ELSEVIER

Journal of Molecular Catalysis A: Chemical 180 (2002) 285–291

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Effects of the addition of titania on the thermal characterization of alumina-supported palladium

Chen-Bin Wang*, Hung-Kuan Lin, Chi-Man Ho

Department of Applied Chemistry, Chung Cheng Institute of Technology, National Defense University,
Tahsi, Taoyuan 33509, Taiwan, ROC

Received 29 May 2001; received in revised form 15 August 2001; accepted 7 November 2001

Abstract

The detailed thermal characterization of $Pd/TiO_2–Al_2O_3$ catalysts under oxygen and hydrogen atmosphere was conducted by means of thermal gravimetric analysis/differential scanning calorimetry (TG/DSC), temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD). A simultaneous TG/DSC measurement revealed that the heat evolved during oxygen adsorption at 25 °C varied slightly with the supports and had a higher value for the smaller palladium crystallite. Hydrogen chemisorption and BET measurements revealed that the coating of Pd/Al_2O_3 catalysts with titania modified the support character to achieve a high dispersion of palladium. TPR and TPD characterizations of oxidized samples further demonstrated that the coating of Pd/Al_2O_3 catalysts with titania promoted the reduction and decomposition of PdO into palladium. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Thermal characterization; TG/DSC; TPR; TPD

1. Introduction

Supported palladium catalysts are the most active for the catalytic combustion of methane [1–6]. Among commonly used supports, alumina is unique because of the ability to retain a high surface area at high temperature and interact strongly with metal [7–10]. Accordingly, we have extensively studied focusing on the alumina-supported ones.

Moreover, the mechanism of Pd/Al_2O_3 towards methane combustion includes an oscillation of the active ingredient between a reduced form (Pd) and an oxidized form (PdO) according to the following equation:

$$2Pd + O_2 \rightarrow 2PdO \qquad (1)$$

$$CH_4 + PdO \rightarrow Pd + CO_2 + H_2O + \text{(adsorbed carbonaceous materials)} \qquad (2)$$

The activity of the methane combustion, therefore, depends heavily on the nature of PdO. A decrease in the strength of the PdO bond should enhance reaction (2) at low temperatures.

The addition of La_2O_3 to the Pd/Al_2O_3 was found by Chou et al. [2] to reinforce the bond strength of PdO on Pd/Al_2O_3 catalysts and reduce the sintering rate of palladium crystallites at high temperatures. Based on the methane combustion activity test, Seo and co-workers [11–13] suggested that the loading of TiO_2 to the Pd catalyst supported on mesoporous materials can promote methane combustion activity. Therefore, we have had interest in coating Pd/Al_2O_3

---

* Corresponding author. Tel.: +886-33-891716; fax: +886-33-891519.
E-mail address: chenbin@ccit.edu.tw (C.-B. Wang).

PII: S1381-1169(01)00450-2

with n-type oxides, TiO_2, and carried out the thermal characterization of the resultant catalysts.

Thermal gravimetric analysis/differential scanning calorimetry (TG/DSC), temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) are valuable techniques for investigating the thermal properties of supported catalysts [14–16]. However, no systematic study has been made of the thermal characterization for the $Pd/TiO_2–Al_2O_3$ catalysts. The aim of the this work is to pursue a more detailed thermal characterization of the $Pd/TiO_2–Al_2O_3$ catalysts by means of oxygen adsorption, oxidation, reduction and thermal decomposition.

2. Experimental

2.1. Sample preparation

Titania-modified alumina supports ($x\%TiO_2–Al_2O_3$ with $x\%$ of TiO_2 in weight) of various TiO_2 loading were prepared by impregnation of γ-Al_2O_3 (Merck, surface area $= 108\,m^2\,g^{-1}$) with appropriate solution of $Ti(O–i\text{-}C_3H_7)_4$ dissolved in 2-propanol. The impregnated samples were subsequently dried overnight at 110 °C, calcined at 600 °C for 6 h and stored as carriers for preparing supported palladium catalysts. Palladium was impregnated on various supports (Al_2O_3 and $x\%TiO_2–Al_2O_3$) by the incipient wetness method with hot H_2PdCl_4 (99%, Aldrich) solution. Pd catalyst was obtained by drying up overnight at 110 °C followed by calcinations at 500 °C for 4 h before storing as testing samples. These palladium catalysts are designated as fresh samples.

