Journal of Catalysis **196,** 200–204 (2000)
doi:10.1006/jcat.2000.3022, available online at http://www.idealibrary.com on IDEAL®

RESEARCH NOTE

Low-Temperature CO Oxidation over New Types of Sn–Pt/SiO_2 Catalysts

J. L. Margitfalvi,*[,1] I. Borbáth,* M. Hegedűs,* E. Tfirst,* S. Gőbölös,* and K. Lázár†

*Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Pusztaszeri út 59-67, 1025 Budapest, Hungary; †Institute of Surface Science and Catalysis, Chemical Research Center, Hungarian Academy of Sciences, P.O. Box 77, 1525 Budapest, Hungary

Received June 28, 2000; revised August 1, 2000; accepted August 8, 2000

Sn–Pt/SiO_2 catalysts prepared by using controlled surface reactions are highly active in the low-temperature oxidation of CO. The results indicate that the high activity of these catalysts can be attributed to (i) the stabilization of tin–platinum alloy phases on the silica support, and (ii) the formation of "*Sn^{4+}–Pt*" *ensemble sites* during the oxidation of CO. It is suggested that Sn^{4+} species formed *in situ* are involved in the activation of the CO molecule adsorbed at the neighboring Pt site. This activation strongly resembles that of the carbonyl group in unsaturated aldehydes over this type of Sn–Pt/SiO_2 catalysts. © 2000 Academic Press

Key Words: **Sn–Pt/SiO_2 catalysts; CO oxidation; low-temperature oxidation; Mössbauer spectroscopy; Sn^{4+}–Pt ensemble sites.**

INTRODUCTION

Literature Background

Pt/SnO_2 (1, 2) and Pd/SnO_2 (3, 4) catalysts are widely used as low-temperature CO oxidation catalysts. With respect to these catalysts, as far as neither the noble metal nor tin oxide can catalyze low-temperature oxidation of CO, a synergism between the oxide and the metal phases has been suggested (1–4). Bond *et al.* proposed a bifunctional mechanism based on the spillover of both CO and oxygen from the noble metal to tin oxide (3). Sheintuch *et al.* also considered a spillover, but it was related only to CO (4). In another study the formation of the SnPt alloy phase has been suggested (5). Local temperature increase of Pt sites and the activation of CO on adjacent SnO_2 sites had also been suggested (6). Recently an alternative reaction mechanism has been proposed suggesting the involvement of the Pt–SnO_2 interface in the activation of CO (7).

Working Hypothesis

Recently we have shown that Sn–Pt/SiO_2 catalysts prepared by using anchoring type controlled surface reactions (CSRs) between tin tetraalkyls and hydrogen adsorbed on platinum are highly active and selective in gas-phase hydrogenation of crotonaldehyde into crotylalcohol (8). The selective hydrogenation of the carbonyl group resulted in S_{CO} selectivities as high as 90%, the highest value ever reported on supported Sn–Pt catalysts (9). The S_{CO} selectivity of Sn–Pt/SiO_2 catalysts strongly depended on the Sn/Pt (at./at.) ratio and increased in the time on stream (TOS) period (9–11). *In situ* Mössbauer spectroscopy measurements indicated (9) that in the first hour of TOS the Sn–Pt alloy phase poor in tin was oxidized by crotonaldehyde, and a correlation was found between the S_{CO} selectivity and the formation of Sn^{4+} sites. The S_{CO} selectivity of Sn–Pt/SiO_2 catalysts has been attributed to the Sn^{4+} species formed *in situ*, which activates the carbonyl group (10–12).

The comparison of the activation of the CO molecule and the carbonyl group shows distinct similarities. In both cases the activation can be related to the atomic closeness of Pt and Sn^{4+} sites; i.e., the activation is due to the presence of "*Sn^{4+}–Pt*" *ensemble sites* formed *in situ* during the reaction.

