Asian Journal of Chemistry; Vol. 25, No. 4 (2013), 2289-2292

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13923

Catalytic Performance of M_x(M = Ni, Co, Cu)$O_y/(MgO)_{0.9}(CeO_2)_{0.1}$ for Combustion of Methane

SHU ZHENG[1,*] and YUHUA GUO[2]

[1]Henan Mechanical and Electrical Engineering College, Xinxiang 453002, Henan Province, P.R. China
[2]Huzhou Teachers College, School of Life Science, Huzhou 313000, Zhejiang, P.R. China

*Corresponding author: E-mail: shuer45@163.com

(*Received*: 18 April 2012; *Accepted*: 23 October 2012) AJC-12333

A series of catalysts M_x(M = Ni, Co, Cu)$O_y/(MgO)_{0.9}(CeO_2)_{0.1}$ have been prepared by a sol-gel method. The effect of the activity of M_x(M = Ni, Co, Cu)$O_y/(MgO)_{0.9}(CeO_2)_{0.1}$ on combustion of methane was investigated and characterized by BET, XRD and TEM techniques. In view of activity and stability of a catalyst, $NiO/(CeO_2)_{0.1}$-$(MgO)_{0.9}$ catalyst shows the highest catalytic activity and the best thermal stability for methane combustion. The structure of the catalyst calcined at 1000 ºC does not have any change, only size increases slightly from TEM photos. It still has a specific surface area of 14.32 $m^2\ g^{-1}$ and high activity as well as good thermal stability.

Key Words: Catalytic combustion of methane, $(MgO)_{0.9}(CeO_2)_{0.1}$ support, M_x(M = Ni, Co, Cu)O_y.

INTRODUCTION

In the combustion field of methane, the catalytic activity of Pt, Pd and other noble metal which have been studied maturely[1-3] are very high, but poor stability, facile volatilization and decomposition in high temperature make their activity are reduced remarkably. The activity of metal-oxide[4,5] is close to noble metal catalyst and its high thermal stability, low cost raw materials and easy availability cause people's extensive concern, so, people hope to replace noble metal catalysts with it.

The melting point of MgO is 2850 ºC and being able to maintain a large surface area[6] compared to most other oxides, so, MgO should be relatively good catalyst carrier in high temperature. MgO is mainly added into methane combustion catalyst as auxiliary at present, Such as MgO has been added into perovskite in the research of Saracco *et al.*[7,8], Kirchnerova and Klvana[9] and Ciambelli *et al.*[10], Addition of MgO into Al_2O_3 in the research of Yang *et al.*[11] and Qi *et al.*[12], which can enhance the thermal stability of Al_2O_3 to some extent. The research of MgO as carrier focus mainly on Fe/MgO catalyst of Spretz *et al.*[13] and Co/MgO catalyst of Ulla *et al.*[14]. The research is major modification of CeO_2 on MgO in research group, to out best of knowledge[15].

However, no study on mixed oxide CeO_2-MgO composite for methane combustion has been reported.We added appropriate proportion of CeO_2 as auxiliary into MgO composite carrier, with transition metal (Ni, Co, Cu)-oxides as active components, to make a comprehensive survey in the combustion performance of the series catalysts for methane combustion, hoping have a good understanding of MgO-CeO_2 support.

EXPERIMENTAL

Preparation of the catalysts: Preparing carrier $(MgO)_{0.9}(CeO_2)_{0.1}$ with sol-gel method. Dissolving $Mg(NO_3)_2{\cdot}6H_2O$ and $(NH_4)_2Ce(NO_3)_6$ into anhydrous ethanol in molar ratio of 9:1, adding certain amount of surface active agent. An excess of aqueous solution of NH_4OH was added to the mixed nitrate solution dropwise and stirring vigorously. The resulting suspension was stirred for 3 h and then left for 24 h. Filtering and washing gel, the obtained gel was dried in supercritical condition (260 ºC, 8 MP) with alcohol as medium, aerogel sample is acquired. Impregnation of $Ni(NO_3)_2$, $Co(NO_3)_2$, $Cu(NO_3)_2$ according to sample quality percentage 12 % at same volume. The sample was dried at 120 ºC for 6 h and then calcined at 600 ºC or 800 ºC or 1000 ºC for 3 h respectively.