2.2. Calorimetric measurements

Isothermal energy changes and amounts of oxygen uptake during oxygen adsorption were measured using a Setaram TG/DSC 111 dual port calorimeter. The apparatus has been described in detail elsewhere [17–22]. Before the adsorption measurement, each $Pd/x\%TiO_2–Al_2O_3$ sample was pre-reduced in flowing hydrogen gas at 150 °C (300 °C for Pd/Al_2O_3 samples) for 1 h and subsequently evacuated for 1 h at 200 °C (350 °C for Pd/Al_2O_3 samples).

2.3. Adsorption measurements

BET surface area was measured through physisorption of nitrogen at -195 °C on samples pretreated with evacuation at 300 °C. Dispersion (D, percentage of atoms exposed to surface) of palladium crystallites on reduced $Pd/x\%TiO_2–Al_2O_3$ samples were estimated by the hydrogen chemisorption measurements performed on a vacuum system at 25 °C under an assumption that $H/Pd^s = 1.1$ [23] for the monolayer chemisorption. Prior to chemisorption measurement, each $Pd/x\%TiO_2–Al_2O_3$ sample was reduced by flowing hydrogen and evacuated at 150 °C (300 °C

Table 1
Dispersion and heats of adsorption of oxygen on palladium measured at 25 °C

Sample	Hydrogen chemisorption		Oxygen chemisorption	
	D^a	d^b (nm)	$N_O^{ad}/N_{Pd}{}^c$	$-\Delta H_{ad}$ (kJ mol^{-1} O_2)
$10.09\%Pd/Al_2O_3$	0.14	7.9	0.10	253
$4.72\%Pd/Al_2O_3$	0.21	5.2	0.14	293
$0.98\%Pd/Al_2O_3$	0.38	2.9	0.27	308
$1.07\%Pd/Al_2O_3$	0.52	2.1	0.33	334
$1.08\%Pd/Al_2O_3$	0.80	1.4	0.48	346
$2.47\%Pd/TiO_2$	0.20	5.5	0.13	270
$1.95\%Pd/TiO_2$	0.33	3.3	0.22	265
$1.10\%Pd/TiO_2$	0.50	2.2	0.31	272
$0.98\%Pd/6\%TiO_2–Al_2O_3$	0.60	1.8	0.41	280
$1.02\%Pd/10\%TiO_2–Al_2O_3$	0.75	1.5	0.49	282
$0.96\%Pd/20\%TiO_2–Al_2O_3$	0.80	1.4	0.46	285

[a] Dispersion of palladium metals.

[b] Average particle size.

[c] Uptake of oxygen atoms on palladium at 25 °C.

for Pd/Al_2O_3 samples). Dispersions of palladium on reduced samples are shown in Table 1.

2.4. TPR/TPD measurements

Both TPR and TPD studies were performed in a fixed bed apparatus. For TPR characterizations, a 30 ml min^{-1} flow of 10% H_2 in Ar was used as the reducing gas when the sample temperature was raised from −60 to 180 °C at a constant rate of 7 °C min^{-1}. The rate of hydrogen consumption during sample reductions was monitored by a thermal conductivity detector (TCD). For TPD characterizations, a flow of He (purity 99.999%) was used in the experiments to purge away the oxygen desorbed from the oxidized samples upon heating from 25 to 1000 °C at a rate of 10 °C min^{-1}. The rate of oxygen desorption was monitored by the TCD in the downstream of the He flow.

3. Results and discussion

3.1. Calorimetric measurements

A typical TG/DSC time profile on reduced 4.72% Pd/Al_2O_3 sample during oxygen chemisorption at 25 °C is shown in Fig. 1. The rate of adsorption is fast at the initial stage, but decreases with the reaction time. The oxygen uptake in each adsorption, N_O^{ad}, is confined to the palladium metal surface and determined according to the Δm_{ox} (where Δm_{ox} denotes the weight gain after an oxidation time reached 2×10^3 s). Integral heats of adsorption of O_2 measured at 25 °C, ΔH_{ad}, are listed in Table 1. This study has shown that integral, isothermal O_2 heats of adsorption on palladium can be easily and reproducibly measured for the catalysts in situ pretreated before the adsorption measurement. Despite some scatter among the data, observed heat varies with the palladium dispersed on $x\%TiO_2$–Al_2O_3 supports and the palladium dispersion. The results are consistent with previous studies on supported palladium [20,24,25] and unsupported bulk palladium [26–30].

