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Characterization of Pd–CeO_x interaction on α-Al₂O₃ support

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Abstract

The Pd–Ce interaction was studied over CeO₂ (0.3–2.5 wt.%)–Pd (1 wt.%) / α-Al₂O₃ catalysts used in the reforming reaction of CH₄ with CO₂. The samples were characterized by using high resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS). The activity and selectivity behavior was in good agreement with that of other supported metal catalysts (Ni and Pd) modified with different promoters. The preliminary results of HRTEM would indicate that the CeO_x forms small crystallites around the Pd particle. The XPS analysis for the regions of Ce 3d and Pd 3d, gives an account of Ce being present mostly as Ce³⁺ and a high binding energy for Pd 3d_{5/2} (335.3 eV), an evidence of Pd–Ce chemical interaction. The Pd/Al XPS intensity ratios vs. the Pd average particle size, determined by TEM, show an excellent correlation for fresh and used catalyst. These results indicate that the diminution of the Pd/Al ratios was due to Pd sintering. Consequently, the small amounts of CeO_x species do not cover the Pd particle, in agreement with the HRTEM results. The overall results stand for the promoter action mechanism of the CeO_x for the reforming reaction with CO₂.

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1. Introduction

The reforming reaction of CH₄ with CO₂ has motivated the accomplishment of numerous studies in search of active and selective catalysts, considering the existence of great natural gas deposits with high CO₂ content that could be used to produce synthesis gas and from this liquid fuels. The reaction displays some disadvantages that limit their potential application such as its strong endothermic character, which demands high reaction temperature to obtain reasonable conversion levels. This operating condition produce the sintering of metallic particle, and deactivation by the formation and accumulation of carbonaceous deposits. It was demonstrated that metal supported catalysts like Pt/ZrO₂, Rh/Al₂O₃ and Rh/MgO [1–3] are active and selective for a dry reforming reaction,

but the high cost of active metals limits their application. Some cheaper metals like Ni and Pd, can be used for reforming with CO₂ using special supports or adding promoters like LaO₃, CaO, and CeO₂, which prevent or reduce the carbon formation. The use of Pd as an active metal is particularly attractive by its remarkable activity for the decomposition of CH₄ [4] at high temperature, favoring the production of H₂ and the formation of carbonaceous deposits. Nagaoka and Aika [5] studied the effect of the aggregate of CeO_x (Ce/Pd = 5) in the activity and stability of a Pd(2 wt.%) / γ-Al₂O₃ catalyst at 1023 K, demonstrating that the formation of carbonaceous deposits is remarkably reduced. On the basis of this study we have recently shown [6] that the addition of 2.5 wt.% of Ce to a Pd(1 wt.%) / α-Al₂O₃ catalyst practically eliminates the carbon deposition, with a slight increase in the CO/H₂ ratio. In this case, a slow diminution of the activity level as a function of time has been verified, with tendency to a constant value, related fundamentally to metal sintering. The possibility of using a support of proven thermal stability in the preparation of the catalyst, such as α-Al₂O₃, confers additional importance to these results. On the basis of them we have recently investigated

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the effect of the load of Ce in greater detail, having verified that it can be reduced to smaller values than the Pd content, without altering its capacity to inhibit the carbon formation. In order to be able to explain the role of the Ce in the reforming reaction, it is necessary to know the degree of interaction with Pd. Previous studies by TEM, made with Pd/ α -Al₂O₃ catalysts with a high load of Ce (5–30 wt.%), indicated that the promoter would be located either in the neighborhoods or in contact with Pd particles [7]. Therefore, the inhibition of C formation in the reforming reaction cannot be explained by supposing that the Ce aggregates limit the activation of CH₄ on the Pd particles. In this work, we have investigated the Ce–Pd interaction in CeO_x (0.3–2.5 wt.%)–Pd(~1 wt.%)/ α -Al₂O₃ catalysts of proven activity, selectivity and stability in the reforming reaction of CH₄ with CO₂. The characterization of the catalysts, in particular the phase CeO_x–Pd, has been made by means of high resolution transmission electron microscopy (HRTEM) and X-ray photoelectrons spectroscopy (XPS) techniques.