Tests of the catalytic activities: Catalytic activity tests were carried out at atmospheric pressure in a fixed-bed quartz microreactor (internal diameter = 12 mm). Catalyst (40-60) dosages: 0.50 g, raw gas volume ratio: $V_{CH_4}:V_{Air}$ = 1:25, flow rate: 30 mL min^{-1}. Reaction temperature rises up to 850 ºC from room temperature at 2 ºC min^{-1}, analysis of reaction tail gas on line with GC-930 gas chromatograph of Shanghai Haixin company, hydrogen flame detector (FID), chromatographic column is carbon molecular sieve, column is connected with methane reformer including Ni catalyst.

Characterization of the catalysts: X-ray powder diffraction analysis was performed on the catalyst samples with a D/max-

TABLE-1
CATALYTIC ACTIVITIES AND SPECIFIC SURFACE AREAS OF M_x(M = Ni, Co, Cu)$O_y/(MgO)_{0.9}(CeO_2)_{0.1}$ CATALYSTS

Sample	$S_{BET}/m^2 \cdot g^{-1}$	$Vp/cm^3 \cdot g^{-1}$	dp/nm	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)
$NiO/(MgO)_{0.9}(CeO_2)_{0.1}$ (**I**)	63.98	0.3	19.04	346	413	478
(**II**)	30.92	0.26	34.35	384	458	528
$CuO/(MgO)_{0.9}(CeO_2)_{0.1}$ (**I**)	64.57	0.24	14.92	337	410	464
(**II**)	6.56	0.04	28.35	444	530	612
$Co_xO_y/(MgO)_{0.9}(CeO_2)_{0.1}$ (**I**)	58.46	0.3	20.74	329	416	484
(**II**)	33.6	0.18	21.69	392	488	564

Note: Catalysts was calcined at 600 °C; Temperature (°C) with methane conversion of 10 %, 50 %, 90 % denoted as $T_{10\%}$, $T_{50\%}$, $T_{90\%}$ respectively; (**I**) means first evaluation; (**II**) means second evaluation

2200 PC X-ray diffractometer, Cu rake, pipe pressure: 30 KV, pipe flow : 20 mA, scan rate: 8° min^{-1}, scan scope: 20-90°, step: 0.08°.

Determination of sample specific surface area with Micromeritics ASAP 2010 adsorption instrument, BET specific surface area is measured with N_2 gas isothermal adsorption method.

Determination of TEM of catalyst: The profile, average grain size and dispersion of sample is performed on Philip Tecnai20 transmission electron microscopy.

RESULTS AND DISCUSSION

Effects of different active components to performance of carrier

Evaluation of catalyst activity and stability: Methane conversions as a function of reaction temperature are showed in Fig. 1, the catalyst M_x(=Ni, Co, Cu)$O_y/(MgO)_{0.9}(CeO_2)_{0.1}$ are prepared after heating at 600 °C. The first evaluation appears to be that the catalytic activities of these catalysts are very similar at low temperature,and catalyst activity of load Cu is higher and that of load Co is lower in high temperature. It has apparent activity difference in second evaluation, catalyst stability of load Ni is best, which is 45 °C at $\Delta T_{50\%}$, followed by load Co catalyst, 72 °C at $\Delta T_{50\%}$, catalyst stability of load Cu is lowest. The effect of load Ni with $(MgO)_{0.9}(CeO_2)_{0.1}$ as carrier is most superior among three kinds of active component. The catalytic activity of $Co_xO_y/(MgO)_{0.9}(CeO_2)_{0.1}$ is better than Co_xO_y/MgO catalyst as reported[16] with similar preparation condition, the temperature of complete methane conversion decreases 86 °C, the results here demonstrate that cerium component is in favour combustion of methane.

Catalyst specific surface characterization: The corresponding activity evaluation data and specific surface data are showed in Table-1. It can be found from specific surface data of sample (Table-1) that the specific surface difference of load of Cu, Ni catalyst is little and slightly larger than that of load Co catalyst, but specific surface of load Cu catalyst in second evaluation is only 6.56 m^2g^{-1}, because Cu oxide may congregate on the surface of carrier after 850 °C reaction. The catalyst specific surface is greatly reduced its activity is also greatly reduced which can be seen from activity evaluation. After second evaluation, the decreased amplitude of specific surface area of load Ni catalyst is slightly higher than that of load Co catalyst. The atomic number of Co, Ni, Cu is nearly same and they have very high activity on methane combustion, but the catalyst with MgO as carrier is not suitable for load Cu oxide as active component.