The results discussed above firmly suggest that our Sn–Pt/SiO_2 catalysts can also be effectively used in CO oxidation. It has been proposed that in an oxidative atmosphere "*Sn^{4+}–Pt*" *ensemble sites* can easily be formed from supported nanoclusters containing different Sn–Pt alloy phases.

In order to prove the above hypothesis Sn–Pt/SiO_2 catalysts with different Sn/Pt (at./at.) ratios were prepared using CSRs between tin tetraethyl and hydrogen adsorbed on platinum (8, 9, 11) and were tested in CO oxidation.

EXPERIMENTAL PART

A 3% Pt/SiO_2 catalyst (CO/Pt = 0.52) was used as a parent catalyst (8). Tin tetraethyl and tin tetramethyl were applied as tin precursor compounds (catalysts (I) and (II), respectively). The tin anchoring was carried out in benzene at 50°C in a hydrogen atmosphere for 2 h. Details of the surface chemistry involved in this type of catalyst

---

[1] To whom correspondence should be addressed. Fax: 36-1-325-7554. E-mail: joemarg@cric.chemres.hu.

0021-9517/00 $35.00

modification can be found elsewhere (8, 13, 14). The decomposition of multilayer organometallic complex (MLOC) was accomplished in both oxidative and reductive atmospheres by the temperature-programmed reaction (TPRe) technique (16) (heating rate = 5°C/min, temperature ramp from 25 to 300°C). The use of a reductive atmosphere provides alloy type Sn–Pt nanoclusters (15), while an oxidative one should give finely dispersed SnO_x ($x = 2$ or 4) over platinum (14). These two types of catalysts will be distinguished as (H) and (O) type catalysts, respectively.

Chemisorption measurements using CO were done using ASDI RXM-100 equipment. TPRe was also used to study the oxidation of CO with oxygen (heating rate = 5°C/min, temperature ramp from 25 to 300°C). In TPRe experiments 0.150 g of catalyst was applied using a gas mixture of 78.8 Torr CO and 40.4 Torr oxygen in helium. In time on stream (TOS) experiments a gas mixture of 5.6 Torr CO and 3.0 Torr oxygen in helium was applied. The space velocity was 28,000 and 24,000 $\mathrm{ml} \cdot (g_{cat})^{-1} \cdot h^{-1}$ in TPRe and TOS experiments, respectively. The TPRe curves were monitored by recording the $m/e = 28$, 32, and 44 signals of CO and oxygen consumed and CO_2 formed, respectively, while in TOS experiments the products were detected by GC. Prior to the reaction the catalysts were re-reduced at 340°C for 1 h in a hydrogen atmosphere.

Mössbauer spectra were recorded at 80 K with a constant acceleration spectrometer using a $Ba^{119}SnO_3$ source. All isomer shifts were referred to SnO_2. A standard least-squares minimization routine was used to fit the spectra as a superposition of Lorentzian lines. The catalyst samples were treated *in situ* and measured in the Mössbauer cell (17). The duration of treatment in a hydrogen atmosphere at 200°C and 300°C was 90 min.

The interaction of the CO molecule with $Sn^{(n)}$ ions was studied at the *ab initio* Hartree–Fock level with the 5.1.3 version of Wavefunction Spartan program system. Full geometry optimization was made for the whole systems with total charge *n*, using the standard, built-in STO-3G and 3-21G(*) basis sets. The core electrons of the tin atoms were taken into consideration explicitely. Further details can be found elsewhere (18).

RESULTS AND DISCUSSION

Characteristic features of Sn–Pt/SiO_2 catalyst are given in Table 1. Data given in Table 1 show that the introduction of tin strongly reduces the chemisorption of the CO. Figure 1 shows selected TPRe results obtained in the oxidation of CO. The temperature at which 50% CO conversion has been achieved (T_{50}) was used to compare the activities of the catalysts; these values are also included in Table 1.

