Pd/SiO$_2$, $R = 6.4$; (3) Na–Pd/SiO$_2$, $R = 25.6$.

Infrared spectra of hydroxyl groups were performed to confirm this picture. As shown in Fig. 4, the integrated absorbance of OH groups per catalyst weight unit (free OH at 3745 cm^{-1} and hydrogen-bonded OH over the 3700–3400 cm^{-1} range) decreases as the sodium additive content increases, indicating that a fraction of the hydroxyl groups of the silica support has been transformed into -O–Na. This confirms that a part of the silica support is covered with sodium ions, the other remaining free from the alkali additive.

A coherent picture of the promoted Pd/SiO$_2$ catalyst emerges from these techniques. A certain amount of the sodium promoter decorates the palladium surface, while the remainder is deposited on the silica support, some places being free from sodium, others reacting with sodium ions to give -O–Na groups. This conclusion is very similar to that reached for similar catalytic systems, such as alkali promoted Ni/SiO$_2$ catalysts (18) and *K*-promoted Pd/SiO$_2$ catalysts (6).

Pd/Natural Pumice

Figure 5 shows that the peak area of palladium obtained by LEIS increases with time and that after 5–10 min it remains almost constant. Neither sodium nor potassium atoms were detected, excluding the hypothesis of an alkali promoter decoration of palladium particles as for the case of Na–Pd/SiO$_2$. The peaks of oxygen and Si + Al atoms grow with increasing time. A blank experiment was carried out with a natural pumice before palladium deposition; only oxygen and Si + Al atoms were detected, showing that alkali atoms are located inside the pumice structure and not on the surface.

EDX experiments performed on sample 4 (Pd = 0.37 wt%) have shown that sodium ions are preferentially located in the vicinity of palladium particles. No palladium is observed without sodium; sometimes areas rich in both palladium and sodium are detected. Obviously, during the preparation palladium is selectively deposited in the sodium-rich part of the pumice although the initial pumice surface is free from alkali ions.

Thus, in contrast to Na–Pd/SiO$_2$ catalysts, alkali ions in Pd/pumice do not decorate metal particles. However, as for the latter catalyst, the alkali promoters are associated with palladium. It is speculated that they are located beneath the metal particle. On palladium deposition, and reduction under hydrogen at 298 K, they probably demonstrate some mobility, migrating from the bulk to the vicinity of

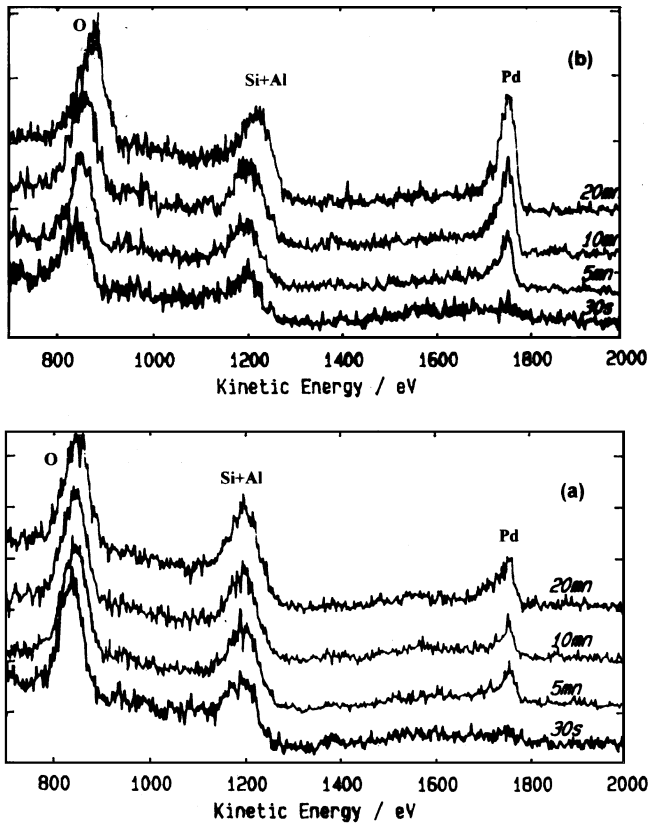

FIG. 5. LEIS spectra of Pd/natural pumice at different analysis times: (a) Pd = 0.37 wt.%; (b) Pd = 0.86 wt.%.

metal particles, since no alkali atoms are present on the pumice surface before impregnation. It is difficult to state whether or not they are in direct contact with palladium particles.

Pd/Model Pumice

The LEIS spectra of sample 6 does not reveal the presence of palladium and sodium. The peak intensity of oxygen and $Si + Al$ atoms does not vary significantly with time.

Nitrogen adsorption–desorption isotherms at 77 K have shown that the sample synt$_2$ is porous (pore volume $= 0.435$ cm^3 g^{-1}) in contrast to natural pumice which has a pore volume of 0.00465 cm^3 g^{-1}.

Electron microscopy confirms the presence of pores with diameters spanning the 30–80 nm range. It is suggested that palladium particles are within pores so that they cannot be detected by LEIS. This phenomenon, however, does not lead to different adsorptions of CO on Pd/model pumice (7) since, due to the large dimensions of the pores, the accessibility of CO to palladium is not altered. Moreover, the IR spectra of CO chemisorbed at 298 K on Pd/synt$_2$ and Pd/synt$_3$ catalysts, despite some differences of the samples in porosity and surface areas of the supports, are well accounted for by the difference of alkali amounts: on increasing the amount of sodium ions in the structure of model pumices, a decreased adsorption of CO occurs.

