Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Catalysis 236 (2005) 168–171

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Research Note

New type of rhodium gem-dicarbonyls formed in Rh-ZSM-5: An FTIR spectroscopy study

Elena Ivanova [a], Mihail Mihaylov [a], Frederic Thibault-Starzyk [b], Marco Daturi [b], Konstantin Hadjiivanov [a,*]

[a] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*
[b] *Laboratoire Catalyse et Spectrochimie, CNRS-ISMRA, Université de Caen, 6, bd. Maréchal Juin, 14050, Caen cedex, France*

Received 12 July 2005; revised 13 September 2005; accepted 14 September 2005

Abstract

CO adsorption on Rh-ZSM-5 leads to the formation of both the well-known $Rh^+(CO)_2$ gem-dicarbonyls and another kind of dicarbonyl species as yet unknown. The latter are most probably formed with the participation of Rh^{n+} ($n > 1$) ions in cationic positions in the zeolite. These species are characterized by $\nu_s(CO)$ at 2176 cm^{-1} and $\nu_{as}(CO)$ at 2142 cm^{-1}. The dicarbonyl structure is proven by ^{12}CO–^{13}CO coadsorption. In excellent agreement with the theoretically expected values, the mixed complexes, $Rh^{n+}(^{12}CO)(^{13}CO)$, were characterized by $\nu(^{12}CO)$ at 2164 cm^{-1} and $\nu(^{13}CO)$ at 2106 cm^{-1}. In contrast to the classical gem-dicarbonyls, the new species are destroyed in the presence of water. This is consistent with the proposed higher oxidation state of rhodium in this case.

Keywords: Adsorption; Carbon monoxide; FTIR spectroscopy; Rhodium; Dicarbonyls; Zeolites

1. Introduction

The carbonyl complexes of supported rhodium have been a subject of steady interest [1–26]. It is well established that CO adsorption of rhodium-containing catalysts results in the formation of $Rh^+(CO)_2$ species characterized by $\nu_s(CO)$ at 2120–2075 and $\nu_{as}(CO)$ at 2053–1990 cm^{-1} [1–25]. Most of the investigations of CO adsorption on supported rhodium catalysts have been performed with prereduced samples. Because of the high stability of the gem-dicarbonyls of Rh^+, they are produced via oxidation of metallic rhodium, and most authors believe that the support surface hydroxyl groups are involved in the process [20–25]. There have been few studies of nonreduced rhodium-containing samples [21,26]. Several authors have reported carbonyl bands at relatively higher frequencies and assigned them to Rh^{n+}–CO species ($n > 1$) [7–9,19,20,26]. In this paper we report the formation of new types of rhodium dicarbonyl complexes formed with rhodium cations in an oxidation state higher than 1+. These species are produced in an Rh-ZSM-5 sample, and presumably the high coordinative unsaturation of cations in zeolites contributes to their formation. Indeed, some authors have reported [26] that Rh^+ cations in Rh-ZSM-5 are low coordinated and can accommodate up to four CO molecules. In this paper we report on the formation of the as-yet unknown rhodium dicarbonyl species.

The starting H-ZSM-5 material, supplied by Degussa, had a Si/Al ratio of 26.8. Rh-ZSM-5 was prepared by solid-state ion exchange; 1.5 g of H-ZSM-5 was mixed with 0.15 g $RhCl_3 \cdot nH_2O$, the mixture was ground in an agate mortar, and then placed in a quartz reactor and heated to 773 K in a nitrogen flow for 1 h. The nominal rhodium concentration in the sample was 3.7 wt% Rh and corresponded to an exchange degree of ca. 60%.

The IR spectra were recorded on a Nicolet Avatar 360 spectrometer at a spectral resolution of 2 cm^{-1} and accumulation of 128 scans. A self-supporting pellet (ca. 15 mg cm^{-2}) was prepared from the sample powder and treated directly in a purpose-made IR cell. The latter was connected to a vacuum-adsorption

---

[*] Corresponding author. Fax: +359 2 8705024.
E-mail address: kih@svr.igic.bas.bg (K. Hadjiivanov).