2. Experimental

2.1. Catalyst preparation

A Pd catalyst with a metallic content near 1 wt.% was prepared, by means of the successive impregnating of α -Al₂O₃ (Rhône Poulanc, BET area = 10 m²/g) with a solution of acetyl acetate of Pd in toluene (3.0×10^{-3} g Pd/ml). The support was kept in contact with the solution for 24 h, then filtered, dried in flow of N₂ and calcined in air at 773 K for 1 h. The preparation was then reduced in flow of H₂ at 573 K. The first impregnation incorporates a load of approximately 0.24 wt.% of Pd. By means of two additional charges, repeating the stages of calcination and reduction, the content of Pd rose to 1 wt.%, obtaining the catalyst named Pd0. A portion of this preparation was calcined in air at 1009 K and later reduced at the same temperature with a H₂(5%)/Ar mixture for 1 h, with the purpose of increasing the Pd particles size, obtaining the sample Pd5. By using the Pd0 and Pd5 catalysts we prepared different CeO_x–Pd/ α -Al₂O₃ catalysts by impregnation with aqueous solutions of Ce(NH₄)₂(NO₃)₆. After a drying stage the preparations were calcined in air at 773 K or 1009 K. Some of them were stored in the oxidized form and others were reduced in H₂(5%)/Ar mixture for 1 h. In this way, the samples Ce–Pd3, Ce–Pd9, and Ce–Pd11 were obtained from Pd0 and Ce–Pd6 from Pd5.

2.2. Catalyst characterization

The determination of the Pd and Ce content was made by atomic absorption and inductive coupled plasma spectrometry respectively.

The exposed Pd fraction in the different catalysts was determined by H₂ chemisorption in a volumetric equipment, using the method of the double isotherm.

XPS measurements were made using a PHI 548 spectrometer using the incident radiation Al K α of 1486.6 eV at 250 W, 20 mA, and 50 eV of pass energy. This system has a pre-chamber for samples introduction and *in situ* heat treatment,

which was evacuated until 2×10^{-7} Torr for sample transfer to the analysis chamber, where the base pressure was always inferior to 5×10^{-10} Torr. The Al 2p binding energy was taken as a charge reference, fixed at 74.0 eV. The signal deconvolution was made with XPSPEAK Ver. 4.1 program, using Shirley type background subtraction and sum of Gaussian–Lorentzian asymmetric functions. The obtained binding energies were determined with a precision of ± 0.5 eV. The atomic ratio estimations were done relating the peak areas after the background subtraction and corrected relative to the corresponding atomic sensitivity factors to an approximated absolute error of 20%.

Fresh and used samples of different catalysts were examined by TEM in a Philips CM200 UT microscope, operating at 200 kV at room temperature. The samples were dispersed in ultrasound and placed on an amorphous C film.

2.3. Activity and selectivity test

The activity and selectivity of the catalysts were investigated in a flow reactor operated at 923 K and 1300 Torr, which was fed with a CH₄/CO₂/Ar (25/25/50 mol%) mixture. Catalyst loads of 0.4 g diluted with an equal amount of α -Al₂O₃ were placed inside a quartz tube of 4 mm of internal diameter in a horizontal electrical oven. Using a total flow of 200 ml/min, the gas hourly space velocity was 23250 h⁻¹. The catalyst temperature was measured by a thermocouple located at the end of the reactor. The catalysts were reduced at room temperature with a H₂(5%)/Ar mixture, with subsequent temperature elevation up to 923 K in Ar.

The reactants and products analysis were made by gas chromatography (GC) using two instruments with thermal conductivity detectors. In one of the GC a silica gel column (6 ft \times 1/8 in.) at 90 °C with He as carrier was used to separate CO₂. In another unit, the content of H₂, CO and CH₄ was analyzed using a Chromosorb 102 column (14 ft \times 1/8 in.) with Ar flow. The water formed by the reverse water gas shift reaction (RWGS) CO₂ + H₂ \rightleftharpoons CO + H₂O was separated by a bed of silica gel. The concentration of H₂O in the out flow stream was estimated from the O₂ balance.

3. Results and discussion

Table 1 summarizes the main physicochemical characteristics of the catalysts used in this work. Considering the high load of Pd in relation to the support area, the dispersion of the base catalyst, Pd0, calcined in air at 773 K is high. When the temperature of calcination and reduction was 1009 K, the dispersion diminished significantly, as observed for the sample Pd5. This behavior was attributed to the growth of Pd particles by sintering. In Ce presence the diminution of the Pd exposed fraction of the catalysts Ce–Pd3, Ce–Pd6 and Ce–Pd9 is not so important in spite of the treatments at high temperature, which seems to indicate that the promoter attenuates the sintering process.