The results summarized above show that the Pt/SiO_2 catalyst is quite inactive. However, the introduction of tin significantly increased the activity of the catalysts, resulting in a pronounced decrease of the T_{50} values. These results show also that the T_{50} values strongly depend on the tin content; however, only a slight difference between (H) and (O) type catalysts has been observed. From the above results it can be assumed that, as has been expected, the "*Sn^{4+}–Pt*" *ensemble sites* formed during the oxidation of CO are highly active in the oxidation of CO.

TABLE 1

Composition, CO Chemisorption, and Activity of Sn–Pt/SiO_2 Catalysts

Catalysts	Sn/Pt, at./at.[a]	CO/Pt[b] (H) type	CO/Pt[b] (O) type	T_{50}, °C[c] (H) type	T_{50}, °C[c] (O) type
Pt/SiO_2	—	0.550		177	
Sn–Pt/SiO_2 (I-1)	0.23	N.A.	0.28	103	100
Sn–Pt/SiO_2 (I-2)	0.42	0.25	0.21	69	63
Sn–Pt/SiO_2 (II-3)	0.68	N.A.	0.20	63	64
Sn–Pt/SiO_2 (I-3)	0.87	0.17	0.16	N.A.	60
Sn–Pt/SiO_2 (I-4)	1.00	N.A.	0.18	117	131

[a] Sn/Pt (at./at.) values calculated from the actual Pt and Sn content determined by AAS.

[b] Chemisorption data.

[c] Activity of the catalysts measured in TPRe experiments, expressed as the temperature at which 50% CO conversion has been obtained.

Additional experiments were carried out to investigate the stability of Sn–Pt/SiO_2 catalysts (see Fig. 2). After the first TPRe experiment the catalyst was reused without any re-reduction step, resulting in the shift of the T_{50} value from 103 to 138°C. However, the original TPRe pattern of this catalyst (with T_{50} = 100–102°C) was restored after subsequent re-reduction in a hydrogen atmosphere at 340°C. These experiments strongly indicate that the activity of these Sn–Pt/SiO_2 catalysts is controlled by the surface composition of the Sn–Pt nanoclusters and the reduced form of

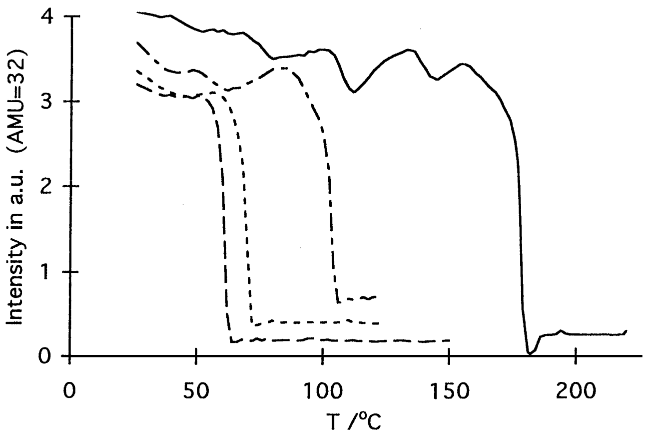

FIG. 1. Oxidation of CO on different Sn–Pt/SiO_2 catalysts. Temperature-programmed reaction (TPRe) results. Catalysts: —, Pt/SiO_2; –·–, I-1(H); - - -, I-2(H); – – –, I-3(O).