0021-9517/$ – see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2005.09.017

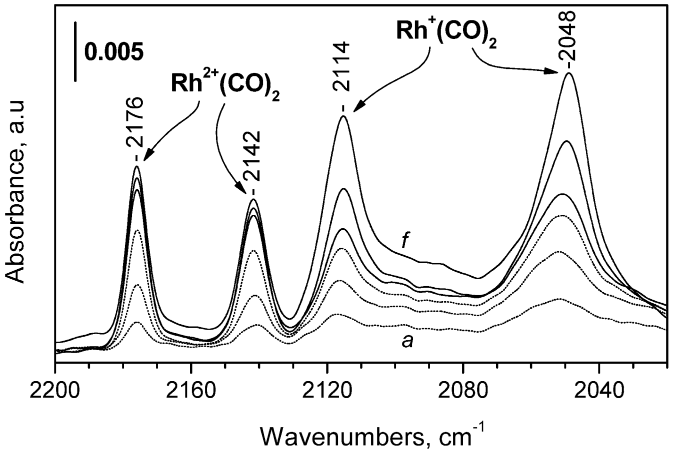

Fig. 1. FTIR spectra taken after introduction of small doses of CO (1 dose = 0.11 µmol) to reduced Rh-ZSM-5: 2, 3, 4, 5, 16 and 70 doses (a–f).

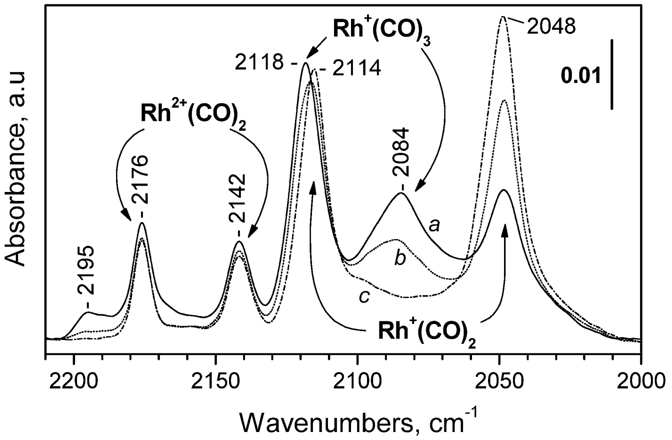

Fig. 2. FTIR spectra of CO adsorbed on reduced Rh-ZSM-5. Equilibrium pressure of 1730 (a) and 65 Pa (b) and after short evacuation (c).

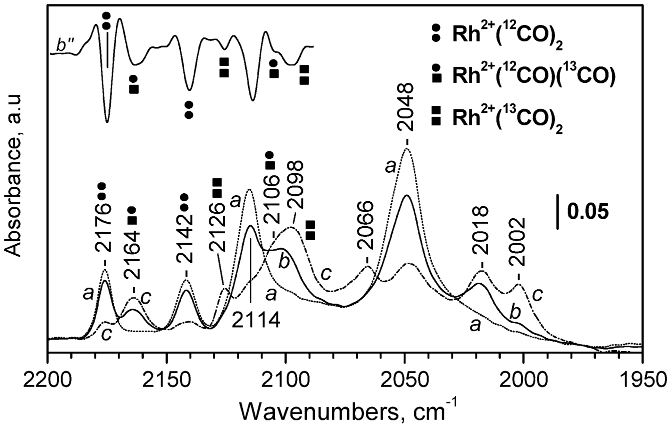

Fig. 3. FTIR spectra of ^{12}CO and ^{13}CO co-adsorbed on reduced Rh-ZSM-5. Spectrum taken after evacuation of ^{12}CO (1730 Pa equilibrium pressure) (a); introduction of 0.22 µmol of ^{12}CO–^{13}CO mixture (molar ratio of 1:1) to the sample; equilibrium pressure of 44 Pa ^{12}CO–^{13}CO mixture (c). The second derivative of spectrum b is presented as b″.

apparatus with a residual pressure $<10^{-3}$ Pa. Carbon monoxide (>99.997) and nitrogen monoxide (>99.9) were supplied by Air Liquide, France. Labeled carbon monoxide (^{13}C isotopic purity of 92.9 at%) was delivered from CEA-ORES, France. Before use, carbon monoxide and oxygen were passed through a liquid nitrogen trap.

Before the adsorption measurements, the sample was activated by 24-h evacuation at ambient temperature, followed by 1 h of heating at 673 K in oxygen, evacuation for 1 h at the same temperature, and reduction in CO (13.3 kPa) at 523 K. Then CO was evacuated initially at ambient temperature and then at 523 K. No carbonyl bands were detected in the IR spectrum after this treatment.