Fig. 2 correlates the $-\Delta H_{ad}$ of oxygen adsorption measured from the TG/DSC with the average diameter (*d*) of palladium crystallites dispersed on Al_2O_3 and TiO_2–Al_2O_3 supports. Apparently, the heat evolved upon adsorption of oxygen on palladium crystallites varies significantly with the supports and the diameter. For Pd/Al_2O_3 catalysts, the evolved heats of adsorption increased by about 100 kJ mol^{-1} O_2 as the size of palladium crystallites decreased from 8.0 to 1.5 nm. The crystallite size clearly affects the heats of oxygen adsorption on Pd/Al_2O_3 catalysts that may be due primarily to an electronic effect. However, for Pd/TiO_2–Al_2O_3, the evolved heats of adsorption

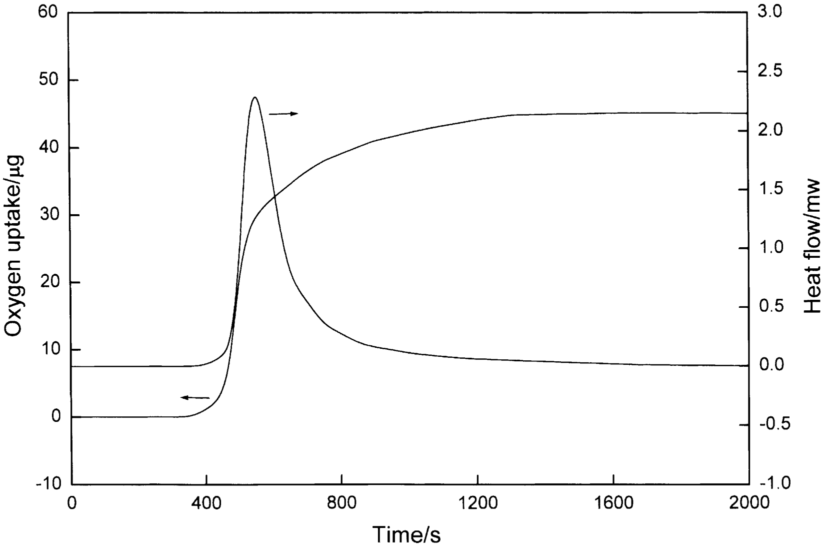

Fig. 1. The TG/DSC results of oxygen adsorption on $4.72\%Pd/Al_2O_3$ sample at 25 °C.

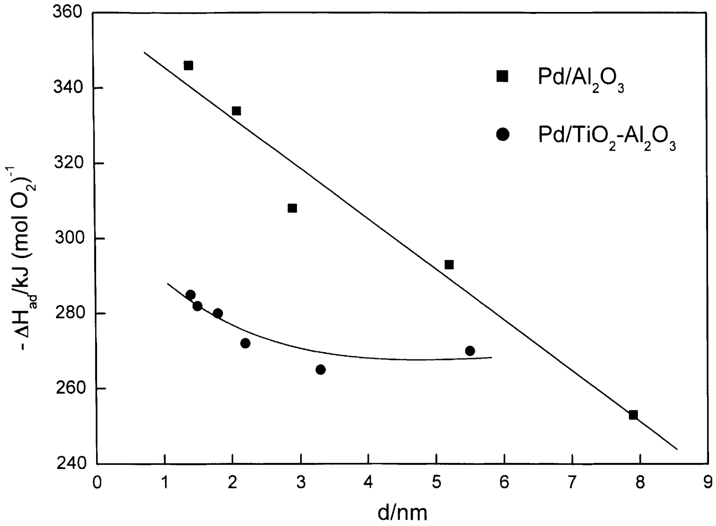

Fig. 2. Variations of $-\Delta H_{ad}$ of oxygen adsorption with the average diameter of various supported palladium metal crystallites: Pd/Al_2O_3 (■) and Pd/x%TiO_2–Al_2O_3 (●).

increased by only about 20 kJ mol^{-1} O_2 as the size of palladium crystallites decreased from 5.5 to 1.5 nm. In the small variations of ΔH_{ad} for oxygen adsorption on Pd/TiO_2–Al_2O_3 catalysts, crystallite size independence is assumed. In a microcalorimetric study of oxygen adsorption on supported palladium, Chou and Vannice [25] observed the variations in the Pd–O bond strength. They concluded that changes in the electronic properties of small palladium crystallites are mainly responsible for the observed increase in the Pd–O bond strength. Comparison of above values, the $-\Delta H_{ad}$ for oxygen adsorption on Pd/TiO_2–Al_2O_3 are smaller than on Pd/Al_2O_3 mainly due to a significant difference in the Pd–O bond strength. The coating of Pd/Al_2O_3 catalysts with TiO_2 can weaken the bond strength of Pd–O.

