Thermochimica Acta, 133 (1988) 175–189
Elsevier Science Publishers B.V., Amsterdam

PROBING THE ELECTRONIC INTERACTION BETWEEN METAL AND SUPPORT ON Pd/TiO_2 CATALYST WITH ADSORPTION OF HYDROGEN

CHENG-CHUNG HONG and CHUIN-TIH YEH

Department of Chemistry
National Tsinghua University
Hsinchu, Taiwan, Republic of China

ABSTRACT

The formation of palladium hydride and its decomposition into constituents were studied with volumetric and TPD methods on a Pd/TiO_2 catalyst reduced at temperatures below 773 K. The hydrogen sorption isotherm of the volumetric study showed that the hydrogen pressure required for the formation of palladium hydride at room temperature for the catalyst reduced at elevated temperatures was higher than that for the catalyst reduced at room temperature. The TPD study under hydrogen isobar conditions showed that the temperature for the desorption of hydrogen from palladium hydride decreased with the increasing of reduction temperature. Both studies founs that the solubility of hydrogen into palladium crystallites of the catalyst was decreased by reduction treatment. These results were interpreted with a transfer of electrons from reduced support to palladium crystallites because of the reduction pretreatments. This transfer raised Fermi level of valence band of palladium crystallites and diminished electron vacancies remained in the valence band of Pd. The $Pd-H_2$ adsorption/desorption phenomenon is a convenient indicator for monitoring electronic interactions between metal crystallites and support on supported Pd catalysts.

INTRODUCTION

Palladium not only adsorbs hydrogen on its surface but also absorbs hydrogen to form non-stoichiometric hydride, PdH_y, in the bulk. Many fundamental researches on this subject may be found in the literature (1-5). According to the reported pressure-composition-temperature (P-C-T) relationships (3), palladium is in the form of α-phase hydride (y~.01) under low hydrogen pressure at room temperature. As the hydrogen pressure is higher than 10 torr, the α-hydride dissolves more hydrogen and transforms into hydrogen rich β-hydride (y~.60), i.e.,

$$PdH_a + (b-a)/2\ H_2 \rightleftharpoons PdH_b \qquad (1)$$

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

where a and b are the y value in α and β-hydride, respectively. The hydrogen pressure required for the α to β-hydride phase transition, P_{tr}, increases with the system temperature. At 352 K, P_{tr} becomes 76 torr.

However, the amount of hydrogen dissolved into Pd/TiO_2 may be suppressed by a treatment of hydrogen reduction on the catalyst. Burch et al. (6) found that the y value of Pd/TiO_2 catalyst reduced at 473 K (Low Temperature Reduction, LTR) was 0.45. After a reduction at 773 K (High Temperature Reduction, HTR), this value was decreased to 0.11. Baker et al. (7) found that the hydrogen uptake in the bulk of Pd was decreased with increasing reduction temperature on 2-8 % Pd/TiO_2 catalysts. Chang et al. (8) investigated the TRS (Temperature Resolved Sorption) phenomena of palladium catalyst. They also reported an increasing suppression of hydrogen absorption on Pd/TiO_2 with reduction temperature between 623 and 843 K. The reason for this suppression was suggested as a contamination of palladium particles with the reduced support during the reduction treatment (6,7).

Neverthless, Spencer (9) pointed out that the rate of segregation of titanium suboxide (TiO_x, $x<2$) across Pt was negligible (the Wittig temperature of Pt and TiO_2 are 681 K and 709 K respectively) for Pt/TiO_2 catalyst under LTR. Interdiffusion between TiO_x and palladium (with a Wittig temperature of 608 K) crystallites should be insignificant as the Pd/TiO_2 catalyst was reduced by hydrogen at $T < 600$ K. The purpose of this study is to reinvestigate and interpret the suppression of hydrogen absorption on the Pd/TiO_2 catalyst below HTR. A volumetric method was used to acquire quantitatively informations on hydrogen uptake at isothermal condition. A TPD setup was utilized to get information for phase transition temperature at hydrogen isobar condition for the reverse of reaction (1).

EXPERIMENTAL

Two palladium samples, Pd powders and Pd/TiO_2 catalyst, were used in this study.

