ISSN 0023-1584, Kinetics and Catalysis, 2012, Vol. 53, No. 2, pp. 247–252. © Pleiades Publishing, Ltd., 2012.

The Structure—Reactivity Relationship for Metathesis Reaction between Ethylene and 2-Butene on WO_3/SiO_2 Catalysts Calcinated at Different Temperatures[1]

S. Chaemchuen[a], S. Phatanasri[a], F. Verpoort[c], N. Sae-ma[a], and K. Suriye[b]

[a] *Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand*

[b] *SCG Chemicals Co., Ltd., Bangkok, Thailand*

[c] *State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, China*

e-mail: s_phatanasri@yahoo.com

Received March 2, 2011

Abstract—The WO_3/SiO_2 catalyst for propylene production by metathesis of ethylene and 2-butene was preheated at different temperatures to investigate the effect of calcination temperatures on the active species and elucidate the structure—reactivity relationship. The influence of calcination temperatures on the physicochemical properties of the catalyst, relating to the active species, was deduced from an array of characterization results. It has been found that the surface tetrahedral tungsten species with high metal—support interaction were formed on the catalyst calcined at 550°C as confirmed by Raman, UV-Vis and TPR-H_2 spectra.

DOI: 10.1134/S0023158412020024

One of the processes used for the production of propylene is the metathesis reaction between ethylene and 2-butene in the presence of a suitable catalyst. Several researchers have reported tetrahedral tungsten oxide species as the active sites for metathesis reaction of ethylene and 2-butene [1, 2]. Huang et al. [3–5] found that Brønsted acidity promotes the formation of active species for metathesis. Liu et al. [6] reported that the moist air accelerates the transformation of bulk WO_3 to surface oxide and reduces the calcination time needed for the preparation of a highly active catalyst. Spamer et al. [7] found that the active tungsten surface compound is involved in the interaction with the support. Roosmalen et al. [2] suggested that the acidity needed for the formation of the initial metal carbene is available from a Lewis site—alkene complex located on the transition metal ion. Nevertheless, the effect of calcination temperatures on the metathesis activity has not been extensively investigated and the structure—reactivity relationship of the silica-supported tungsten catalyst has not been reported earlier. Therefore, this study has been focused on the influence of calcination temperatures on the nature of tungsten species of WO_3/SiO_2 that are active in the formation of propylene and by-products by the metathesis reaction of ethylene and 2-butene.

EXPERIMENTAL

Preparation of Catalysts

Silica gel, Davisil grade 646 (pore volume 1.15 cm^3/g, supplied by "Aldrich") was used as a support. The precursor of 8%WO_3/SiO_2 was prepared by impregnation of the silica with an aqueous solution of ammonium metatungstate hydrate ("Aldrich", 99.9%). The sample was dried at 110°C for 12 h and calcinated at temperatures from 450 and 750°C for 8 h in static air. The samples were denoted as W(450), W(550), W(650) and W(750), respectively.

Catalyst Characterization

Raman spectra were collected by projecting a continuous wave YAG laser of Nd (810 nm) through the samples at room temperature. A scanning range of 200–1400 cm^{-1} with a resolution of 2 cm^{-1} was applied.

Ammonia temperature programmed desorption (**TPD-NH_3**) was used to determine the acid strength and amount of acid in the WO_3/SiO_2 samples. The amount of ammonia effluent was determined by measuring the areas of the desorption profiles obtained from a Micromeritic Chemisorb 2750 automated system attached with Chemi Soft TPx software.

Temperature programmed reduction by hydrogen (**TPR-H_2**) was carried out by heating the samples in the presence of flowing 10% H_2/Ar with a flow rate of 50 mL/min in the temperature range from 40 to 600°C with ramping rate of 10°C/min following the pretreatment in flowing Ar at 250°C for 2 h.

Catalytic Performance Tests

The catalyst sample was placed at the center of a reactor with an ID of 7.5 mm. The catalyst was pre-

---

[1] The article is published in the original.