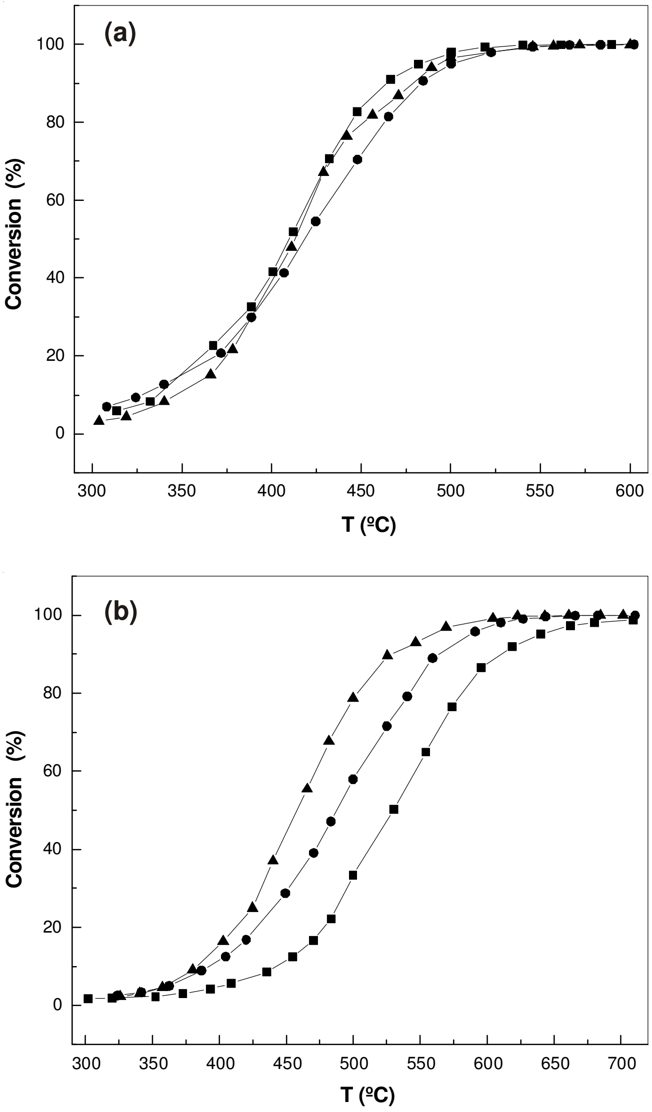

Fig. 1. Conversion of CH_4 over M_x(M = Ni, Co, Cu)$O_y/(MgO)_{0.9}(CeO_2)_{0.1}$ samples; (a) First evaluation; (b) Second evaluation; ●:$Co_xO_y/(MgO)_{0.9}(CeO_2)_{0.1}$, ▲:$NiO/(MgO)_{0.9}(CeO_2)_{0.1}$, ■:$CuO/(MgO)_{0.9}(CeO_2)_{0.1}$

Catalyst composition: The XRD patterns of the M_x(M = Ni, Co, Cu)$O_y/(MgO)_{0.9}(CeO_2)_{0.1}$ catalysts are shown in Fig. 2. Characteristic diffraction peaks of fresh catalyst have clear width, amorphous enhancement, catalyst crystal tends to be complete after second evaluation. MgO and Co_3O_4 both have diffraction peak in 2θ = 37.02°, while it is the strongest characteristic diffraction peak position to Co_3O_4. The difference of diffraction peak intensity of load Co catalyst and that of other

TABLE-2
CATALYTIC ACTIVITIES AND SPECIFIC SURFACE AREAS OF NiO/$(MgO)_{0.9}(CeO_2)_{0.1}$
CATALYSTS CALCINED AT DIFFERENT TEMPERATURE

Samples	S_{BET}/$m^2 g^{-1}$	Vp/$cm^3 g^{-1}$	dp/nm	$T_{10\%}$ (ºC)	$T_{50\%}$ (ºC)	$T_{90\%}$ (ºC)
600 ºC (I)	63.98	0.3	19.04	346	413	478
(II)	30.92	0.26	34.35	384	458	528
800 ºC (I)	34.03	0.22	26.82	416	496	574
(II)	24.78	0.21	34.39	437	530	600
1000 ºC (I)	14.32	0.12	34.3	458	541	617
(II)	13.89	0.13	37.26	457	547	622