Pd powders were obtained from Merck and used without further purification. The particle size of these powders is around 60 μm

2.33 wt% Pd/TiO_2 catalyst was prepared by impregnating TiO_2 (Degussa P-25) with $PdCl_2$. The impregnated catalyst was dried in an oven at 378 K. After a calcination in air at 673 K for 4hrs, the catalyst was stored in a dessicator. The dispersion of the catalyst reduced at room temperature was 30% according to a TEM measurement.

Isotherms of hydrogen sorption on the Pd/TiO_2 was measured on a conventional volumetric sorption apparatus equipped with a Texas Instruments precision gauge. The catalyst was prereduced at a desired temperature in flowing hydrogen for 2 hrs. The reduced catalyst was then evacuated for 2 hrs below $1*10^{-5}$ torr at room temperature before each measurement. Uptake isotherms were also measured at room temperature.

The TPD measurements were performed in a flow system described elsewhere (10). The carrier gas of the flow system was 10% H_2/Ar mixture at 1 atm (the hydrogen pressure was 76 torr). The uptake or desorption of hydrogen by the Pd samples was monitored by a thermal conductivity detector. The volume of the reactor was scaled down (from previous 50 ml) to 10 ml to improve the peak resolution of TPD spectrum. The reactor can be disconnected from the flow system and attached to a vacuum system for evacuation treatment to the sample.

RESULTS AND DISCUSSION

1.Volumetric measurement for Pd/TiO_2 catalyst

Figure 1 shows obtained hydrogen sorption isotherms on the Pd/TiO_2 sample reduced at three different temperatures. The sorption isotherms were measured after the catalyst had been reduced at a desired temperature and then evacuated at room temperature. Because strongly chemisorbed hydrogen could not be outgassed at room temperature, the observed hydrogen uptake therefore consisted of weakly chemisorbed (H_w) and absorbed hydrogens (H_b) (11). Based on the curve shape of the sorption isotherms, the uptake of hydrogen above and below 10 torr of hydrogen pressure was assumed to be H_b and H_w respectively. The three sorption isotherms shown in the figure 1 clearly indicated that the amount of hydrogen absorbed was decreased and the P_{tr} required for the hydride formation was increased with the elevation of reduction temperature. Certain interactions between metal and support must occur during the reduction treatments to influence chemical properties of Pd particles on the catalyst.

Since Tauster et al. (12,13,14) reported the SMSI phenomena on HTR supported metal catalyst, electronic interaction (12) and metal-support interdiffusion (15) were proposed as the two main reasons for the metal-support interactions. The latter reason is the most widely accepted model to account for the observation till now (16). As the palladium crystallites were encapsulated or

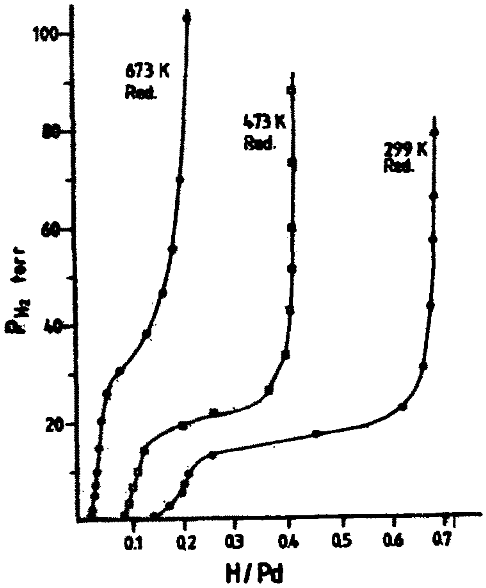

Figure 1. Isotherms of hydrogen uptake for Pd/TiO_2 catalyst reduced at indicated temperatures. After each reduction, the catalyst was evacuated at 299 K. Quantitative data from the figure are summarized in Table 1.

all the "portholes" on the surface of some palladium crystallites were blocked by TiOx, the solubility of hydrogen in palladium crystallites on the catalyst might be suppressed. However, pure encapsulation should not affect the variation of P_{tr} required for the hydride formation. Therefore the increase of P_{tr} in the experiment must be induced by some other reasons.

There are many theoretical advantages for metallic catalyst dispersed on supports. Modification the electronic property of active metals by supports has been proposed as one of these advantages (17,18). Many experimental methods, i.e., ESCA (19), EXAFS (20), magnetization (21), calorimetry (22), etc., have been found in literatures to detect this electron interaction for TiO_2

Table 1. Quantitative data obtained from the volumetric adsorption (figure 1).

