CO hydrogenation on rhodium catalysts as studied by temperature programmed desorption and reaction

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The addition of promoters to rhodium catalysts has been studied for CO hydrogenation. Differences in temperature programmed desorption and reaction show that the support and promoter have an influence on the dissociation of carbon monoxide. A low temperature methane peak appears at 110°C in the CO temperature programmed hydrogenation on the unpromoted catalyst. The mechanistic implications of these results are discussed.

Keywords: CO hydrogenation; supported rhodium catalysts; temperature programmed desorption; temperature programmed surface reaction; metal promoter interaction

1. Introduction

The addition of promoters or the use of different supports to rhodium containing catalysts is well known to change drastically the reactivity and selectivity in $CO + H_2$ reactions [1–8]. However, the mechanism of the promoting effects is still not well understood and various models have been proposed to explain these changes both in selectivity and activity. The results of the literature must be taken with care, since recently Nonnemann et al. [9] have drawn the attention on the importance of the impurities in the studies in promoting effects. Thus, many discrepancies in the literature results may be explained by differences in purity of the used silica supports. The proposed models for the promotion effects have been summarized and critically reviewed by Ponec [10] and Hindermann et al. [11].

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In many works, CO is reported to dissociate more easily on promoted catalysts [8,12–14]. Such an increased dissociation probability has also been observed by Lavalley et al. [15] for ceria promoted catalysts. However, these last authors have shown an apparent discrepancy between an enhanced CO dissociation and a sharp drop in hydrocarbon, essentially methane, activity upon promotion. They attributed this to a possible difference of reactivity of the formed surface carbon species. Orita et al. [16] have observed three forms of surface carbon on Rh/TiO_2 catalysts. The aim of the present paper is to examine more thoroughly this point and more specially to study the reactivity of the surface carbon.

2. Experimental

2.1. CATALYST PREPARATION

The catalysts have been obtained by a conventional impregnation method from an aqueous solution of $RhCl_3 \cdot nH_2O$ (Johnson Matthey) on a pure silica (Roth 0201 100 mesh, BET surface area 289 m^2/g). The analysis of the silica has shown that the Na, K and Fe contents are less than 100 ppm. CeO_2 (BET surface area 46 m^2/g) has been obtained by calcining $Ce(NO_3)_3 \cdot 6H_2O$ (Fluka) during 6 h at 550°C. Promoters have been introduced by coimpregnation of the corresponding nitrates.

2.2. CATALYST CHARACTERIZATION

Rhodium metal particle size has been measured after reduction at 450°C in a hydrogen flow. Three methods have been used: pulse CO adsorption, H_2 adsorption and transmission electron microscopy (TEM, Philips EM 300G). The composition and homogeneity on the catalysts have been studied by microprobe scanning electron microscopy.

2.3. ACTIVITY MEASUREMENTS

0.5 g of catalyst is placed in a continuous flow fixed bed glass reactor of 10 mm inner diameter and reduced at 300 or 400°C during 10 h in a 2 $\ell\,h^{-1}$ g cat^{-1} H_2 flow. The reaction is performed at 220°C with a total gas flow of 4 or 6 $\ell\,h^{-1}$ g cat^{-1} and a CO/H_2 molar ratio of 0.5 at atmospheric pressure (0.1 MPa). The gas flows are regulated by Brooks mass flowmeters (5850). Products are analyzed on line by gas chromatography. The conversion is expressed as number of CO moles converted to the given product versus total number of introduced CO times 100 and given after 8 h on stream.

2.4. TEMPERATURE PROGRAMMED DESORPTION (TPD) AND SURFACE REACTION (TPSR)

TPD and TPSR are performed as follows: 0.5 g of the catalyst is placed into a quartz tube and reduced in situ at 450°C during 10 h under a 2 ℓ h^{-1} hydrogen flow. The inlet gas flows are controlled by Brooks mass flowmeters. Two thermal conductivity GOW-MAC cells placed at the entrance and the outlet of the reactor allow to record any change in the outlet gas composition. The outlet gases are more thoroughly analyzed by two on-line GC apparatuses. CO, CO_2 and CH_4 are detected by a TCD cell, whereas $CH_4, CH_3CHO, C_2H_5OH, CH_3COCH_3$ ... are measured by a FID. The chromatographic conditions are the following:

– CO, CO_2, CH_4: Column Chromsorb 102, 1.5 m length, diameter: 3.2 mm. He carrier gas 40 ml/min, room temperature.