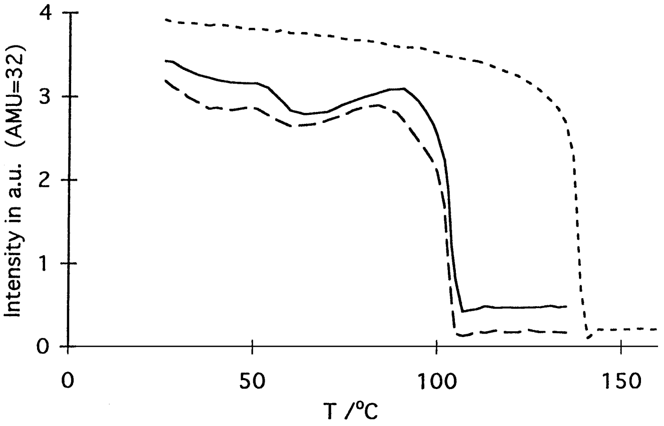

FIG. 2. Investigation of the regeneration of Sn–Pt/SiO_2 catalysts. Catalyst: I-1 (H). —, First run; - - -, second run without re-reduction in hydrogen; – – –, third run after re-reduction in hydrogen at 340°C.

the Sn–Pt nanoclusters is more active than the fully oxidized form.

Further results verified also that the activity of these catalysts was strongly influenced by the reduction temperature. The corresponding results given in Table 2 show that type (O) catalysts are particularly sensitive to the temperature of reduction in a hydrogen atmosphere. This is an indication that Sn^{4+} species formed after decomposition of MLOC in an oxygen atmosphere are stable in the presence of hydrogen even at 200°C. The full reduction of Sn^{4+} species requires temperature above 300°C. This behavior of (O) type catalysts was also confirmed by the temperature-programmed reduction technique.

The results of preliminary time on stream experiments carried out at 25°C are shown in Table 3. Slight or pronounced deactivation of the catalysts has been observed. Both the activity and the deactivation pattern of the catalysts strongly depend on the Sn/Pt ratio, showing a definite maximum for the activity and a minimum for the deactivation. The original high activity of these catalysts could be restored by their treatment in pure hydrogen for 15 min at room temperature. No measurable activity changes were observed after four CO oxidation–room temperature hydrogen treatment cycles (catalyst II-3) or when the CO/O_2 molar ratio was altered in the range of 0.75–1.5.

Further characterization of our (H) and (O) types of Sn–Pt/SiO_2 catalysts was accomplished by Mössbauer spectroscopy. The catalyst samples were analyzed as received and after reduction in a hydrogen atmosphere at 200 and 300°C, respectively. These results are summarized in Table 4.

TABLE 2

Influence of the Temperature of Reduction on the Activity of Catalyst I-2

Catalytic runs	Catalysts and pretreatments	T_{50},°C
1	(H) type, $T_{H2} = 340$°C	69
2	(H) type, $T_{H2} = 200$°C	69
3	(O) type, $T_{H2} = 340$°C	63
4[a]	(O) type, $T_{H2} = 200$°C	101
5[a]	(O) type, after run 4 followed regeneration at $T_{H2} = 340$°C	68

[a] TPRe experiment with temperature ramp up to 200°C.

TABLE 3

Summary of Results in Time on Stream Experiments at Ambient Temperature

Catalysts	Sn/Pt, at./at.	Conversion of CO, %		Deactivation parameter, n^a	
		After 1 h	After 5 h	First 2 h	Last 2 h
I-1	0.23	21.6	4.7	0.404	1.191
II-1	0.47	38.4	15.1	0.210	0.545
II-2	0.58	32.3	25.4	0.035	0.322
II-3	0.68	14.4	4.3	0.266	0.737

Note: All catalysts are (O) type. Time on stream = 5 h. Total flow rate = 60 cm^3/min. Amount of catalysts = 0.150 g. $T = 25$°C.

[a] The deactivation parameter, n, was calculated from the Voorhies equation (21): $\lg(X_t/X_f) = A - n \lg t$, where X_f is the conversion value measured in the first sample (after 15 min of TOS) and X_t are the conversion values in the t^{th} minute of the TOS experiment.