Adsorption of CO at ambient temperature on the sample was initially performed with small doses added successively into the cell. The first dose of adsorbed CO provoked the appearance of four bands with maxima at 2176, 2142, 2114, and 2048 cm^{-1} (Fig. 1, spectrum a). All bands increased in intensity with the amount of CO introduced into the IR cell (Fig. 1, spectra b–d). Analysis of the spectra shows two sets of bands changing in parallel, at 2176 and 2142 cm^{-1} on the one hand, and at 2114 and 2048 cm^{-1} on the other hand. The bands at 2114 and 2048 cm^{-1} went on increasing after the bands at 2176 and 2142 cm^{-1} reached saturation. Under increasing CO equilibrium pressure, new bands at 2195, 2118 and 2084 cm^{-1} appeared, whereas the bands at 2114 and 2048 cm^{-1} decreased in intensity (Fig. 2, spectra a–c). No changes in the O–H stretching region were detected, indicating that the OH groups were not involved in the formation of the carbonyl species. This situation differs from the case where CO is adsorbed on samples containing metallic rhodium and where oxidation of metallic rhodium by the surface support hydroxyls is well established [16].

The bands at 2114 and 2048 cm^{-1} are unambiguously assigned to the $\nu_s(CO)$ and $\nu_{as}(CO)$ modes, respectively, of the well-known $Rh^+(CO)_2$ gem-dicarbonyls [1–25]. The bands at 2118 and 2084 cm^{-1} characterize tricarbonyls produced by insertion of a third CO molecule into the $Rh^+(CO)_2$ species [21,26]. The band at 2195 cm^{-1} is seen at high equilibrium pressure only (Fig. 2, spectra a and b) and is due to carbonyls of rhodium cations in a high oxidation state (most probably Rh^{3+}) [20,26]. To support this assignment, we studied CO adsorption on a sample reduced at 573 K. In this case the bands at 2176, 2142, 2114, and 2048 cm^{-1} appeared with a slightly reduced intensity after CO adsorption, whereas the band at 2195 cm^{-1} was absent. This finding is consistent with the reduction of the Rh^{3+} sites. In what follows we concentrate on the bands at 2176 and 2142 cm^{-1}.

The two bands at 2176 and 2142 cm^{-1} appeared to change simultaneously, suggesting that they characterize one kind of polycarbonylic species. To prove this hypothesis and to establish the exact number of the CO ligands, we studied ^{12}CO–^{13}CO coadsorption. The cell was evacuated, after which only the bands arising from $Rh^+(CO)_2$ gem-dicarbonyls (at 2114 and 2048 cm^{-1}) and those at 2176 and 2142 cm^{-1} remained in the spectrum (Fig. 3, spectrum a). Then small doses of a ^{12}CO–^{13}CO isotopic mixture (molar ratio of ca. 1:1) were successively added into the cell. The first dose of the isotopic mixture provoked a decrease in the intensity of all four carbonyl bands, most pronounced with the bands arising from $Rh^+(CO)_2$ species (Fig. 3, spectrum b). In addition, a series of new bands

Table 1
Calculated frequencies of $Rh^{n+}(CO)_2$ species after replacing ^{12}CO by ^{13}CO

Species	$Rh^{n+}(^{12}CO)_2$ (Observed bands)	$Rh^{n+}(^{12}CO)(^{13}CO)$	$Rh^{n+}(^{13}CO)_2$
Classic $Rh^{+}(CO)_2$	ν_s at 2114 cm^{-1} ν_{as} at 2048 cm^{-1}	$\nu(^{12}CO)$ at 2098 cm^{-1} $\nu(^{13}CO)$ at 2018 cm^{-1}	ν_s at 2067 cm^{-1} ν_{as} at 2002 cm^{-1}
New species	ν_s at 2176 cm^{-1} ν_{as} at 2142 cm^{-1}	$\nu(^{12}CO)$ at 2164 cm^{-1} $\nu(^{13}CO)$ at 2106 cm^{-1}	ν_s at 2127 cm^{-1} ν_{as} at 2094 cm^{-1}

appeared with maxima at 2164, 2098, 2066, and 2018 cm^{-1}. Increasing the amount of the isotopic mixture added into the cell led to an additional decrease in the intensity of the initially recorded carbonyl bands, and under a certain equilibrium pressure, the bands recorded were at 2176, 2164, 2142, 2126, 2114, 2098, 2066, 2048, 2018, and 2002 cm^{-1} (Fig. 3, spectrum c).