– $CH_4, CH_3CHO, C_2H_5OH, CH_3COCH_3$: Column Haysep, 1.8 m length, 3.2 mm diameter. He carrier, 20 ml/min, isothermal temperature 110°C.

TPD. The catalyst was left under a helium flow during its cooling down from 450°C to room temperature. The catalyst is then saturated by CO. The reactor is again flushed by pure helium until no more CO is observed in the gas phase. The temperature is then increased at a 6°C min^{-1} rate under a 2 ℓ h^{-1} g cat^{-1} flow of helium.

TPSR. The catalyst is treated in the same manner as for the TPD, but it is switched to H_2 before heating up at a 6°C min^{-1} rate. Several tests have been made after partial desorption of CO. These experiments have been performed as follows: after the surface of the catalyst has been saturated by CO, flushed by He, it is heated under helium at a 6°C min^{-1} temperature increase rate as for the TPD measurements; the partial desorption is then interrupted at the given temperature (150, 200 and 250°C). The catalyst is cooled down to room temperature, the helium is switched to H_2 and the experiment is then performed as for the TPSR.

3. Results and discussion

3.1. PARTICLE SIZE MEASUREMENTS

As can be seen in table 1, the particle size measurements are in good agreement for Rh/SiO_2 in the three methods. For the ceria supported catalysts the particle sizes measured by CO adsorption are apparently smaller than those obtained by hydrogen adsorption and electron microscopy. The same difference can be observed between CO and H_2 adsorption measurements for ceria promoted Rh/SiO_2 catalysts. However, Lavalley et al. [15] have shown by FTIR that gem-dicarbonyl species are formed on these catalysts. The assumption of one adsorbed CO molecule for one exposed rhodium atom is no more valid. The formation of

Table 1
Metal particle size

Catalyst	Particle size (nm)		
	TEM	CO adsorption	H_2 adsorption
5%Rh/SiO_2	3.5	3.1	3.1
5%Rh5%CeO_2/SiO_2	–	1.7	4.0
5%Rh/CeO_2	3.3	2.5	3.0

gem-dicarbonyl is accompanied by the disrupture of small metal particles in presence of CO [17–19].

3.2. ACTIVITY MEASUREMENTS

It can be seen from table 2 that the presence of CeO_2 has three effects. The first

Table 2
Activity of catalysts

Catalyst	CO conversion (%)						Selectivity to oxygenates (%)
	CH_4	total HC	MeOH	AcH	EtOH	total	
5%Rh/SiO_2 Tred 300°C							
a	0.94	1.66	0.03	0.09	0.0	1.78	6
5%Rh/SiO_2 Tred 450°C							
a	0.37	0.65	0.02	0.13	0.0	0.80	18
b	0.40	0.68	0.05	0.13	0.0	0.86	20
5%Rh5%CeO_2/SiO_2 Tred 300°C							
a	0.20	0.34	0.04	traces	0.22	0.60	43
b	0.04	0.08	0.03	traces	0.09	0.20	60
5%Rh5%CeO_2/SiO_2 Tred 450°C							
a	0.08	0.12	0.03	traces	0.17	0.32	63
b	0.08	0.12	0.04	traces	0.19	0.35	67
5%Rh/CeO_2 Tred 450°C							
a	0.06	0.10	0.06	0.0	0.18	0.34	71

[a] Gas flow: 4 ℓ h^{-1} g cat^{-1}.
[b] Gas flow: 6 ℓ h^{-1} g cat^{-1}.

one is to depress the overall activity of the catalyst essentially at the dependence of the conversion to methane, even with a very small amount of CeO_2. The second is to enhance the conversion to C_2 oxygenates and the third is to shift the C_2 oxygenates selectivity from almost pure acetaldehyde to pure ethanol. A more detailed discussion on these effects is given in ref. [3]. The selectivity and activity results on the present rhodium/silica catalyst are in very good agreement with those obtained by Nonnemann et al. [9] on very pure silica. This confirms the analysis of the silica used in the present work which shows that the first effect of the studied promoter is to drop sharply the overall activity. This result is somewhat in disagreement with that of Borer and Prins [20], who have observed an increased activity by addition of sodium to a Rh/SiO_2 catalyst. This difference may be ascribed to the used silica. Indeed, Nonnemann et al. [9] have also observed a decrease in activity when sodium is added to a very pure silica containing catalyst with an increase when the amount of sodium is higher. The sharp decrease in overall activity and essentially in hydrocarbon formation is in apparent disagreement with an enhanced dissociation probability since it is commonly believed that the rate determining step is the carbon monoxide dissociation. However, the pulse rate surface analysis experiments of Mori et al. [21] have shown that for rhodium catalysts the rate of CO dissociation is near to that of hydrogenation of the obtained carbonaceous species. Therefore, even a slight change in one of these reaction rates could change the rate limiting step.