Reductn Temp.(K)	$H_t^{(a)}$/Pd	$H_w^{(b)}$/Pd	$F_w^{(c)}$	$H_b^{(d)}$/Pd	$F_b^{(c)}$	P_{tr} (Torr)
299	0.69	0.22	100%	0.47	100%	16
473	0.42	0.12	54%	0.30	60%	21
673	0.22	0.036	16%	0.18	38%	(35)

(a) H_t : Total hydrogen (including weak chemisorption and absorption) uptake after the sample was desorbed in vacuum at room temperature. $H_t=H_w+H_b$.

(b) H_w : Weakly chemisorbed hydrogen. The part of H_t sorbed at $P_{H_2}<10$ torr.

(c) F : Fraction of hydrogen uptake remained for sample reduced at temperature T relative to that reduced at 299 K.

(d) H_b : Absorbed hydrogen, the uptake observed at $P_{H_2}>10$ torr.

supported catalyst. The observed suppression of hydrogen absorption and the increase of P_{tr} with reduction temperature may be accounted qualitatively by the transfer of electrons from the reduced TiO_2 to the supported palladium crystallites during the reduction. According to "Rigid Band Model" illustrated in figure 2, the 4d and 5s valence bands of palladium have a Fermi level of E_f. On interacting with electron donating materials, palladium crystallites are tempted to accept electrons to fill the d-band vacancies with energy higher than E_f. During the hydride formation, palladium crystallites accept electrons from hydrogen atoms (4). Each dissolved hydrogen atom donates one electron to the valence band of palladium crystallite (23). The Fermi level of the metal is thus increased until energy E_h is reached to form the saturated palladium hydride $PdH_{0.6}$. As palladium crystallites on the catalyst accept electrons from the reduced TiO_2, the E_f of palladium crystallites was raised to E_f' (figure 2B). The average potential energy for the remained vacancies in the 4d valence band is also raised. Consequently, less electrons donated from hydrogen are accepted (with y value < 0.60) and higher hydrogen partial pressure is required for the PdH_y formation.

Table 1 lists some quantitative results obtained from the figure 1 to show the variation in hydrogen uptake with reduction condition. In this table, not only the amount of H_b but also that of H_w was shown suppressed for the catalyst reduced at elevated temperature. The H_w has been suggested as those hydrogens adsorbed on the interstitial sites at the subsurface of Pd crystallites and the precursors for the absorbed hydrogen (11). Besides, H_w was suggested to be protonic, i.e., it also donates electron to the valence band of Pd. The amount of H_w, like that of H_b, should be suppressed by electronic interaction. The migration of TiO_x onto the surface of Pd crystallites during the reduction may block these sites and cause an additional suppression to the amount of H_w. A comparison between suppression factors (F, defined in Table 1) may indicate the contribution for migration. Table 1 shows that F_w is close to F_b for 473 K reduced catalyst. A negligible site blockage was indicated for catalyst reduced at this temperature. Nevertheless, the ratio of F_w/F_b fell below 0.5 for 673 K reduced Pd/TiO_2 catalyst. Site blockage thus became an important factor on suppressing the amount of H_w for the catalyst reduced around 673 K.

2.TPD study of Pd powders and Pd/TiO_2 catalyst

Figure 3 showed obtained spectrum due to the desorption and sorption of hydrogen in a typical TPD-TRS experiment on palladium powders. According to the P-C-T relationships of Pd-H_2 system, the powders were saturated with dissolved hydrogen and in the form of β-hydride at 307 K and 0.1 atm H_2 (4). Two hydrogen desorption peaks were found from this sample as the temperature