TABLE 4

Mössbauer Parameters of Catalyst I-4

Catalyst sample	Species	IS, mm s^{-1}	QS, mm s^{-1}	FWHM, Mm s^{-1}	RI, %
(H) form as received	Sn^{4+}	0.09	0.64	0.86	55
	Sn–Pt(a)	1.25	—	1.45	27
	Sn–Pt(b)	1.98	—	1.03	18
(H) form $T_{H2} = 200$°C	Sn^{4+}	0.43	0.19	0.80	8
	Sn–Pt(a)	1.30	—	1.17	38
	Sn–Pt(b)	2.17	—	1.31	54
(H) form $T_{H2} = 300$°C	Sn–Pt(a)	1.32	—	1.44	49
	Sn–Pt(b)	2.21	—	1.46	51
(O) form as received	Sn^{4+}	0.08	0.72	0.99	100
(O) form $T_{H2} = 200$°C	Sn^{4+}	0.48	—	1.57	16
	Sn–Pt(a)	1.24	—	1.30	33
	Sn–Pt(b)	2.35	—	1.56	44
	Sn^{2+}	2.60	1.42	1.44	7
(O) form $T_{H2} = 300$°C	Sn^{4+}	0.62	—	0.83	7
	Sn–Pt(a)	1.20	—	1.20	23
	Sn–Pt(b)	2.17	—	2.17	70

IS, isomer shift, mm s^{-1}; QS, quadrupole splitting, mm s^{-1}; FWHM, full width at half-maximum, mm s^{-1}; RI, relative spectral area (%). Errors on IS, QS, and RI values are 0.03 mm s^{-1} and ±10 rel.%, respectively.

The contribution of the Sn–Pt bimetallic component in most of the Mössbauer spectra of Sn–Pt/SiO$_2$ catalysts was composed of two singlets: one with isomer shifts (IS) around 1.20–1.30 mm s^{-1}, and the other at 1.98–2.35 mm s^{-1}. Attempts to fit the bimetallic compound with one singlet resulted in worsening of the fitting quality, and, on the other hand, inclusion of a third singlet to this particular line was not successful either. These two components are denoted as Sn–Pt(a) and Sn–Pt(b), respectively.

According to Charlton *et al.* (19) the Sn–Pt(a) component may be assigned to Sn substitutional alloy (with a solubility of a few weight percent Sn) in cubic Pt, while the Sn–Pt(b) can be attributed to various intermetallic alloys (NiAs type PtSn, hexagonal Pt_2Sn_3, CaF_2 type $SnPt_2$, and orthorombic $PtSn_4$) which exhibit different isomer shifts in a linear dependence of the tin content (20).

In all reduced samples the tin-rich phase (Sn–Pt(b)) is the main component; however, ionic forms of tin exist in all samples except sample (H)$_{300}$. The contribution of the tin-rich phase is different in all samples, varying in the range of 17–70%. This variation is negligible in (H) type catalyst after hydrogen treatment; however, it is very pronounced in (O) type sample. The (H) type sample as received also has a tin oxide phase, due to its contact with air. However, the results show that this ionic form of tin can easily be reduced and after reduction at 300°C the Sn–Pt alloy phase is fully restored.

As emerges from the data given in Table 4, the Mössbauer spectra of (H) and (O) type Sn–Pt/SiO$_2$ catalysts are different. The (O) type catalyst as received contains only Sn^{4+} species. After reduction of this sample at 200°C it still contains Sn^{4+} and Sn^{2+} species. Moreover, the reduction of (O) type sample at 300°C cannot fully restore the alloy phase. These results explain why the activity of (O) type catalyst shows a strong dependence on the temperature of hydrogen treatment (see Table 2).

The results obtained in this study unambiguously demonstrate that Sn–Pt/SiO$_2$ catalysts prepared by using CSRs are highly active in the oxidation of CO at low temperature. The activity of the catalysts is strongly controlled by the surface composition of supported alloy type nanoparticles. The surface composition of Sn–Pt/SiO$_2$ catalysts depends on (i) the Sn/Pt (at./at.) ratio, (ii) the temperature of hydrogen treatment prior to the reaction, and (iii) the temperature of CO oxidation.