Note: Temperature (ºC) with methane conversion of 10 %, 50 %, 90 % denoted as $T_{10\%}$, $T_{50\%}$, $T_{90\%}$ respectively; (I) means first evaluation; (II) means second evaluation

two kinds of catalyst in 2θ=37.02º is little, so, there are two possibilities: First, Co_3O_4 highly dispersed on catalyst surface and XRD does not detect it, Secondly, Co^{2+} into MgO lattice to replace Mg^{2+} position, forming CoO-MgO solid solution. Highly dispersive Co_3O_4 or Co^{2+} of MgO lattice may form methane combustion activity[16]. Load Cu catalyst appears weak CuO characteristic diffraction peaks in 2θ = 35.58º and 2θ = 38.71º, which show that there exist some free CuO. However the diffraction peaks of CuO disappear after second evaluation. It is likely that this catalyst, which has been strongly sintered (6.56 m^2 g^{-1}), has dissolved copper ions as reported in the literature for numerous transition metal ions[17], it is consistent with that specific surface is greatly reduced and catalytic activity is also significantly reduced. NiO diffraction peak is not appeared in load Ni catalyst diagram. On one hand is the NiO might be dispersed too thin to be detected by using XRD or the NiO might be simply an amorphous solid. On the other hand, NiO and MgO are completely miscible at arbitrary proportion in high temperature and form an ideal solid solution since they pose cubic structures and their lattice parameters are similar[18,19] (the lattice constants of NiO and MgO respectively are 0.417 nm and 0.412 nm), therefore, the diffraction peak of $MgNiO_2$ and MgO appears in spectrum, it can be seen from activity evaluation that the solid solution improves sintering capacity of catalyst NiO/MgO and enhances stability.

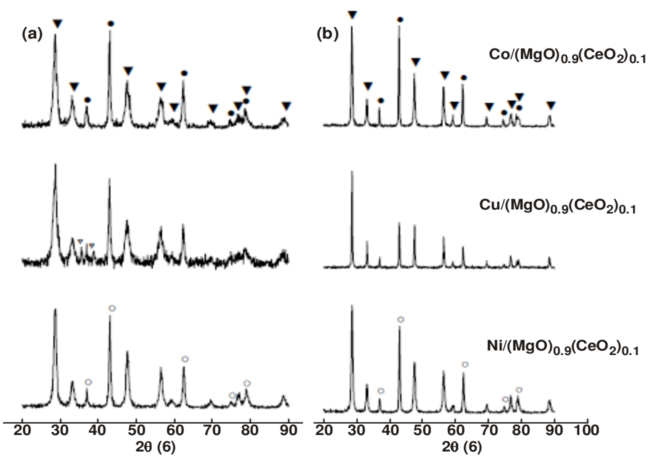

Fig. 2. XRD patterns of M_x(=Ni, Co, Cu)O_y/$(MgO)_{0.9}(CeO_2)_{0.1}$ catalysts; (a) Fresh catalysts, (b) Old catalysts; o: MgO and $MgNiO_2$, ▼: CeO_2, ▽: CuO, ●: MgO and CoO-MgO

Effect of the calcination temperature on NiO/$(MgO)_{0.9}(CeO_2)_{0.1}$: In view of activity and stability of a catalyst, NiO/$(MgO)_{0.9}(CeO_2)_{0.1}$ catalyst was selected as a specimen and calcined at 600 ºC, 800 ºC and 1000 ºC respectively to study roasting temperature influence on catalyst performance. The specific surface area and evaluation results of catalytic activity at different roasting temperature of NiO/$(MgO)_{0.9}(CeO_2)_{0.1}$ catalyst are showed in Table-2.