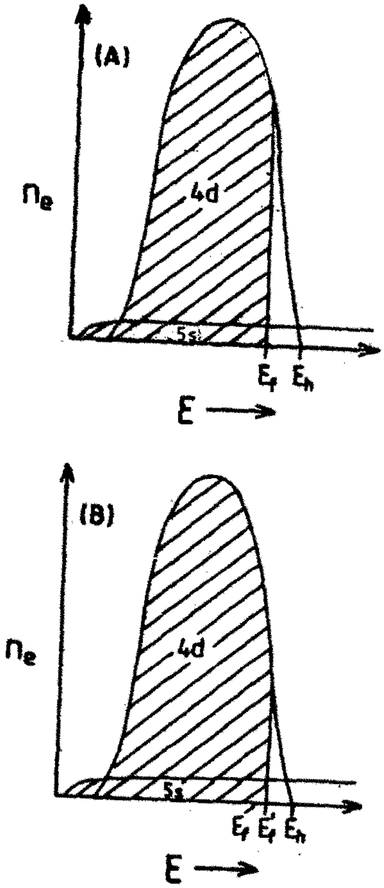

Figure 2. Schematic rigid band model for the valence band of palladium. A). Normal palladium crystallites have a Fermi level of E_f. E_h is the highest energy for 4d orbital. The electron density becomes very low at Energy higher than E_h. B). The Fermi level of palladium is raised to E_f as some electrons are accepted from TiO_2 during reduction. The electron vacancy below E_h is diminished and the average energy in the vacancy is increased.

was raised during TPD. A small peak around 323 K was the desorption of extra hydrogen in the β-phase. A major peak at 362 K resulted from the hydrogen desorbed during the phase transition (reaction 1). Since the dispersion of these powders was less than 0.1%, the desorption and sorption of the chemisorbed hydrogen did not produce any detectable peak in this spectrum. The average desorption temperature (T_d) of the peaks closely agreed with the temperature reported for the phase transition of bulky palladium crystals under 0.1 atm hydrogen pressure (4).

The same TPD-TRS experiment has been performed on the Pd/TiO_2 catalyst. The peak area of TRS or TPD spectra represents the relative amount of absorbed hydride. These two spectra were checked and indeed showed good quantitative consistency with each

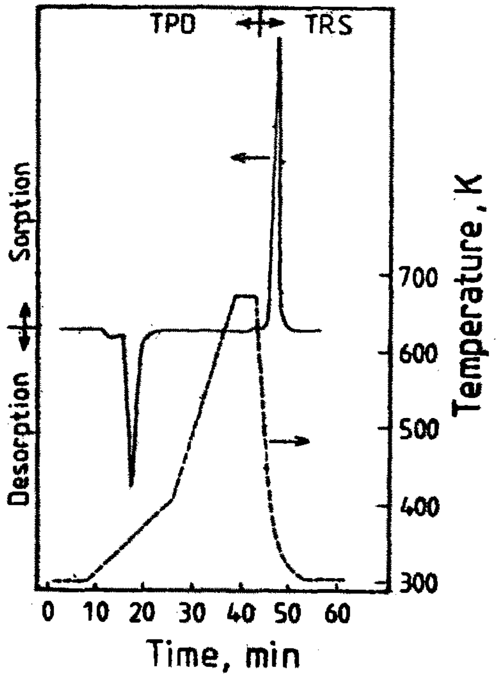

Figure 3. TPD and TRS spectrum for palladium powders. The heating rate below and above 393 K was 5 and 10 K/min respectively.

other. Obtained TPD spectrum was found varying with the condition of pretreatment. Feature R2 in figure 4 showed that the shape and T_d in TPD spectrum of the Pd/TiO_2 catalyst reduced at room temperature was similar to those of Pd powders shown in Figure 3. The diffusivity of the absorbed hydrogen in Pd was obviously high enough (4) so that the desorption rate of the dissolved hydrogen was independent of the metal particle size in the range from nm to µm. The desorption temperature found in TPD therefore directly reflected the decomposition temperature of the palladium hydride.

TREATMENT CONDITION	TPD SPECTRA 362K	REL. AREA	$\bar{T}_d$ K
H_2/Ar 298 K 20 min.	R2 	1.00	359
evacu. 573K 1 hr.	E5 	.943	357
evacu 673K 1 hr.	E6 	.871	354
O_2 298 K 1 hr.	C2 	.900	358
O_2 393 K 1 hr.	C3 	1.00	361
H_2/Ar 573K 1 hr.	R5 	.821	354
H_2/Ar 573 K 9 hr.	R5' 	.764	353

Figure 4. Consecutive TPD spectra for the desorption of hydrogen from a Pd/TiO_2 catalyst after the indicated pretreat condition. T_d denotes average desorption temperature.