3.3. TEMPERATURE PROGRAMMED DESORPTION AND SURFACE REACTION

3.3.1. Temperature programmed desorption and hydrogenation of the formed carbon

Fig. 1, curve a, shows the TPD spectrum after CO adsorption at room temperature. Two main peaks are observed with maxima around 100 and 330°C. The first peak corresponds to the desorption of carbon monoxide and that at 330°C to a coincident CO_2 and CH_4 desorption. This second peak has been attributed to CO dissociation followed by the hydrogenation of the formed carbon by residual hydrogen from the reduction of the catalyst. Recently, Koerts et al. [22] made measurements with labeled CO to determine if the formed CO_2 was coming from the Boudouard reaction. They concluded that CO_2 formation can be attributed to an exchange with an active oxygen species of the surface. They excluded the formation of CO_2 by CO dissociation since the sites for isotopic scrambling were not the bridge bonded CO for vanadium promoted rhodium catalysts and since these bridged sites are believed to be the precursors of CO dissociation. However, it must be taken into consideration that on vanadium containing catalysts the centre of CO dissociation might be at the interface of Rh and promoter through a C and O coordinated CO, whose existence has been evidenced by infrared spectroscopy [3,12,23–26]. Furthermore, Koerts et al. [22] evidenced that the exchange between CO or CO_2 and the oxygen of the surface must be very fast since upon $C^{18}O$ adsorp-

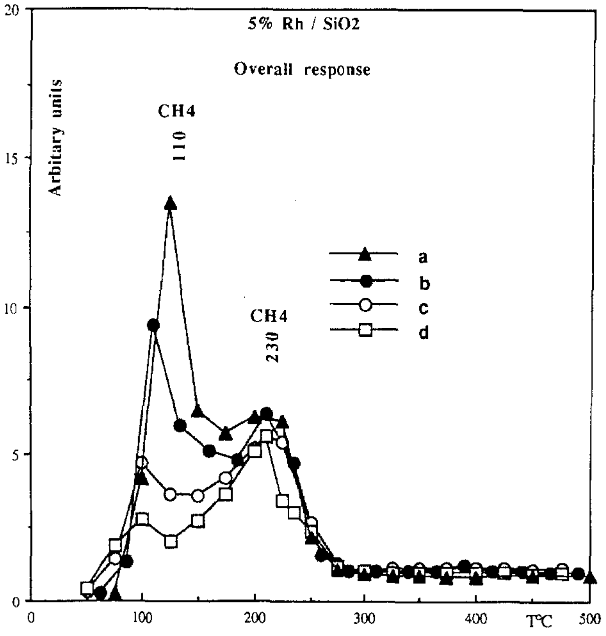

Fig. 1. TPD after CO adsorption and hydrogenation of the formed carbon on Rh/SiO_2.

tion essentially $C^{16}O_2$ is formed. An alternative explanation to that of Koerts et al. could be that CO is dissociated at the Rh–V interface, a second CO molecule removes the oxygen and the thus formed CO_2 might exchange its oxygens very rapidly with active oxygen species of the surface. The infrared spectra of scrambling of Koerts et al. have been taken on an impure Grace type silica and that might be of significance. In the case of the present catalyst CH_4 is formed simultaneously to CO_2 desorption, and hence this second peak is rather in agreement with CO dissociation.

After TPD, the catalyst was cooled under helium. Helium is then switched to hydrogen at room temperature and then the catalyst is heated under a hydrogen flow of 2 ℓ h^{-1} g cat^{-1} at 6°C min^{-1}. The carbon formed during the TPD up to 450°C is hydrogenated at about 230°C as shown in fig. 1, curve b.

The same procedure was applied to the ceria promoted rhodium/silica catalyst. The peak for coincident CO_2 and CH_4 desorption during TPD after CO adsorption is shifted down to 275°C (fig. 2, curve a). The carbon formed during this TPD is hydrogenated at 175°C compared to 230°C for rhodium on silica (fig. 2, curve b).