3.2. BET surface area and dispersion measurements

The BET surface area of x%TiO_2–Al_2O_3 supports and dispersion of Pd/x%TiO_2–Al_2O_3 catalysts for various contents of TiO_2 are collected in Table 2. The addition of TiO_2 decreases the surface area of the Al_2O_3 support. This may be due to the fact that a certain number of the pores of Al_2O_3 support are plugged by TiO_2. Although the surface area of TiO_2 support is lower than the Al_2O_3 support, the dispersion of palladium on the Pd/x%TiO_2–Al_2O_3 catalysts increases with TiO_2 loading. It increases abruptly from 38 to 80% with x from 0 to 20 on the Pd/x%TiO_2–Al_2O_3 catalysts. This indicates that the TiO_2 support has a strong interaction with palladium. The coating of TiO_2 on the high

Table 2
The surface area of x%TiO_2–Al_2O_3 supports and the dispersion of Pd/x%TiO_2–Al_2O_3 catalysts

Support	BET surface area (m^2 g^{-1})	Catalyst	Hydrogen chemisorption	
			D	*d* (nm)
Al_2O_3	234	0.98%Pd/Al_2O_3	0.38	2.9
TiO_2	53	1.10%Pd/TiO_2	0.50	2.2
6%TiO_2–Al_2O_3	188	0.98%Pd/6%TiO_2–Al_2O_3	0.60	1.8
10%TiO_2–Al_2O_3	170	1.02%Pd/10%TiO_2–Al_2O_3	0.75	1.5
20%TiO_2–Al_2O_3	158	0.96%Pd/20%TiO_2–Al_2O_3	0.80	1.4

surface area of Al_2O_3 can modify the character of the support to achieve a high dispersion of palladium.

3.3. TPR measurements

Assuming that oxygen and hydrogen atoms can diffuse readily through the well dispersed palladium crystallites ($d < 3\,nm$) in our samples, the relative strength of the Pd–O bond may be compared by the temperature required for reaction (1) as well as the following reduction reaction. For comparison the TPR spectra of Pd/Al_2O_3, Pd/TiO_2 and $Pd/x\%TiO_2–Al_2O_3$ catalysts are displayed. Fig. 3 shows the characteristic TPR spectra of these catalysts oxidized at 500 °C to study the effect of support composition. The amount of oxygen atom (N_O) reduced in TPR experiments has been calibrated with the hydrogen consumption and converted to N_O/N_{Pd} (where N_{Pd} denotes the number of palladium atom in each sample). The N_O/N_{Pd} in Fig. 3 are determined to be 0.90, 1.00, 1.02 and 1.13, respectively, for $0.98\%Pd/Al_2O_3$, $0.98\%Pd/6\%TiO_2–Al_2O_3$, $0.96\%Pd/20\%TiO_2–Al_2O_3$ and $1.10\%Pd/TiO_2$. This shows that the dominant species upon oxidation at 500 °C is PdO.

A positive peak is observed around 30 °C for $0.98\%Pd/Al_2O_3$. This peak around 30 °C is attributed to both reactions (3) and (4) for hydrogen consumption during the reduction of PdO to palladium

$$1.5H_2 + Pd^sO \rightarrow Pd^sH + H_2O \quad (3)$$

$$(1 + \tfrac{1}{2}x)H_2 + Pd^bO \rightarrow Pd^bH_x + H_2O \quad (4)$$

$$Pd^bH_x \rightarrow Pd^b + \tfrac{1}{2}xH_2 \quad (5)$$

A negative peak around 80 °C is assigned to the desorption of absorbed hydrogen from Pd^bH_x according to the reaction (5) [31]. The onset temperature of the main reduction stage decreased in the sequence Pd/Al_2O_3, $Pd/x\%TiO_2–Al_2O_3$ and Pd/TiO_2. Increasing the coating of TiO_2 on $Pd/x\%TiO_2–Al_2O_3$ catalysts cause distinct shifts of the reduction peak to lower temperature. Profile for $0.98\%Pd/6\%TiO_2–Al_2O_3$ displays that an additional peak of hydrogen consumption occurs around 0 °C besides the peak around 30 °C. The temperature of this new peak shifted to a lower temperature and its intensity relative to that of the peak around 30 °C is increased as the amount of added TiO_2 is increased. The TPR profile for $1.10\%Pd/TiO_2$ shows that the catalyst is reduced below 0 °C. Apparently, observed changes of the TPR profiles in Fig. 3 indicate variations in the distribution of palladium oxide with support composition. The peak around 0 °C should be the PdO dispersed on titania-rich grains and the peak around 30 °C should be the PdO dispersed on alumina-rich grains. Probably, the coating of Pd/Al_2O_3