TiO_2 is a n-type semiconductor. Its electric conductivity depends on oxygen partial pressure and temperature. Under elevated temperature, TiO_2 is unstable and produces oxygen vacancies according to the following eqúation :

$$TiO_2 \text{ (unperturbed lattice)} = |O|^{\bullet\bullet} + 2\,e^- + 1/2\ O_2\ (g) \qquad (3)$$

where $|O|^{\bullet\bullet}$ represents a site of oxygen vacancy. Excess electrons in the equation enter the conduction band and increase the conductivity of TiO_2 (24). The electronic interaction for metal contacting with n-type semiconductor has also been studied for Ni deposited TiO_2 and Pt deposited $SrTiO_3$ with ESCA (Electron Spectroscopy for Chemical Analysis). A transfer of electron from support to metal was found on these samples heated in the temperature range of 673 K to 888 K (25,26). Palladium has an electron negativity comparable to nickel and platinum. As the Pd/TiO_2 catalyst was heated under vacuum, some electrons should

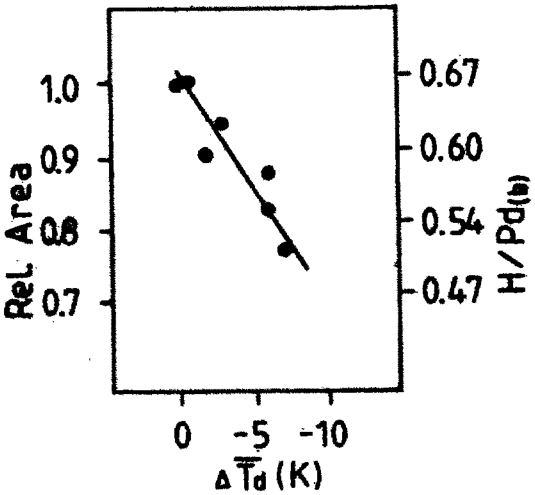

Figure 5. The correlation between the fraction of hydrogen remained in the palladium hydride verse the variation of the desorption temperature for Pd/TiO_2 catalyst with various pretreatment at T<773 K.

also transfer to Pd crystallites. Consequently the P-C-T relationship for palladium hydride formation was changed. Features E5 and E6 in the figure 4 are TPD spectra for the desorption of hydrogen from the Pd/TiO_2 pretreated with evacuation treatment at 573 and 673 K, respectively. The shape of these peaks are indeed different from that of R2. The amount of desorbed hydrogen was decreased (by a ratio of RA) and T_d was shifted to a low temperature (by a difference ΔT_d). The higher the evacuation temperature, the larger was the observed variation in RA and ΔT_d. Since the oxygen atoms lost in the high temperature evacuations might be reversed back to the support by a subsequent recalcination. Palladium crystallites on this recalcined catalyst should therefore restore the original hydrogen desorption properties. This restoration was again confirmed by TPD features of C2 and C3 in the figure 4.

Feature R5 and R5' in figure 4 showed that a hydrogen reduction treatment on the Pd/TiO_2 catalyst at 573 K induced a larger variation in RA and ΔT_d than an evacuation pretreatment at the same temperature (feature E5). The difference comes from the formation of excess hydroxyl ions and/or oxygen vacancies due to the hydrogen spillover onto the support. Extra electrons were transferred from the hydrogen reduced TiO_2 to palladium crystallites because of the spillover (27).

A correlation between the relative amount of desorbed hydrogen and the ΔT_d obtained in the TPD measurement for the evacuated, recalcined and hydrogen reduced Pd/TiO_2 catalyst was shown in figure 5. The amount of desorbed hydrogen apparently decreased parallelly with the variation of temperature of phase transition regardless the pretreatment conditions for this study. According to the "Rigid Band Model" mentioned above, electrons transferred from support to valence band of Pd results in a rise of Fermi level of this metal. At the same time, the dissolved hydrogen became less stable and desorbed at low temperature.

The present TPD system is a simple and sensitive in situ method to investigate the variation of absorption of hydrogen in Pd on Pd/TiO_2 catalysts or promoter added Pd catalysts (28). Metal-support interactions for Pd supported on the other n-type semiconductor (e.g., ZnO, CeO_2), p-type semiconductor (e.g., Cr_2O_3, NiO), and insulator (e.g., Al_2O_3, SiO_2) could also be studied. This method, however, is un-suitable for the other noble metals because of their low hydrogen solubility (4).