Table 2 summarizes some physicochemical characteristics of the catalysts after a long run test, where the diminution in the percentual conversion for the Pd0 sample is mainly due to

Table 1
Physicochemical properties of Pd/ α -Al₂O₃ and Ce-Pd/ α -Al₂O₃ catalysts

Catalyst ^a	Ce (wt.%)	Treatment		H/Pd ^b
		Air (K)	H ₂ (K)	
Pd0	–	773	773	0.18
Ce-Pd3	0.47	1009	–	0.14
Pd5	–	1009	1009	0.06
Ce-Pd6	0.47	1009	1009	0.10
Ce-Pd9	0.33	773	–	0.15
Ce-Pd11	2.5	1009	1009	0.075

^a In all samples the Pd content is ~1 wt.%.

^b All catalysts were reduced at 573 K in pure H₂ for chemisorption measurements.

the build-up of carbon deposits as determined by thermo gravimetric analysis. On the other hand, the important effect of the addition of a small load of CeO_x on carbon formation is observed. The decrease in dispersion is attributed to Pd particle sintering in the reaction process.

The role of Ce, as a promoter, in the reforming reaction with CO₂ can be explained on the basis of the existence of Ce₂O₃ species on the catalyst surface. CO₂ can oxidize these species to CeO₂ producing CO, whereas C produced by the activation of CH₄ would be responsible for the reduction of CeO₂ to Ce₂O₃. This change in the oxidation state of CeO₂ is evident from the results obtained by XPS for Ce 3d region. Fig. 1 shows the spectra corresponding to the catalyst Ce-Pd9 taken as a reference, since the rest of the analyzed samples showed a similar behavior.

The great complexity of the observed structures is due to the hybridization of Ce 4f with ligand orbitals and the partial occupation of valence state orbitals 4f [8] that can be solved in eight components. Using the notation of Burroughs et al. [9] the peaks can be assigned: v, v', v'' and v''' for Ce 3d_{5/2} and u, u', u'' and u''' for Ce 3d_{3/2}. Shyu et al. investigated the systems Pd and Pt/ γ -Al₂O₃ modified with Ce [10,11] and CeO₂/ γ -Al₂O₃ [12] correlating the amount of CeO₂ with the peak u''' coming from the transition between 4f0 initial and final states. Therefore, u''' becomes the fingerprint of Ce⁴⁺ species, since Ce⁺³ (Ce₂O₃) does not have 4f0 configuration.

Assuming a uniform mixture of Ce³⁺ and Ce⁴⁺, the intensity relative to the sum of the eight contributions of Ce 3d to the u''' peak can be used to quantify the Ce⁴⁺ present in the sample [10,11].

The comparison of the spectra of Fig. 1a and b, corresponding to the oxidized and reduced *in situ* catalyst at 823 K, shows a clear diminution of the signal u''' indicating that, in these conditions of reduction, most of the superficial Ce is in +3 oxidation state. Nevertheless, signals corresponding to the peak

Table 2
Physicochemical properties of used Pd/ α -Al₂O₃ and Ce-Pd/ α -Al₂O₃ catalysts

Catalyst	H/Pd	Deactivation (%) ^a	C (wt.%)
Pd0	–	72	54.5
Ce-Pd3	0.035	14	–
Ce-Pd9	0.054	14	0.5

^a Deactivation ratio = $\{1 - [(\text{CH}_4 \text{ conversion at } t = 24 \text{ h})/(\text{CH}_4 \text{ conversion at } t = 0)]\} \times 100$.