To assign the new IR bands, we calculated, using an approximate force-field model [27], the expected frequencies after partial and full exchange of the ^{12}CO ligands with ^{13}CO of both the well-known $Rh^{+}(CO)_2$ gem-dicarbonyls and the species characterized by bands at 2176 and 2142 cm^{-1}, assuming that they were dicarbonyls as well. The results are presented in Table 1. Comparing the calculated frequencies with the observed frequencies clearly shows that the bands at 2176 and 2142 cm^{-1} characterize dicarbonyl species. Indeed, the molar ratio of the isotopic mixture that we used presupposes a ratio between the $Rh^{n+}(^{12}CO)_2$, $Rh^{n+}(^{12}CO)(^{13}CO)$, and $Rh^{n+}(^{13}CO)_2$ species of 1:2:1. Hence the two most intense bands for the new dicarbonyls should be located at 2164 and 2106 cm^{-1}. Indeed, inspection of Fig. 3, spectrum c, confirms the existence of a band at 2164 cm^{-1} of approximately twice the intensity than the bands at 2176 and 2142 cm^{-1}. Because of the overlap with the other bands in the region, we could not perform a detailed analysis of the band at 2106 cm^{-1}. The intensity of the band at 2126 cm^{-1} [characterizing the $Rh^{n+}(^{13}CO)_2$ species] appears to be as expected. Indeed, this band is hardly observable when the amount of isotopic mixture added into the cell is negligible and the concentration of the complexes with two ^{13}CO ligands is expected to be very low.

It is well known that the second derivatives of the spectra allow a more exact determination of the band maxima, especially in the case of overlapping bands. The second derivative of spectrum b is presented in Fig. 3. A band at 2106 cm^{-1}, arising from the $\nu(^{13}CO)$ modes of the $Rh^{n+}(^{12}CO)(^{13}CO)$ species, is clearly observable. We also point out that the observed new frequencies of the $Rh^{+}(CO)_2$ species also agree very well with the calculated frequencies, and that under CO equilibrium pressure, we would expect some $Rh^{+}(CO)_3$ species with various numbers of ^{12}CO and ^{13}CO ligands, which complicates spectrum c in Fig. 3.

The fact that the new dicarbonyl species easily exchange CO ligands can be explained by three hypotheses:

- Equilibrium exists between the dicarbonyls and the corresponding monocarbonyls, allowing rapid replacement of the ligand. However, we were not able to detect any monocarbonyl species, which indicates that the dicarbonyls are *complex-specified* [28].
- Equilibrium exists between the dicarbonyls and the corresponding unstable tricarbonyls (which also allows rapid ligand exchange). In contrast to what was observed for the $Rh^{+}(CO)_2$ species, we have seen no conversion between di- and tricarbonyls of Rh^{n+} even at low temperature.
- The dicarbonyls are characterized by a relatively low stability and are in equilibrium with "empty" sites. This hypothesis is supported by our results. Indeed, it was found that the bands at 2176 and 2142 cm^{-1} slowly decreased in intensity under evacuation even at ambient temperature.

An interesting phenomenon is the comparable intensity of the bands at 2176 and 2142 cm^{-1}. Usually, the symmetric modes of dicarbonyl species are less intense than the antisymmetric modes. Using the values of the integral absorption of the respective bands, we calculated the angle between the two CO molecules in the $Rh^{+}(CO)_2$ species to be 103° and that in the new dicarbonyls species to be 87°. Recently, dicarbonyls with an angle between the two CO molecules $<90°$ were reported for platinum cations in Pt-ZSM-5 [29].