The XRD spectrum of NiO/$(MgO)_{0.9}(CeO_2)_{0.1}$ at different roasting temperature are showed in Fig. 3, with increasing calcination temperature, diffraction peaks become sharper and crystal phase tend to be complete, but NiO diffraction peak doesn't appear. On one hand as a result of active component on the surface of carrier is highly dispersed or amorphous, on the other hand, because NiO and MgO are cubic system, the lattice constants respectively are 0.417 nm and 0.412 nm, they can inter-solve at arbitrary proportion at high temperature, to form $MgNiO_2$ solid solution on catalyst surface, therefore, the diffraction peak of $MgNiO_2$ and MgO appears in spectrum. It can be seen from activity evaluation that the solid solution improves sintering capacity of catalyst NiO/MgO and enhances stability. Thus, the catalyst still maintains relatively large specific surface and catalytic activity at 1000 ºC.

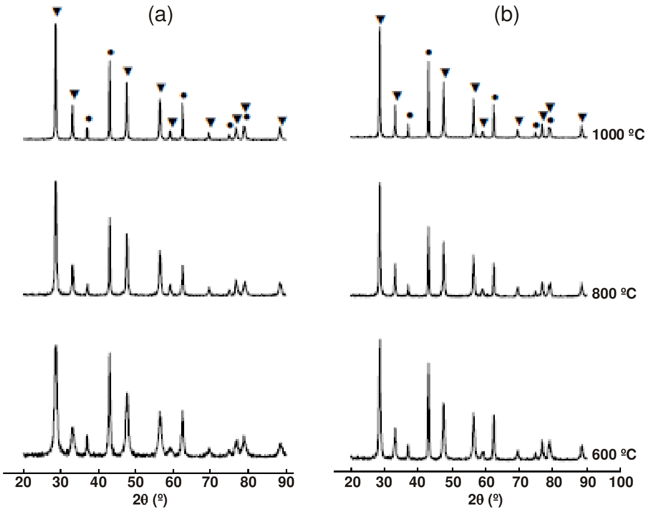

Fig. 3. XRD patterns of NiO/$(MgO)_{0.9}(CeO_2)_{0.1}$ catalysts calcined at different temperature; (a) Fresh catalysts, (b) Old catalysts ●: MgO and $MgNiO_2$, ▼:CeO_2

TEM analysis: The TEM micrographs of NiO/$(CeO_2)_{0.1}$-$(MgO)_{0.9}$ catalyst in different state are showed in Fig. 4. It can be seen from the pictures that the profile of sample is mainly ball structure and NiO highly disperses on the surface of carrier, so, XRD doesn't detect these NiO. Ce auxiliary added decreases average size of NiO/MgO catalyst particles. After second evaluation of the catalyst, average particle size increases slightly, obvious agglomeration doesn't appear. After roasting at 1000 ºC, the catalyst average particle size increases, agglomeration phenomenon is not obvious. These show that the powder material has good resistance ability of sintering, which is consistent with activity evaluation, XRD and results of BET.

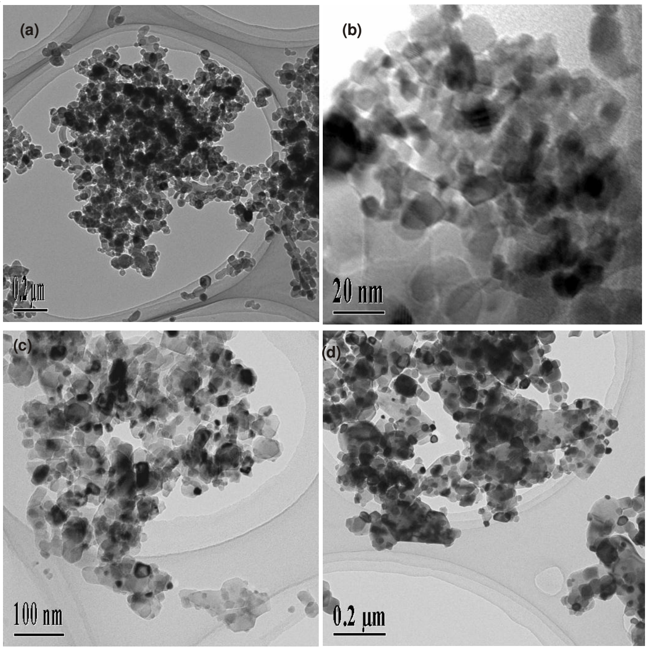

Fig. 4. TEM images of NiO/M_xO_y-MgO catalysts; a: NiO/MgO, b: Fresh NiO/$(CeO_2)_{0.1}$-$(MgO)_{0.9}$, c: After second evaluation NiO/$(CeO_2)_{0.1}$-$(MgO)_{0.9}$, d: 1000 ºC NiO/$(CeO_2)_{0.1}$-$(MgO)_{0.9}$