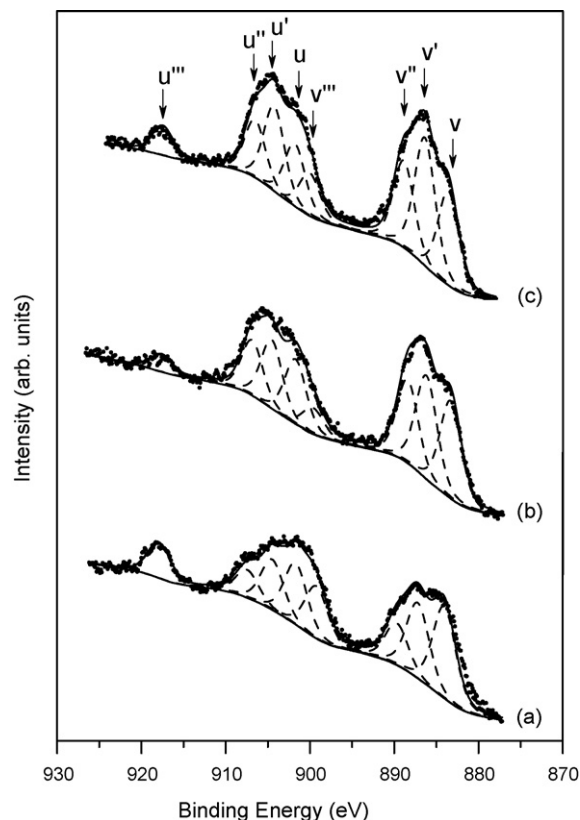


Fig. 1. Ce 3d XPS spectra for the Ce-Pd9 sample: (a) oxidized *in situ* at 823 K, (b) reduced *in situ* at 823 K, and (c) after 34 h reaction as received.

v and v'' are still present which can be due to the formation of nonstoichiometric Ce oxides [12].

Fig. 1c corresponds to the spectra of the Ce-Pd9 sample used for 34 h. Unlike the fresh sample, this was analyzed as removed from the reactor, without any temperature treatment. The coexistence of both states of oxidation is observed there, giving account for Ce promotional mechanism, previously proposed.

Table 3 summarizes the XPS results obtained for the different samples studied as a function of the *in situ* heat treatment and Fig. 2a–c, show the XPS spectra for Pd 3d region corresponding to the catalysts Ce-Pd9, oxidized and reduced *in situ* at 823 K, and Pd0, reduced *in situ* at 823 K, respectively. The high Pd 3d_{5/2} binding energy (335.2 eV) for the Ce-Pd9 catalyst in comparison with the obtained for the Pd0 catalyst (334.6 eV), after a reduction treatment, gives an evidence of the Pd–CeO_x interaction. The presence of CeO_x maintains the Pd particle partially oxidized. Nevertheless, when comparing the values of the binding energies obtained for Pd5 and Ce-Pd6 catalysts (Table 3) we can see that this tendency is not fulfilled, probably due to the greater particle size (low dispersion, see Table 1) which enhances the Pd metallic character. On the other hand, the Ce-Pd11 catalyst is a particular case in which, in spite of the fact that the Pd particle is larger than the ones of other catalysts, the interaction is again evident due to the greater amount of Ce (2.5 wt.%), revealing a compromise situation between Pd particle size and Ce loading. Table 3 also shows the Ce/Al XPS ratios, which are in good correlation with the Ce loads.

Table 3
XPS analysis results as function of *in situ* thermal treatment

Catalyst	Treatment ^a	Pd/Al $\times 10^2$	Ce/Al $\times 10^2$	Ce ⁴⁺ (%)	Pd 3d _{5/2} BE (eV)
Pd0	Air	3.1	–	–	336.9
	H ₂	3.0	–	–	334.6
Ce-Pd9 ^b	Air	3.3	1.9	51	336.8
	H ₂	2.6 (1.4)	1.7 (2.0)	26 (38)	335.2 (335.3)
Ce-Pd11	Air	2.4	3.6	76	337.3
	H ₂	1.9	3.5	32	335.3
Pd5	Air	2.0	–	–	336.7
	H ₂	1.7	–	–	334.7
Ce-Pd6	Air	2.8	2.4	46	336.7
	H ₂	2.3	2.8	0	334.9

^a All the thermal treatments were made at 823 K.

^b The quantities between brackets correspond to a sample with a reaction time of 35 h.

An excellent correlation of the present results can be observed by plotting the Pd/Al XPS ratios as a function of Pd particle diameter (see Table 3), obtained from TEM and H₂ chemisorption (see Tables 1 and 2, columns labeled H/Pd).

In Fig. 3, the open square represents the particle diameters derived from the relation $d_{H/Pd} = 1.12/(H/Pd)$ assuming the hemispherical particle model and a surface atom density of