The same trend can be observed for rhodium supported on ceria with an even larger shift of coincident CO_2 + CH_4 formation down to 235°C.

These results seem to indicate that both the carbon monoxide dissociation and surface carbon hydrogenation are easier on the promoted catalysts. The question arises to explain the discrepancy between this result and a decreased reactivity for low amounts of promoters.

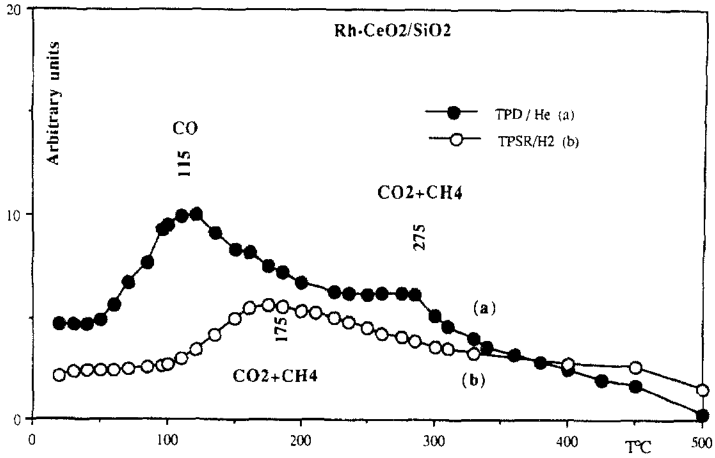

Fig. 2. TPD after CO adsorption and hydrogenation of the surface carbon formed during TPD on $Rh–CeO_2/SiO_2$.

A more systematic study of the temperature programmed surface reaction of adsorbed carbon monoxide was therefore undertaken.

3.3.2. Temperature programmed surface reaction TPSR

The obtained results for the Rh/SiO_2 catalyst are given in fig. 3. Curve a corresponds to the TPSR of carbon monoxide adsorbed at room temperature. It can be seen that two methane peaks are observed: one at 110°C and another at 230°C. The

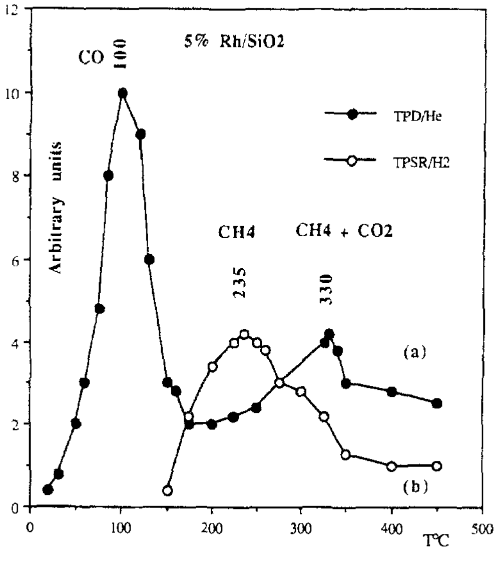

Fig. 3. TPSR experiments on Rh/SiO_2.

methane peak at 230°C corresponds to that of surface carbon hydrogenation after TPD up to 450°C. The first peak at 110°C decreases if part of the carbon monoxide is desorbed as indicated in the experimental part prior to the TPSR experiment. Curves b–d are obtained after partial desorption at 150, 200 and 250°C respectively. The amount of methane formed at 230°C is almost the same as for curve a. The TPD experiment shows (fig. 1) that only CO is desorbed between 100 and 250°C.

It seems therefore that hydrogenation of CO could occur through a non-dissociative pathway on the present Rh/SiO_2 catalyst under these reaction conditions. This low temperature methane formation could not be observed by Koerts et al. [27] and Ponec et al. [28] during the TPSR of CO adsorbed at room temperature. It appears only after desorption of CO at 250°C. This must probably be due to the difference in the silica used. The silica used in the present study has a very high specific area and the metal particle size is very low. As can be seen in fig. 4 only one peak of methane formation is observed for the ceria supported catalysts (175°C). This peak corresponds to that of carbon hydrogenation after TPD. It seems therefore that on these catalysts the low temperature methane formation is suppressed. For a ceria promoted rhodium/SiO_2 catalyst the same shift is observed.

The addition of trace amounts of Fe to Rh/SiO_2 has the same effect: the low temperature peak is shifted to 150°C (fig. 5).