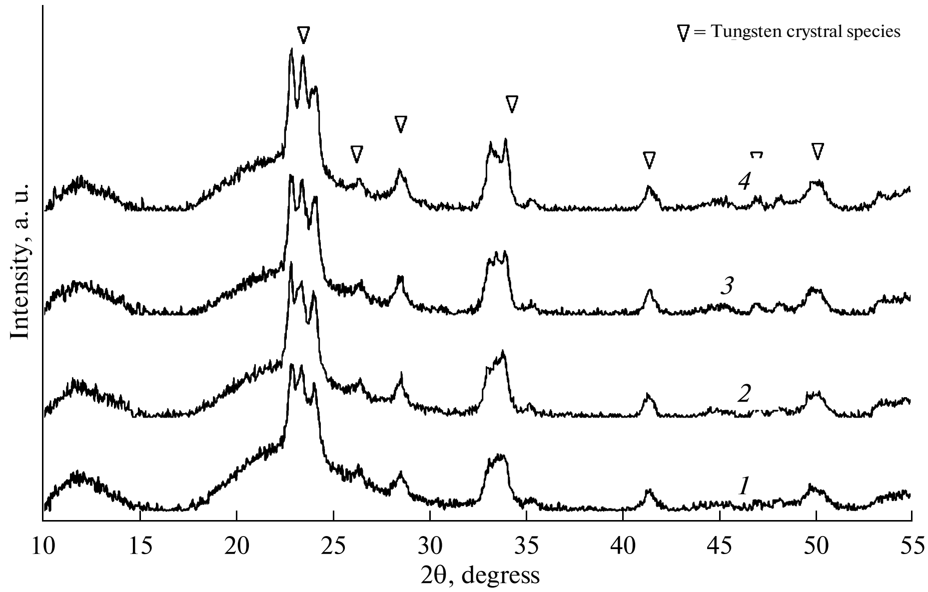

Fig. 1. X-ray diffraction patterns of the silica-supported tungsten catalysts calcined at 450 (*1*), 550 (*2*), 650 (*3*) and 750°C (*4*).

treated at 500°C under nitrogen flow for 1 h and then it was allowed to cool down under the same atmosphere to each reaction temperature ranging between 300 and 500°C. The reaction conditions were as follows: pressure 0.1 MPa, C_2H_4/*trans*-2-C_4H_8 = 2 : 1. The sampling was made after 8 h of operation, and sample analysis was performed on a Shimadzu GC 2014 gas chromatograph equipped with a column of packed 10% silicone SE-30 and a FID detector.

RESULTS AND DISCUSSION

Catalyst Characterization

In order to determine the range of suitable calcination temperatures, thermogravimetric analysis of uncalcinated WO_3/SiO_2 was made by temperature programmed heating in air at which devolatilization of precursor impurities occurs. The weight loss of approximately 5% during the heating from the onset temperature to 400°C was observed. This may be attributed to desorption of precursor impurities as well as to some amount of water physically adsorbed on the catalyst surface. No further weight loss occurred from 450 to 1000°C, indicating that no tungsten metal is lost from the surface over this temperature range. Thus, the temperature range of 450–750°C was adopted for the study of calcination effect.

Table 1. Specific surface area of WO_3/SiO_2 catalysts calcinated at different temperatures

Sample	S_{BET}, m^2/g
Pure SiO_2	256.9
W(450)	234.1
W(550)	238.9
W(650)	222.2
W(750)	173.9

The XRD patterns of catalysts are shown in Fig. 1. All catalysts exhibited the characteristic peaks of WO_3 crystallites at 2θ of 23.12°, 23.60° and 24.38°. It has been found that the XRD peaks tend to increase in their intensities with increasing calcination temperature. It appears that various tungsten oxide species, other than tungsten crystal WO_3, are formed during the calcination. As shown in Table 1, the BET surface area (S_{BET}) of the catalyst decreased with increasing calcination temperature. This may be due to either the sintering of tungsten metal itself and/or tungsten metal and silica support.

The results of the determination of the acidity of catalysts by TPD-NH_3 method are shown in Fig. 2. As the calcination temperature was increased from 450 to 750°C the intensity of the low temperature peak around 200°C attributable to the weak acid sites was reduced by 75%. In accordance with the lowered BET surface area, higher calcination temperatures causes a decrease in acidity.

The Raman spectroscopy was adopted as a good tool for determination of the structure of tungsten species in supported WO_3/SiO_2 catalysts calcinated at different temperatures. As shown in Fig. 3, the Raman band characteristics at 498, 602, 808 and 1060 cm^{-1} were assigned to oscillation of four- and three-membered silica ring and Si–O–Si stretching [8]. The positions of the Raman band for crystalline WO_3 at 263–275, 707–720 and 807–808 cm^{-1} were assigned to the deformation mode of W–O–W, bending mode of W–O, and the symmetric stretching mode of W–O,