These results indicate also that the chemical nature of heterogeneous catalytic activation of both the carbonyl group in aldehydes (9) and the CO molecule should have a common basis. The high activity of catalysts prepared by using CSRs can be related to the activation of the carbonyl moiety by Sn^{4+} species formed during the reaction. The ionic forms of tin stabilized on the platinum surface attract an electron either from the oxygen atom of the CO molecule or the carbonyl group. The flow of electrons from the CO (or carbonyl moiety) to Sn^{4+} strongly weakens the carbon–oxygen triple (or double) bond. Consequently, in CO oxidation over our Sn–Pt/SiO$_2$ catalysts the CO molecule is strongly perturbed and reacts at low temperature.

TABLE 5

Bond Lengths and Mulliken Bond Orders of the Carbon–Oxygen Bond in the Carbon Monoxide Molecule and in CO + Sn$^{(n)}$ Complexes

	Bond length (Å)		Mulliken bond order	
	STO-3G	3-21G(*)	STO-3G	3-21G(*)
CO	1.15	1.13	2.51	2.22
CO + Sn^0	1.15	1.13	2.46	2.10
CO + Sn^{4+}	1.28	1.28	1.61	1.25

The above perturbation of the CO molecule has been modeled and calculated. In the first approach *ab initio* Hartree–Fock calculations were made for some CO + Sn$^{(n)}$ clusters, where $n = 0$, $+2$, and $+4$. The results for the single CO molecule and for the cases $n = 0$ and $+4$ are summarized in Table 5. These data clearly show that the carbon–oxygen bond is weakened in the proximity of the charged tin atom. This weakening effect is proportional to the charge of the tin atom.

In order to study the origin of the above bond-weakening effect of the tin cation, we calculated the Mulliken charges of the contributing atoms. These data are presented in Table 6. As emerges from these data the effect of the neutral tin atom in the proximity of the CO molecule on the atomic charges and bond orders is insignificant. However, when the tin atom is charged, electron transfer occurs from the CO molecule to the tin cation. The charge of the carbon atom in the CO molecule becomes more positive, and this makes the oxygen atom more negative and reduces the positive charge of the tin cation. The increase in the nucleophilic nature of the oxygen atom makes it possible to form a strong interaction between the CO molecule and the tin cation. As shown in Table 7, the Mulliken bond order increases and the distance decreases between the O and Sn$^{(n)}$ atoms if the tin atom is charged. However, the increase of the positive charge on the carbon atom reduces

TABLE 6

Mulliken Atomic Charges in the Carbon Monoxide Molecule and in CO + Sn$^{(n)}$ Complexes

	C		O		Sn	
	STO-3G	3-21G(*)	STO-3G	3-21G(*)	STO-3G	3-21G(*)
CO	0.20	0.44	−0.20	−0.44	—	—
CO + Sn^0	0.24	0.53	−0.21	−0.47	−0.03	−0.06
CO + Sn^{4+}	1.03	1.48	−0.31	−0.64	3.28	3.16

TABLE 7

Distances and Mulliken Bond Orders between the Oxygen and Tin Atoms in CO + Sn$^{(n)}$ Complexes

	Distance (Å)		Mulliken bond order	
	STO-3G	3-21G(*)	STO-3G	3-21G(*)
CO + Sn^0	2.66	2.72	0.08	0.12
CO + Sn^{4+}	1.93	2.01	0.85	0.76

the electronic charge density in the proximity of the carbon nucleus, and thus reduces its ability to form a covalent bond. Hence, the result of these effects is the weakening of the carbon–oxygen bond in the carbon monoxide molecule.

Consequently, the results of the *ab initio* Hartree–Fock calculations strongly support the relevance of our hypothesis with respect to the involvement of the electron transfer from the CO molecule to the Sn^{4+} site in the activation of the CO molecule.