The present results are puzzling, but are in good accordance with the result of Mochida et al. who observed that most of the methane formed on Rh/SiO_2 was produced by a reversibly adsorbed CO species [29] whereas on Rh/TiO_2 it was an irreversibly adsorbed CO species which was the reaction intermediate.

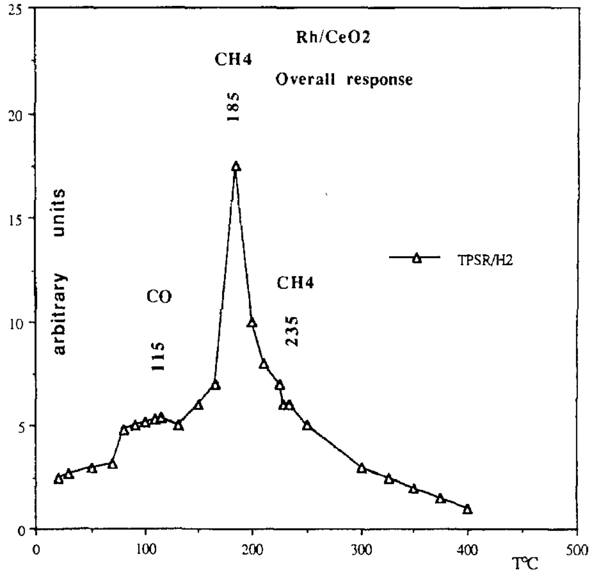

Fig. 4. TPSR after CO adsorption on Rh/SiO_2.

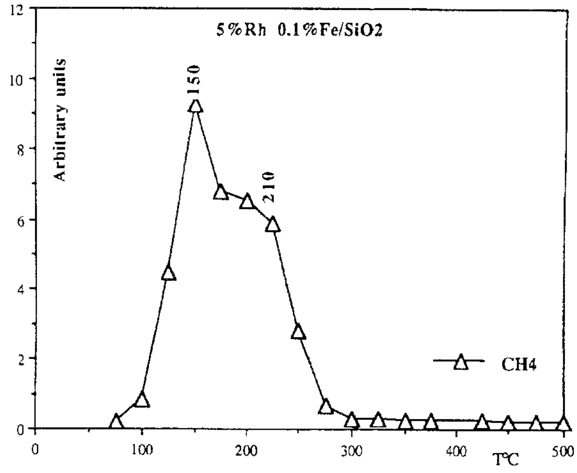

Fig. 5. TPSR after CO adsorption for 5%Rh0.1%Fe/SiO_2 catalyst.

These results lead to conclude that a reaction pathway to methane through a non-dissociative mechanism could be possible on Rh/SiO_2. The FTIR spectra of adsorbed CO show that an absorption peak at 1914 cm^{-1} corresponding to CO adsorbed in a bridging position on the Rh(100) face disappears when promoters are added to the silica catalysts [5]. The bridged bonded CO on the Rh(100) face or on defects of this face could be the active species in this low temperature methane formation. Ren and Liu [30] have observed that if the density of defects is high CO dissociation might occur on the rhodium surface. It cannot be excluded that the difference of activity of the promoted catalyst might be ascribed to altering the surface restructuring during CO adsorption as observed on promoted Rh/SiO_2 catalysts by Kraus et al. [31] and on Pd catalysts [32,33]. The roughness of the Pd surface seems to play a role in CO dissociation [34]. The disappearance of this species could possibly also explain that the scrambling of oxygen in CO as observed by Koerts et al. [22] is not the same for the bridged bonded CO on Rh/SiO_2 and vanadium promoted catalyst.

As a conclusion, a puzzling low temperature methane formation peak is observed on Rh/SiO_2. This methane formation peak seems to be related to a non-dissociative CO hydrogenation to methane. The suppression of this pathway in presence of the promoter could explain the apparent discrepancy between an enhanced dissociation probability, an increased reactivity of the formed surface carbon and the drop of activity in presence of the promoter. The presence of the promoter could also favour the dissociative pathway. However, the presence of special sites for a low temperature CO dissociation on the rhodium/silica catalyst in presence of hydrogen cannot entirely be excluded. Experiments to explain the difference between the present results and those of other authors are underway.

References

[1] M. Ichikawa, Bull. Chem. Soc. Japan 51 (1978) 2268.

[2] M. Ichikawa, Bull. Chem. Soc. Japan 51 (1978) 2273.