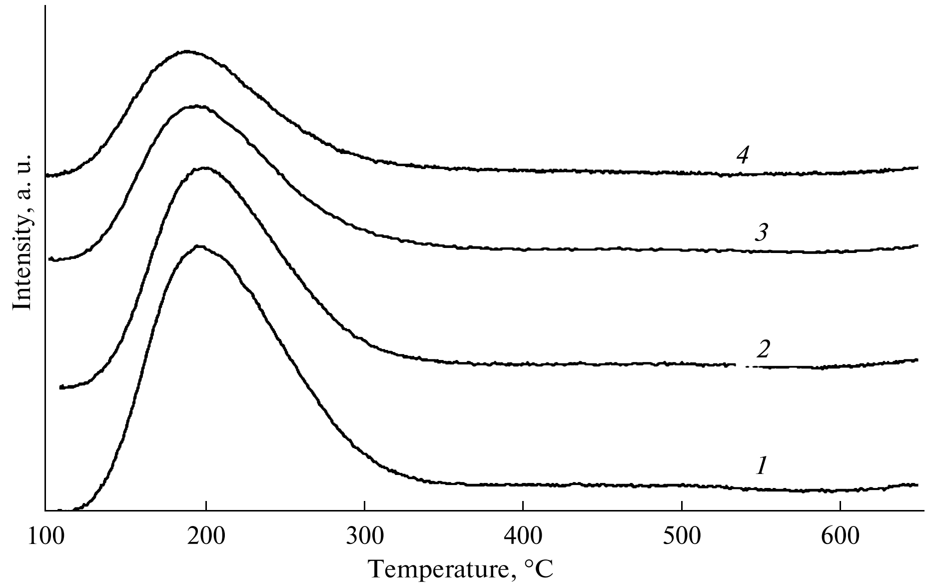

Fig. 2. TPD-NH_3 profiles for catalysts calcined at 450 (*1*), 550 (*2*), 650 (*3*) and 750°C (*4*).

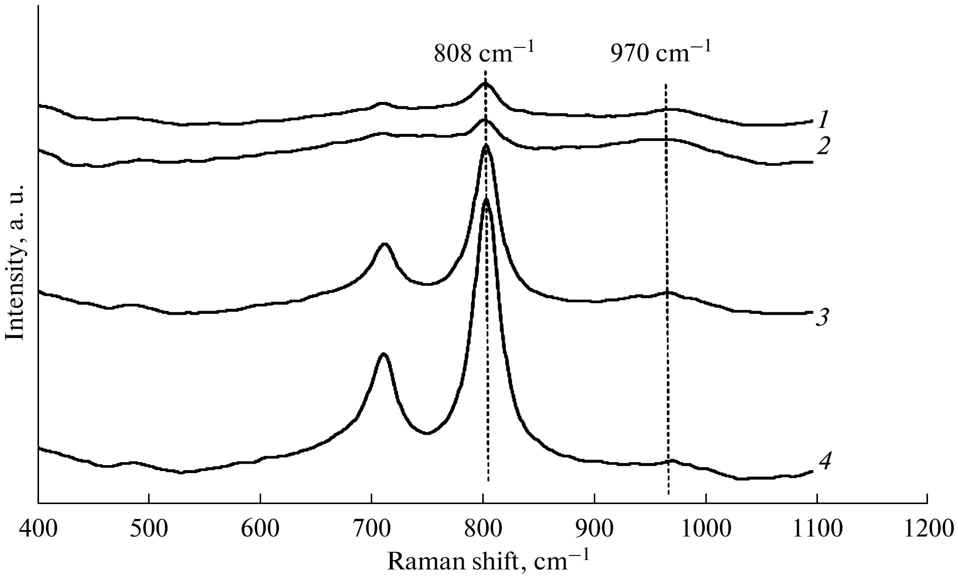

Fig. 3. Raman spectra of catalysts calcined at 450 (*1*), 550 (*2*), 650 (*3*) and 750°C (*4*).

respectively [9]. The band at 970 cm^{-1} was assigned to the surface tungsten oxide species—the active species for metathesis reaction [4], This band was ascribed to the O=W=O band of the isolated surface tetrahedral tungsten oxide species [10]. Bands around 710, 808 and 970 cm^{-1} differed in intensity were observed (Fig. 3). Since the tungsten content for all the catalysts is the same, we suggest that the amount of surface tungsten oxide compound can be estimated from the relative intensities (I) of Raman bands between 970 and 805 cm^{-1} as adopted by some researchers [4, 11]. It has been found that the maximum ratio of I_{970}/I_{805} was achieved for the catalyst calcinated at 550°C, as shown in Table 2.