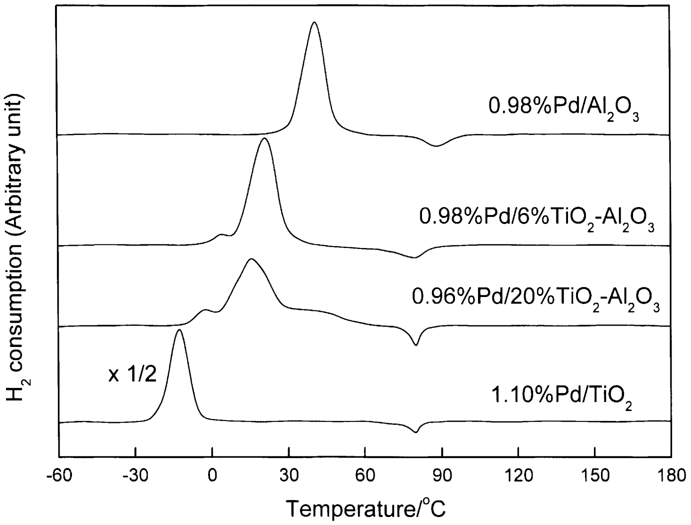

Fig. 3. TPR profiles of different supported palladium catalysts.

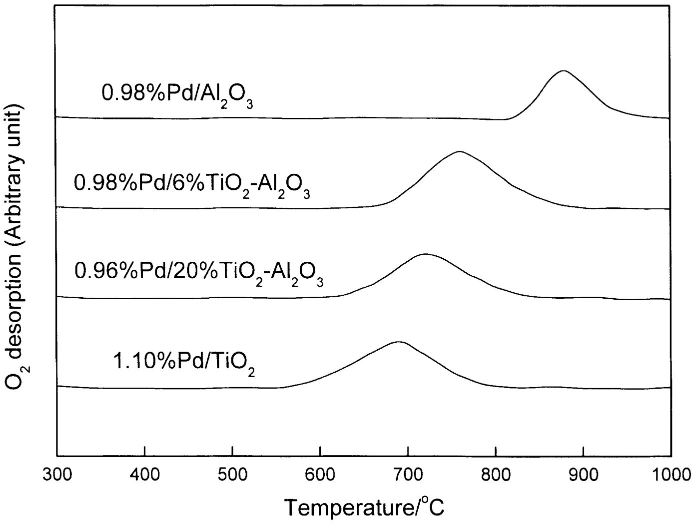

Fig. 4. Oxygen TPD profiles from PdO/x%TiO_2–Al_2O_3 catalysts.

catalysts with TiO_2 can increase the titania-rich grains to decrease the reduction temperature.

3.4. TPD measurements

The effect of TiO_2 coating on Pd/Al_2O_3 can also be characterized with the TPD technique. Fig. 4 indicates a series of TPD spectra of oxygen obtained from PdO/Al_2O_3, PdO/TiO_2 and PdO/x%TiO_2–Al_2O_3. The N_O/N_{Pd} in Fig. 4 are determined to be 0.63, 1.08, 0.89 and 0.96, respectively, for 0.98%Pd/Al_2O_3, 0.98%Pd/6%TiO_2–Al_2O_3, 0.96%Pd/20%TiO_2–Al_2O_3 and 1.10%Pd/TiO_2. Since the desorption of oxygen is not complete at 1000 °C, the N_O/N_{Pd} for 0.98%Pd/Al_2O_3 is small than 1.

The oxygen desorption temperature has shifted towards a higher temperature in the sequence PdO/TiO_2, PdO/x%TiO_2–Al_2O_3 and PdO/Al_2O_3. The supported PdO/Al_2O_3 becomes unstable at $T > 800\,^{\circ}C$ and was thermally decomposed into metallic palladium in the heating process according to reaction (1). The degree of the shift towards a lower temperature obviously increased with the loading of titania. The temperature gradually lowers from 800 to 600 °C with increasing loading amount of titania from 0 to 100 on the 1%Pd/x%TiO_2–Al_2O_3 catalysts. This improvement is ascribed to the interactions between palladium and titania through oxygen that enhances the decomposition of palladium oxide at low temperature.