EDX analysis of sample 6 shows that sodium atoms are non-uniformly deposited on the catalyst, the sodium to $Si + Al$ atom ratio varying from 0.5 to 12%. We were unable to establish a clear correlation between the location of Na^+ and that of Pd.

As can be seen, LEIS and electron microscopy lead to a picture of Pd/model pumices which is less clear than for the other catalysts. Some features, however, seem well established. Palladium particles are likely to be located in the pores of the support (sample 6) and some facetting of metal particles, which can reveal epitaxial phenomena, occurs for the case of sample 7. Nevertheless, these techniques alone are not able to tell us whether sodium ions decorate palladium particles and how they are arranged with respect to the metal surface. However, some information can be deduced on the basis of the different adsorptions of CO and CO_2 on Pd/pumices and Na–Pd/SiO$_2$ catalysts (7). Since the behaviour of Pd/model pumices is very close to that of Pd/natural pumice if the different amount of sodium in the structures is considered, it can be speculated that the sodium ions do not decorate the palladium particles and are located preferentially beneath the metal.

CONCLUSIONS

This work confirms that the different behaviour manifested in the adsorption and reactivity of CO and CO_2 on alkali-promoted Pd catalysts (7) is due to the different locations of the alkali metal ions on the supported catalysts. The addition of sodium to the Pd/SiO$_2$ catalysts results in a presence of the additive which is not uniform on the support and on the supported-palladium which is partly decorated by the additive. Similar experiments on natural pumice indicate that the alkali metal ions are located in the structure of the support itself; they are not detected on the surface of pumice. After deposition of palladium, results show that the alkali metal ions are nearby the palladium crystallites, the surface of palladium remaining free from alkali ions.

Although definitive results on Pd/model-pumices are not obtained on the basis of LEIS and TEM experiments, owing to a porosity and to the difference of surface area between the synthetic supports and the natural pumice, it seems established that no palladium is present on the external surface. Furthermore, there are good indications, especially considering the qualitatively similar reactivity of palladium supported on natural and model pumices (7), that decoration of the palladium crystallites by the alkali metal ions does not occur in the Pd/model-pumice catalysts.

Several studies of catalytic hydrogenations over Pd/model-pumice catalysts to settle the influence of the alkali ion content and of the morphological characteristics on activity and selectivity are now in progress. Preliminary results on hydrogenations of unsaturated organic substrates confirm the trend previously found (3) with Pd/pumice catalysts as a function of the metal dispersion and the alkali ion content in the structure.

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REFERENCES

1. Derrien, M., *in* “Catalytic Hydrogenation” (L. Červený, Ed.), p. 613. Elsevier, Amsterdam, 1987.
2. Fagherazzi, G., Benedetti, A., Deganello, G., Duca, D., Martorana, A., and Spoto, G., *J. Catal.* **150**, 117 (1994).
3. Deganello, G., Duca, D., Martorana, A., Fagherazzi, G., and Benedetti, A., *J. Catal.* **150**, 127 (1994).
4. Duca, D., Liotta, L. F., and Deganello, G., *J. Catal.* **154**, 69 (1995).
5. Liotta, L. F., Venezia, A. M., Martorana, A., Duca, D., and Deganello, G., to be submitted.
6. Pitchon, V., Gallezot, P., Nicot, C., and Praliaud, H., *Appl. Catal.* **47**, 357 (1989).
7. Liotta, L. F., Martin, G. A., and Deganello, G., *J. Catal.* **164**, 322 (1996).
8. Pitchon, V., Guénin, M., and Praliaud, H., *Appl. Catal.* **63**, 333 (1990).
9. Deganello, G., Duca, D., Liotta, L. F., Martorana, A., and Venezia, A. M., *Gazz. Chim. It.* **124**, 229 (1994).

10. Vicarini, M. A., Nicolaon, G. A., and Teichner, S. J., *Bull. Soc. Chim. Fr.* 1466 (1979).
11. Carturan, G., and Strukul, G., *J. Catal.* **57**, 516 (1979).
12. Yermakov, Y. I., *Catal. Rev.* **13**, 77 (1986).
13. Venezia, A. M., Floriano, M. A., Deganello, G., and Rossi, A., *Surf. Interface Anal.* **18**, 532 (1992).
14. Brongersma, H. H., and Mul, P. M., *Surf. Sci.* **35**, 303 (1973).
15. Nichus, H., Heiland, W., and Taglauer, E., *Surf. Sci.* **17**, 213 (1993).
16. Jacobs, J.-P., Lindfors, L. P., Reintjes, J. C. H., Jylhä, O., and Brongersma, H. H., *Catal. Lett.* **25**, 315 (1994).
17. Brongersma, H. H., Bergmans, R. H., Buijs, L. G. C., Jacobs, J.-P., Kruseman, A. C., Severijns, C. A., and van Welzenis, R. G., *Nucl. Instr. Meth. B* **68**, 207 (1992).
18. Brum-Pereira, E., and Martin, G. A., *in* "Natural Gas Conversion II" (H. E. Curry-Hyde and R. F. Howe, Eds.), p. 349. Elsevier, Amsterdam, 1994.