It is well known that the higher the oxidation state of the cation, the higher the frequency of CO adsorbed on it [29–33]. Hence we can conclude that the rhodium oxidation state in the new dicarbonyl species is higher than 1+. This could account for the smaller angle between the adsorbed CO molecules compared with that in the $Rh^{+}(CO)_2$ species. It is well known that an increase in oxidation state leads to a decrease in the cationic radius. Thus, for steric reasons, the angle between the CO molecules is expected to be lower for the $Rh^{2+}(CO)_2$ species. In addition, the higher oxidation state of rhodium in the new dicarbonyl species can explain two other phenomena:

- The lower stability of the new complexes compared with the $Rh^{+}(CO)_2$ species. This arises from the weaker π back-bonding resulting from the higher charge of the cation.
- The weaker interaction between the CO molecules (i.e., smaller difference between the symmetric and antisymmetric modes). This again is evidently due to the weaker π back-bonding [29–33].

The hypothesis of the participation of Rh^{n+} cations in the new species is also consistent with the fact that these cations are not stable in the presence of water. Introduction of water vapor (50 Pa equilibrium pressure) to the sample with preadsorbed CO led to disappearance of the bands at 2176 and 2142 cm^{-1}. The $Rh^{+}(CO)_2$ bands at 2114 and 2048 cm^{-1} were hardly affected. Only in the presence of higher equilibrium pressure (400 Pa) the latter were red-shifted to 2108 and 2041 cm^{-1}. This shift was previously reported and assigned to coordination of a water molecule to the Rh^{+} cation from the geminal species [26]. It is now well established that water can replace preadsorbed CO only when the π back-donation in the carbonyl species is negligible, that is, when the cation is in a high oxidation state [34]. In contrast, CO can replace water from univalent cations providing that these cations have d-electrons for π back-donation.

The average position of the symmetric and asymmetric modes of the $\mathrm{Rh}^{n+}(\mathrm{CO})_2$ species, ν_{av}, was 2159 cm^{-1}. This value is 78 cm^{-1} higher than the ν_{av} of the $\mathrm{Rh}^{n+}(\mathrm{CO})_2$ gem-dicarbonyls (2081 cm^{-1}). A similar difference (70 cm^{-1}) was been found by means of DFT studies of $\mathrm{Rh}^{2+}(\mathrm{CO})_2$ and $\mathrm{Rh}^{+}(\mathrm{CO})_2$ species (results not reported here for brevity). The difference between the stretching modes of Ni^{2+}–CO and Ni^{+}–CO species in Ni-ZSM-5 is about 100 cm^{-1} [35], and that of Co^{2+}–CO and Co^{+}–CO species in Co-ZSM-5 even larger, 130 cm^{-1} [36]. This comparison strongly supports the assumption that the oxidation state of rhodium in the $\mathrm{Rh}^{n+}(\mathrm{CO})_2$ species is 2+. The smaller difference between the ν_{av} of the carbonyl complexes of the univalent and divalent cations in the case of rhodium can be explained by a significant π back-donation in the $\mathrm{Rh}^{2+}(\mathrm{CO})_2$ species.

We believe that the Rh^{2+} cations forming the new dicarbonyl species observed in this study are most probably in a cationic position in ZSM-5, which explains their high coordinative unsaturation and ability to coordinate several small molecules simultaneously. We can speculate that these cations have occupied such positions during the gentle activation procedure applied.

In conclusion, the results reported in this communication contribute to our understanding of the carbonyl chemistry of rhodium and of when and why more than one molecule can be attached to one site, which is an important question for understanding the mechanism of different catalytic reactions. In addition, the stabilization of Rh^{2+} cations in a zeolite matrix may be very important with a view to the importance of Rh^{2+} cations in particular catalytic reactions, for example, decomposition of α-diazo carbonyl compounds [37].

Acknowledgment

This work was supported by the French–Bulgarian Rila program.