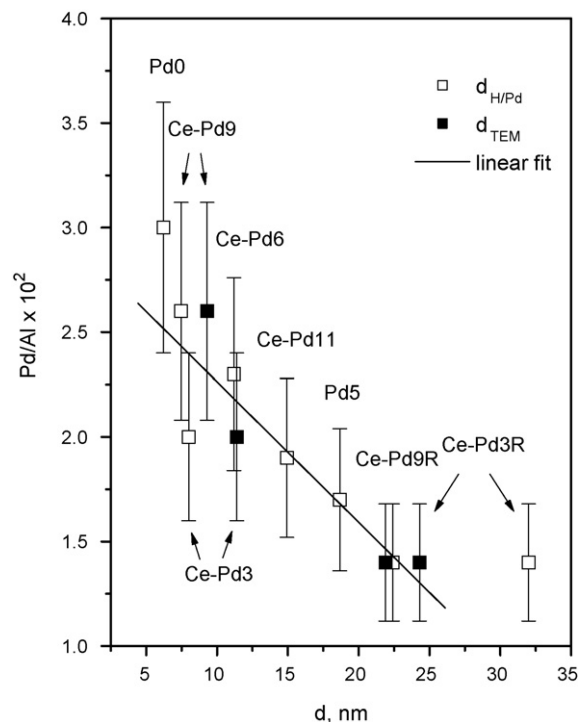


Fig. 3. Pd/Al XPS ratios vs. Pd particle diameter: (□) diameter determined from H₂ chemisorption using the relation $d_{H/Pd} = 1.12/(H/Pd)$; (■) diameter determined from TEM image using the relation $d_{TEM} = \sum n_i d_i^3 / \sum n_i d_i^2$. The error bar represents the absolute error in de Pd/Al XPS ratio determination.

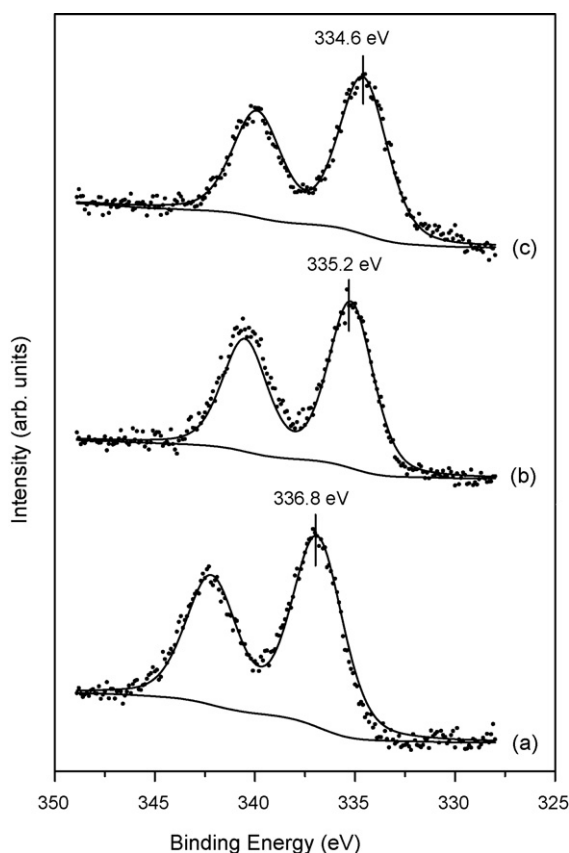


Fig. 2. Pd 3d XPS spectra: (a) Ce-Pd9 sample oxidized *in situ* at 823 K, (b) Ce-Pd9 sample reduced *in situ* at 823 K, and (c) Pd0 sample reduced *in situ* at 823 K.

1.27×10^{19} atoms/m² [13]. The solid square represents the particle diameters derived from the volume/area relation $d_{TEM} = \sum n_i d_i^3 / \sum n_i d_i^2$, where n_i is the number of particles with diameter d_i measured from digitalized TEM images using the equivalent circle particle diameter definition [14]. The linear fit was made considering only the diameters $d_{H/Pd}$ obtained from fresh samples.

As it was expected, when the particle size grows the Pd/Al XPS ratios diminish as a consequence of the exposed area reduction. When we considered the samples Ce-Pd3 and Ce-Pd9 analyzed after reaction (indicated with a capital R in the graph) both samples, within experimental error, maintain the correlation indicating that the Pd/Al XPS ratio diminution is only due to Pd sintering. A great difference in particle size can be noticed in sample Ce-Pd3R depending on the method used for its determination. This apparent discrepancy is due to the process of isotherms evaluations in the H₂ chemisorption experiment for samples with very low dispersions (large particle size).