CONCLUSIONS

The suppression of hydrogen absorbed in Pd on Pd/TiO_2 was observed as the catalyst had been evacuated or reduced in hydrogen below 773 K. The subsequently absorbed hydrogen in this pretreated catalyst was in high energy state. It was reflected with a rise of hydrogen pressure required to accomplish hydride formation under isothermal condition and a lowering of desorption temperature of the hydride decomposition on isobar condition. The results of these observations may be interpreted by a transfer of electrons from the TiO_2 to Pd. The extent of electronic interaction between metal and support on Pd/TiO_2 catalyst can be estimated from the Pd-H_2 absorption/desorption system by volumetric and/or TPD method.

ACKNOWLEDGEMENT

The financial support of this research by the national science council of the Republic of China are appreciated.

REFERENCES

1.Graham, T., Phil. Trans. Roy. Soc. (London) 156, 415 (1866).

2.Flanagan, T. B., Engelhard Ind. Techn. Bull. 7, 9 (1966).

3.Lewis, F. A., "The Palladium Hydrogen System " Academic Press London, New York 1967.

4.Alefeld, G., and Volkl, J. (eds.), (a). "Hydrogen in Metals I. Basic Properties " Topics in Applied Physics, vol.28, (b)."Hydrogen in Metals II. Application-Oriented Properties", Topics in Applied Physics, vol.29, Springer-Verlag, Berlin, Heidelberg, New York 1978.

5.Flanagan, T. B., and Oates, W. A., in "Transition Metal Hydride " ed. Bau, R., Advance in chemistry series 167, Am. Chem. Soc., Washington, D.C. 1977. p.283.

6.Burch, R., and Bracey, J. D., J. Catal. 86, 384 (1984).

7.Baker, R. T. K., Prestridge, E. B., and McVicker, G. B. J. Catal. 89, 422 (1984).

8.Chang, T.-C., Chen, J.-J., and Yeh, C.-T. J. Catal. 96, 51 (1985).

9.Spencer, M. S., J. Catal. 93, 216 (1985).

10.Chen, G., Chou, W.-T., and Yeh, C,-T., Appl. Catal. 8, 339 (1983).

11.Lynch, J., and Flanagan, T. B., J. Phys. Chem. 77, 2628 (1973).

12.Tauster, S. J., Fung, S. C., and Garten, R. L., J. Am. Chem. Soc. 100, 170 (1978).

13.Tauster, S. J., and Fung, S. C., J. Catal. 55, 29 (1978).

14.Tauster, S. J., Fung, S. C., Baker, R. T. K., and Horsley, J. A., Science (Washinhton, D.C.) 221, 1121 (1981).

15.Meriaudeau, P., Ellestad, O. H., Dufaux, M., and Naccache, C., J. Catal. 75, 243 (1982).

16.Sanchez, M. G., and Gazquez, J. L., J. Catal. 104, 120 (1987).

17.Schwab, G. M., Block, J., Muller, W., and Schultze, D., Naturwissenschaften 44, 582 (1957).

18.Szabo, Z. G., and Solymosi, F., in "Proceeding, 2nd International Congress on Catalyst", P. 1627, Technip, Paries, 1961.

19.Fung, S. C., J. Catal. 76, 225 (1982).

20.Short, D. R., Mansour, A. N., Cook, Jr., J. W., Sayers, D. E., and Katzer, J. R., J. Catal. 82, 299 (1983).

21.Hans-Conrad Zur Loye and Angelica, M. Stacy, J. Am. Chem. Soc. 107, 4567 (1985).

22.Herrmann. J. M. Gravelle-Rumeau-Maillot, M., and Gravelle, P. C., J. Catal. 104, 136 (1987).

23.Wagner, C., J. Chem. Phys. 19, 626 (1951).

24.Che, M., Naccache, C., and Imelik, B., J. Catal. 24, 328 (1972).

25.Kao, C. C., Tsai, S. C., Bahl, M. K., and Chung, Y., Surf. Sci. 95, 1 (1980).

26.Bahl, M. K., Tsai, S. C., and Hung, Y. W., Phys. Rev. B. 21, 1344 (1980).

27.Iwaki, T., J. Chem. Soc., Faraday Trans. I, 79, 137 (1983).

28.Ziemecki, S. B., Jonecs, G., and Michel, J. B., J. Catal. 99, 207 (1986).