Conclusion

Different active component has a great effect on the activity and the thermal stability of the catalyst. $(CuO)_{0.1}$-$(MgO)_{0.9}(CeO_2)_{0.1}$-supported Cu catalyst has the highest activity but is sintered by second evaluation, due to strong interaction between copper and the support. Therefore CuO is not a suitable active component on MgO support. The activity of NiO/$(CeO_2)_{0.1}$-$(MgO)_{0.9}$ catalyst was similar to that of CuO/$(CeO_2)_{0.1}$-$(MgO)_{0.9}$ catalyst and NiO/$(CeO_2)_{0.1}$-$(MgO)_{0.9}$ catalyst has the best thermal stability. $(CeO_2)_{0.1}$-$(MgO)_{0.9}$ is deemed to be a good support for NiO. The activity of Co oxide is not good as above and its stability is between them, but after second evaluation, its reduction of specific surface is minimum.

Taking activity and stability of two kinds of factors into account, further study on the nature of NiO/$(MgO)_{0.9}(CeO_2)_{0.1}$, confirms preliminarily that MgO and NiO form $MgNiO_2$ solid solution and TEM shows that Ce auxiliary added decreases obviously average size of NiO/MgO catalyst particles. So the surface of catalyst still is 14.32 $m^2\ g^{-1}$. Through second evaluation, the structure of the catalyst calcined at 1000 ºC does not have any change from that of the fresh catalyst. This catalyst is relatively stable and show high activity as well as have good thermal stability.

REFERENCES

1. R.J. Farrauto, M.C. Hobson, T. Kenelly and E.M. Waterman, *Appl. Catal. A*, **81**, 227 (1992).
2. M. Lyubovsky and L. Pfefferle, *Appl. Catal. A*, **173**, 107 (1998).
3. M. Lyubovsky and L. Pfefferle, *Catal. Today*, **47**, 29 (1999).
4. A.J. Zarur and J.Y. Ying, *Nature*, **403**, 65 (2000).
5. C. J.Zhou, Y.X. Zhu and Y.C. Xie, *Acta Phys.-Chim. Sin.*, **17**, 850 (2001).
6. I. Matsuura, Y. Hashimoto, O. Takayasu, K. Nitta and Y. Yoshida, *Appl. Catal.*, **74**, 273 (1991).
7. G. Saracco, G. Scibilia, A. Iannibello and G. Baldi, *Appl. Catal. B*, **8**, 229 (1996).
8. G. Saracco, F. Geobaldo and G. Baldi, *Appl. Catal. B*, **20**, 277 (1999).
9. J. Kirchnerova and D. Klvana, *Catal. Today*, **83**, 233 (2003).
10. P. Ciambelli, S. Cimino, S. De Rossi, L. Lisi, G. Minelli, P. Porta and G. Russo, *Appl. Catal. B*, **29**, 239 (2001).
11. L.F. Yang, C.K. Shi, X.E. He and J.X. Cai, *Appl. Catal. B*, **38**, 117 (2002).
12. C.X. Qi, L.D. An and H.L. Wang, *Appl. Catal. A*, **140**, 17 (1996).
13. R. Spretz, S.G. Marchetti, M.A. Ulla and E.A. Lombardo, *J. Catal.*, **194**, 167 (2000).
14. M.A. Ulla, R. Spretz, E. Lombardo, W. Daniell and H. Knözinger, *Appl. Catal. B*, **29**, 217 (2001).
15. Y.X. Li, Y.H. Guo and Y.Q. Ji, *Acta Phys.-Chim. Sin.*, **21**, 468 (2005).
16. T.C. Xiao, S.F. Ji, H.T. Wang, K.S. Coleman and M.L.H. Green, *J. Mol. Catal. A*, **175**, 111 (2001).
17 P. Artizzu, E. Garbowski, M. Primet, Y. Brulle and J. Saint-Just, *Catal. Today*, **47**, 83 (1999).
18. H.B. Nussler and O. Kubaschewski, *Z. Phys. Chem., (N.F.)*, **121**, 187 (1980).
19. E. Ruckenstein and Y.H. Hu, *Appl. Catal. A,* **183**, 85 (1999).