Fig. 4 shows a high resolution image of the Ce-Pd9 catalyst used in the reforming reaction for 34 h. The crystallographic planes of two nanoparticles, with lattice spacings 3.25 Å and 3.2 Å are clearly observed. These lattice spacings may correspond to PdO and also to more than one Ce oxide phase. A precise determination of these species requires complementary studies. However, based on the reaction condition and the catalyst history we discard the possibility of PdO existence and we think that these nanoparticles corresponds to CeO_x phases. The HRTEM images obtained from the samples, before and

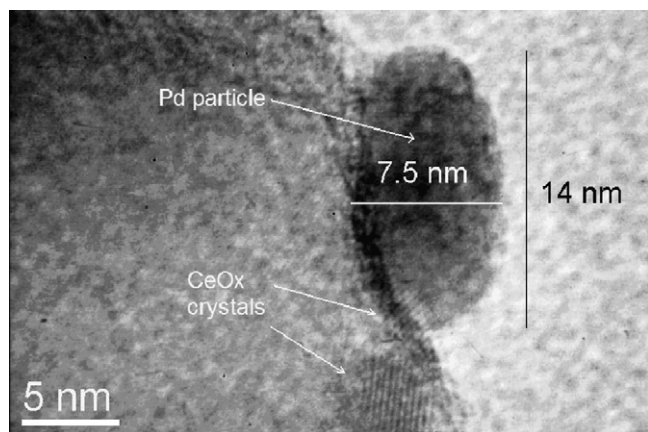


Fig. 4. HRTEM image for Ce-Pd9 catalyst after 34 h reaction (observe the large size of the Pd particle and, next to it, two nanoparticles of CeO_x).

after reaction, did not show lattice spacings corresponding to the formation of a Pd–Ce interface alloy.

These preliminary results allow us to establish that Ce oxide species are actually close, but not on top, of the Pd particle in opposition to the results obtained by other authors for similar systems [7]. On the other hand, this conclusion is in agreement with the H_2 chemisorption and X-ray diffraction result (not shown).

4. Conclusions

The Pd–Ce interaction has been studied on CeO_x -Pd/ α - Al_2O_3 catalysts used in the reforming reaction of CH_4 with CO_2 by means of different characterization techniques. On the basis of the present results we can conclude that this interaction occurs between palladium and reduced species of cerium. In this sense, the XPS determinations show a higher binding energy for Pd when the modified catalysts are reduced and that the cerium valence state, under these conditions, is close to Ce^{3+} as it is demonstrated by the decrease of the u''' peak

intensity observed in the Ce 3d spectrum. The analysis made on the different samples showed that this interaction depends mainly on the Pd particle size and the cerium content. The characterizations by means of H_2 chemisorption and, in preliminary form, HRTEM would indicate that Ce species form small crystals in contact with the Pd particles, which is consistent with the remarkable correlation between XPS Pd/Al ratios and Pd particle size before and after reaction. Also, the HRTEM results did not show the formation of an alloy in the Pd–Ce interface region, limiting the Pd–Ce interaction only to a chemical one in which the reduction of the CeO_x causes the partial oxidation of Pd after the reduction treatment, as demonstrated by the XPS results.

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References

- [1] J.H. Bitter, K. Seshan, J.A. Lercher, *J. Catal.* 171 (1997) 279.
- [2] J. Erdöhelyi, F. Cserényi, Solymosi, *J. Catal.* 141 (1993) 287.
- [3] H.Y. Wang, E. Ruckenstein, *Appl. Catal. A* 204 (2000) 143.
- [4] J.R. Rostrup-Nielsen, J.-H. Bak-Hansen, *J. Catal.* 144 (1993) 38.
- [5] K. Nagaoka, K. Aika, *Bull. Chem. Soc. Jpn.* 74 (2001) 1841.
- [6] P.G. Schulz, M.G. Gonzalez, C.E. Quincoces, C.E. Gigola, *Ind. Eng. Chem. Res.* 44 (2005) 9020.
- [7] J.H. Holles, R.J. Davis, T.M. Murray, J.M. Howe, *J. Catal.* 195 (2000) 193.
- [8] A. Fujimori, *Phys. Rev. B* 27 (1983) 3992.
- [9] P. Burroughs, A. Hamnett, A.F. Orchard, G. Thornton, *J. Chem. Soc. Dalton Trans.* (1976) 1686.
- [10] J.Z. Shyu, K. Otto, W.L.H. Watkins, G.W. Graham, R.K. Belitz, H.S. Gandhi, *J. Catal.* 114 (1988) 23.
- [11] J.Z. Shyu, K. Otto, *J. Catal.* 115 (1989) 16.
- [12] J.Z. Shyu, W.H. Weber, H.S. Gandhi, *J. Phys. Chem.* 92 (1988) 4964.
- [13] J. Anderson, *Structure of Metallic Catalysts*, Academic Press, New York, 1975, p. 296.
- [14] R.J. Matyi, L.H. Schwartz, J.B. Butt, *Catal. Rev.-Sci. Eng.* 29 (1) (1987) 41.