References

[1] M. Primet, J. Chem. Soc., Faraday Trans. I 74 (1978) 2570.
[2] J.F. Goellner, B.C. Gates, G.N. Vayssilov, N. Rösch, J. Am. Chem. Soc. 122 (2000) 8056.
[3] G.N. Vayssilov, N. Rösch, J. Am. Chem. Soc. 124 (2002) 3783.
[4] H. Wang, J.T. Yates Jr., J. Catal. 89 (1984) 79.
[5] M.P. Keyes, K.L. Watters, J. Catal. 100 (1986) 477.
[6] H. Miessner, I. Burkhardt, D. Gutschick, A. Zecchina, C. Morterra, G. Spoto, J. Chem. Soc., Faraday Trans. 85 (1989) 2113.
[7] A. Guerrero-Ruiz, B. Bachiller-Baeza, P. Ferreira-Aparicio, I. Rodrigues-Ramos, J. Catal. 171 (1997) 374.
[8] J. Herrero, C. Blanco, A.R. Gonzalez-Elipe, J.P. Espinos, L.A. Oro, J. Mol. Catal. 62 (1990) 171.
[9] S. Trautmann, M. Baerns, J. Catal. 150 (1994) 335.
[10] T. Chafik, D. Kondarides, X.E. Verykios, J. Catal. 190 (2000) 446.
[11] J.C. Conesa, M.T. Zainz, J. Soria, G. Munuera, V. Rives-Arnau, A. Munoz, J. Mol. Catal. 17 (1982) 231.
[12] J.T. Yates Jr., T.M. Duncan, R.W. Vaughan, J. Phys. Chem. 96 (1992) 7733.
[13] K.A. Almusaiteer, S.S.C. Chuang, J. Phys. Chem. B 104 (2000) 2265.
[14] T.T.T. Wong, A.Yu. Stakheev, W.M.H. Sachtler, J. Phys. Chem. 96 (1992) 7733.
[15] M. Zaki, G. Kunzmann, B.C. Gates, H. Knözinger, J. Phys. Chem. 91 (1987) 1486.
[16] P. Basu, D. Panayotov, J.T. Yates Jr., J. Phys. Chem. 91 (1987) 3133.
[17] T. Beutel, O. Alekseev, A. Ryndin, V. Likholobov, H. Knözinger, J. Catal. 169 (1997) 132.
[18] P. Gelin, Y. Ben Taarit, C. Naccache, J. Catal. 59 (1979) 357.
[19] K. Smith, F. Huguws, A. Theolier, J.M. Basset, R. Ugo, G.M. Zanderighi, J.L. Bilhou, V. Bilhou-Bougnal, W.F. Graydon, Inorg. Chem. 18 (1979) 3104.
[20] H. Miessner, I. Burkhardt, D. Gutschick, A. Zecchina, C. Morterra, G. Spoto, J. Chem. Soc., Faraday Trans. 86 (1990) 2321.
[21] H. Miessner, D. Gutschick, H. Ewald, H. Mueller, J. Mol. Catal. 36 (1986) 359.
[22] R. Dictor, J. Catal. 109 (1988) 89.
[23] J.-C. Lavalley, J. Lamotte, R. Breault, J.P. Hindermann, J. Phys. Chem. 94 (1990) 5941.
[24] P. Basu, D. Panayotov, J.T. Yates Jr., J. Am. Chem. Soc. 110 (1988) 2074.
[25] J.L. Robbins, J. Phys. Chem. 90 (1986) 3381.
[26] E. Ivanova, K. Hadjiivanov, Phys. Chem. Chem. Phys. 5 (2003) 655.
[27] P.S. Braterman, Metal Carbonyl Spectra, Academic Press, London, 1975.
[28] K. Hadjiivanov, E. Ivanova, D. Klissurski, Catal. Today 70 (2001) 73.
[29] K. Chakarova, M. Mihaylov, K. Hadjiivanov, Catal. Commun. 6 (2005) 466.
[30] K. Hadjiivanov, G. Vayssilov, Adv. Catal. 47 (2002) 307.
[31] H. Knözinger, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 2, Wiley–VCH, Weinheim, 1997, p. 707.
[32] E. Payen, J. Grimblot, J.C. Lavalley, M. Daturi, F. Maugé, in: J.M. Chalmers, P.R. Griffiths (Eds.), Handbook of Vibrational Spectroscopy, vol. 4, Wiley, Chichester, 2002, p. 3005.
[33] A. Davydov, Molecular Spectroscopy of Oxide Catalyst Surfaces, Wiley, Chichester, 2003.
[34] K. Hadjiivanov, J. Chem. Soc., Faraday Trans. 94 (1998) 1901.
[35] K. Hadjiivanov, H. Knzinger, M. Mihaylov, J. Phys. Chem. B 106 (2002) 2618.
[36] K. Hadjiivanov, B. Tsyntsarski, Tz. Venkov, M. Daturi, J. Saussey, J.-C. Lavalley, Phys. Chem. Chem. Phys. 5 (2003) 243.
[37] J.M. Mejıra-Oneto, A. Padwa, Tetrahedron Lett. 45 (2004) 9115.