4. Conclusions

Analysis of the TG/DSC, TPR and TPD records proves a useful tool for studying the thermal properties of supported catalysts. The overall results give some evidence for the character of the coating titania on the Pd/Al_2O_3 catalysts. These results reveal that the coating of Pd/Al_2O_3 catalysts with titania can decrease the ΔH_{ad} for oxygen adsorption and promotes the reduction/decomposition of PdO into palladium.

Acknowledgements

The author acknowledges the financial support of this study by the National Science Council of the Republic of China.

References

[1] J.G. McCarty, Catal. Today 26 (1995) 283.
[2] T.Y. Chou, C.H. Leu, C.T. Yeh, Catal. Today 26 (1995) 53.

[3] R. Burch, P.K. Loader, F.J. Urbano, Catal. Today 27 (1996) 243.
[4] J.K. Lampert, M.S. Kazi, R.J. Farrauto, Appl. Catal. B 14 (1997) 211.
[5] M. Lyubovsky, L. Pfefferle, Appl. Catal. A 173 (1998) 107.
[6] M. Lyubovsky, L. Pfefferle, Catal. Today 47 (1999) 29.
[7] R.F. Hicks, H. Qi, M.L. Young, R.G. Lee, J. Catal. 122 (1990) 295.
[8] P. Briot, M. Primet, Appl. Catal. 68 (1991) 301.
[9] R.J. Farrauto, M.C. Hobson, T. Kennelly, E.M. Waterman, Appl. Catal. A 81 (1992) 227.
[10] F.H. Ribeiro, M. Chow, R.A.D. Betta, J. Catal. 146 (1994) 537.
[11] T.G. Kang, J.H. Kim, G. Seo, H.C. Park, Hwahak Konghak 36 (1998) 364.
[12] W.S. Ahn, D.H. Lee, T.J. Kim, J.H. Kim, G. Seo, R. Ryoo, Appl. Catal. A 181 (1999) 39.
[13] T.G. Kang, J.H. Kim, S.G. Kang, G. Seo, Catal. Today 59 (2000) 87.
[14] J.E. Baker, R. Burch, S.E. Golunski, Thermochim. Acta 142 (1989) 329.
[15] B. Fubini, Thermochim. Acta 148 (1989) 37.
[16] F. Janssen, Thermochim. Acta 148 (1989) 137.
[17] P. Leparlouer, Thermochim. Acta 92 (1985) 371.
[18] P. Leparlouer, J. Mercier, B. Jalon, Thermochim. Acta 103 (1986) 21.
[19] P. Leparlouer, Thermochim. Acta 121 (1987) 307.
[20] Y.S. Ho, C.B. Wang, C.T. Yeh, J. Mol. Catal. A 112 (1996) 287.
[21] C.B. Wang, C.T. Yeh, J. Mol. Catal. A 120 (1997) 179.
[22] C.B. Wang, C.T. Yeh, J. Catal. 178 (1998) 450.
[23] K. Masayoshi, I. Yasunobn, T. Nobuo, L.B. Robert, B.B. John, B.C. Jerome, J. Catal. 64 (1980) 74.
[24] C.B. Wang, C.T. Yeh, Appl. Catal. A 209 (2001) 1.
[25] P. Chou, M.A. Vannice, J. Catal. 105 (1987) 342.
[26] D. Brennan, D.O. Hayward, B.M.W. Trapnell, Proc. R. Soc. A 256 (1960) 81.
[27] G. Ertl, P. Rau, Surf. Sci. 15 (1969) 443.
[28] G. Ertl, J. Koch, Z. Phys. Chem. Neue Fol. 69 (1970) 323.
[29] H. Conrad, G. Ertl, J. Kuppers, E.E. Latta, Surf. Sci. 65 (1977) 245.
[30] G.D. Zakumbaeva, N.A. Zakarina, V.A. Naidin, A.M. Dostiyarov, N.F. Toktabaeya, E.N. Litvyakova, Kinet. Catal. 24 (1983) 379.
[31] G. Chen, W.T. Chou, C.T. Yeh, Appl. Catal. 8 (1983) 389.