CONCLUSIONS

The results obtained in this study indicate that alloy type Sn–Pt/SiO$_2$ catalysts prepared by using CSRs are highly active for low-temperature CO oxidation. Both the experimental evidences shown and the calculations done strongly support our hypothesis with respect to the involvement of both the "*Sn^{4+}–Pt*" *ensemble sites* and the electron transfer from the CO molecule to the Sn^{4+} site in the activation of the CO molecule. We suggest that these two phenomena mentioned above are responsible for the increased activity of our alloy type Sn–Pt/SiO$_2$ catalysts prepared by using CSRs in low-temperature CO oxidation. To our knowledge it has been shown for the first time that alloy type Sn–Pt/SiO$_2$ catalysts can be used in low-temperature CO oxidation.

ACKNOWLEDGMENTS

The authors acknowledge the research grants from OTKA (Nos. T23322, T25732). Special thanks are due to A. S. Belyi (Boreskov Institute of Catalysis, Omsk Branch) for providing the Pt/SiO$_2$ catalyst and to Prof. A. Vértes for valuable discussions about the Mössbauer spectra.

REFERENCES

1. Sárkány, J., Bartók, M., and Gonzales, R., *J. Catal.* **81**, 347 (1983).
2. Yu Yao, Y. F., *J. Catal.* **87**, 152 (1984).
3. Bond, G. C., Molloy, L. R., and Fuller, M. J., *J. Chem. Soc., Chem. Commun.* 796 (1975).
4. Sheintuch, M., Schmidt, J., Lechtman, Y., and Yahav, G., *Appl. Catal.* **49**, 55 (1989).
5. Gardner, S., Hoflund, G. B., Davidson, M. R., and Schryer, D. R., *J. Catal.* **115**, 132 (1989).
6. Gangel, N. D., Gupta, M., and Iyer, R. M., *J. Catal.* **126**, 13 (1990).
7. Grass, K., and Linz, H.-G., *J. Catal.* **172**, 446 (1997).
8. Margitfalvi, J. L., Borbáth, I., Tfirst, E., and Tompos, A., *Catal. Today* **43**, 29 (1998).
9. Margitfalvi, J. L., Vankó, Gy., Borbáth, I., Tompos, A., and Vértes, A., *J. Catal.* **190**, 474 (2000).
10. Ponec, V., *Appl. Catal.* **149**, 27 (1997).
11. Margitfalvi, J. L., Tompos, A., Kolosova, I., and Valyon, J., *J. Catal.* **174**, 246 (1998).
12. Yu, W., Liu, H., Liu, M., and Tao, Q., *J. Mol. Catal.* **138**, 273 (1999).
13. Margitfalvi, J. L., Tálas, E., and Gőbölös, S., *Catal. Today* **6**, 73 (1989).
14. Margitfalvi, J. L., Borbáth, I., Hegedűs, M., Gőbölös, S., and Lónyi, F., *React. Kinet. Catal. Lett.* **68**, 133 (1999).
15. Vértes, Cs., Tálas, E., Czakó-Nagy, I., Ryczkovski, J., Gőbölös, S., Vértes, A., and Margitfalvi, J., *Appl. Catal.* **68**, 149 (1991).
16. Bhatia, S., Beltraminki, J., and Do, D. D., *Catal. Today* **7**, 309 (1990).
17. Lázár, K., Matusek, K., Mink, J., Dobos, S., Guczi, L., Vizi-Orosz, A., Markó, L., and Reiff, W. M., *J. Catal.* **87**, 163 (1984).
18. Spartan 5.0, User's Guide, Wavefunction, Inc., Irvine, CA, 1997.
19. Charlton, J. S., Cordey-Hayes, M., and Harris, I. R., *J. Less-Common Metals* **20**, 105 (1970).
20. Kappenstein, Ch., Guérin, M., Lázár, K., Matusek, K., and Paál, Z., *J. Chem. Soc., Faraday Trans.* **94**, 2463 (1998).
21. Voorhies, A., *Ind. Eng. Chem.* **37**, 318 (1945).