[3] A. Kiennemann, R. Breault, J.P. Hindermann and M. Laurin, J. Chem. Soc. Faraday Trans. I 83 (1987) 2119.

[4] A.S. Lisitsyn, S.A. Stevenson and H. Knözinger, J. Mol. Catal. 63 (1990) 201.

[5] A.G.T.M. Bastein, W.J. van den Boogert, B. Schuller, H. Luo and V. Ponec, Appl. Catal. 29 (1987) 243.

[6] A.G.T.M. Bastein, W.J. van den Boogert, B. Schuller, H. Luo and V. Ponec, J. Chem. Soc. Faraday Trans. I 83 (1987) 2103.

[7] B.J. Kip, E.G.F. Hermans and R. Prins, Appl. Catal. 35 (1987) 141.

[8] R.P. Underwood and A.T. Bell, Appl. Catal. 34 (1987) 289.

[9] L.E.Y. Nonnemann, A.G.T.M. Bastein, V. Ponec and R. Burch, Appl. Catal. 62 (1990) L 23.

[10] V. Ponec, Catal. Today 12 (1992) 227.

[11] J.P. Hindermann, G. Hutchings and A. Kiennemann, Catal. Rev.-Sci. Eng. 35 (1993) 1.

[12] W.M.H. Sachtler and M. Ichikawa, J. Phys. Chem. 90 (1986) 4752.

[13] R.P. Underwood and A.T. Bell, J. Catal. 11 (1988) 109.

[14] J.P. Hindermann, A. Kiennemann and S. Tazkritt, Stud. Surf. Sci. Catal. 48 (1989) 481.

[15] J.C. Lavalley, J. Saussey, J. Lamotte, R. Breault, J.P. Hindermann and A. Kiennemann, J. Phys. Chem. 94 (1990) 5941.

[16] H. Orita, S. Naito and K. Tamura, J. Catal. 111 (1988) 464.

[17] H.F.J. van 't Blik, J.B.A.D. van Zon, T. Huizinga, J.C. Vis, D.C. Koningsberger and R. Prins, J. Phys. Chem. 87 (1983) 2264.

[18] P. Johnston, R.W. Joyner, P.D.A. Pudney, E.S. Shpiro and B.P. Williams, Faraday Discussion Chem. Soc. 89 (1990) 91.

[19] F. Solymosi and M. Pasztor, J. Phys. Chem. 89 (1985) 4789.

[20] A.L. Borer and R. Prins, in: *10th Int. Congr. on Catalysis*, Budapest 1992, eds. L. Guczi, F. Solymosi and P. Tétényi (Akadémia Kiado, Budapest, 1993) p. 114.

[21] Y. Mori, T. Mori, T. Hattori and Y. Murakami, Appl. Catal. 66 (1990) 59.

[22] T. Koerts, W.J.J. Welters, J.H.M.C. van Wolput and R.A. van Santen, Catal. Lett. 16 (1992) 287.

[23] B.P. Underwood and A.T. Bell, J. Catal. 111 (1988) 325.

[24] M.N. Bredikhin, Yu. Lokhov and V.L. Kuznetsov, Kinet. Catal. 28 (1987) 671.

[25] H.F.J. van 't Blik, J.B.D.A. van Zon, T. Huizinga, J.C. Vis, D.C. Koningsberger and R. Prins, J. Am. Chem. Soc. 107 (1985) 3139.

[26] S.A. Stevenson, A. Lisitsyn and H. Knözinger, J. Phys. Chem. 94 (1990) 1576.

[27] T. Koerts, PhD Thesis Eindhoven University of Technology, Eindhoven, The Netherlands (1992).

[28] V. Ponec and L.E.Y. Nonnemann, Stud. Surf. Sci. Catal. 61 (1991) 225.

[29] I. Mochida, N.I. Keyama, H.I. Shibashi and H. Fujitsu, J. Catal. 110 (1988) 150.

[30] D.M. Ren and W. Liu, Surf. Sci. 232 (1990) 316, 323.

[31] L. Kraus, M.I. Zaki, H. Knözinger and B. Tesche, J. Mol. Catal. 55 (1989) 55.

[32] R. Raval, S. Haq, M.A. Harrison, G. Blyholder and D.A. King, Chem. Phys. Lett. 167 (1990) 391.

[33] M.H. El-Yakhloufi and E. Gillet, Catal. Lett. 17 (1993) 11.

[34] E. Gillet and V. Matolin, Z. Phys. D 19 (1991) 347.