The relative reducibility of oxygen on catalyst surface by hydrogen, measured by TPR-H_2 technique, was used to investigate the interaction between tungsten species and silica support as shown in Fig. 4. It has been found that the calcination temperature affects both the position and area of reduction peaks for each catalyst. The results are summarized in Table 2. The catalyst calcinated at 550°C exhibits the shift of TPR-H_2 peaks at a relatively higher temperature and shows remarkably less consumption of H_2 compared to other

Table 2. The relative intensities of Raman bands at 970 and 805 cm^{-1} (I_{970}/I_{805}), relative amount of acid sites and relative amount of consumed H_2 for WO_3/SiO_2 catalysts calcinated at different temperatures

Catalyst	Parameter			
	I_{970}/I_{805}	relative amount of acid sites, (mol NH_3)/g_{cat} × 10^{-2}	reducibility by H_2, a.u.	temperature of reduction (maximum), °C
W(450)	0.31	12	1.08	538
W(550)	1.55	10	0.74	560
W(650)	0.53	9	1.18	538
W(750)	0.02	3	1.01	532

samples. This indicates the existence of a strong metal–support interaction for W(550) catalyst and reflects me influence of calcination temperature on the tungsten species obtained. The catalyst calcinated at 550°C was found to show a strong metal–support interaction as clearly indicated by TPR-H_2 result in Fig. 4. Moreover, the existence of surface tetrahedral tungsten oxide species in substantial amounts can be also inferred from the Raman results (Fig. 3). Therefore, there exists some interesting relationship between the formation of tetrahedral species and a strong metal–support interaction.

Catalytic Performance of WO_3/SiO_2 Catalysts

The *trans*-2-butene conversion and propylene selectivity of various catalysts calcinated at different reaction temperatures are shown in Fig. 5. As high as 85.6% of *trans*-2-butene was converted with a 80.6% selectivity for propylene in the presence of the W(550) catalyst at 400°C. It is interesting to note that both *trans*-2-butene conversion and propylene selectivity observed at the same reaction temperature of 400°C are considerably lower for catalysts calcinated at temperatures below or above 550°C. At a reaction temperature of 300°C, a considerably lower *trans*-2-butene conversion and propylene selectivity were observed irrespective of the calcination temperature. As for the reaction temperature of 500°C, a relatively high *trans*-2-butene conversion and propylene selectivity were remained nearly unchanged for all the calcination temperatures studied. The distribution of the observed by-products from metathesis reaction at 400°C on the catalysts calcinated at different temperatures is also shown in Table 3.

DISCUSSION

The results outlined above show the influence of calcination temperatures on the catalyst activity. From these results characterizing a metal–support interaction, acidity and the nature of surface tungsten species some conclusions about structure–reactivity relationship of WO_3/SiO_2 catalysts can be made. It has been

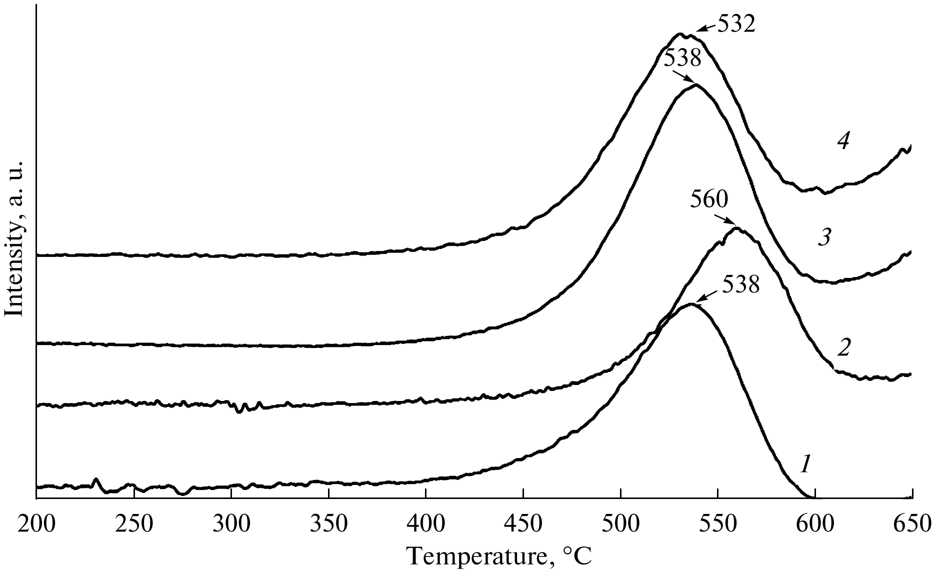

Fig. 4. TPR-H_2 profiles for catalysts calcined at 450 (*1*), 550 (*2*), 650 (*3*) and 750°C (*4*).

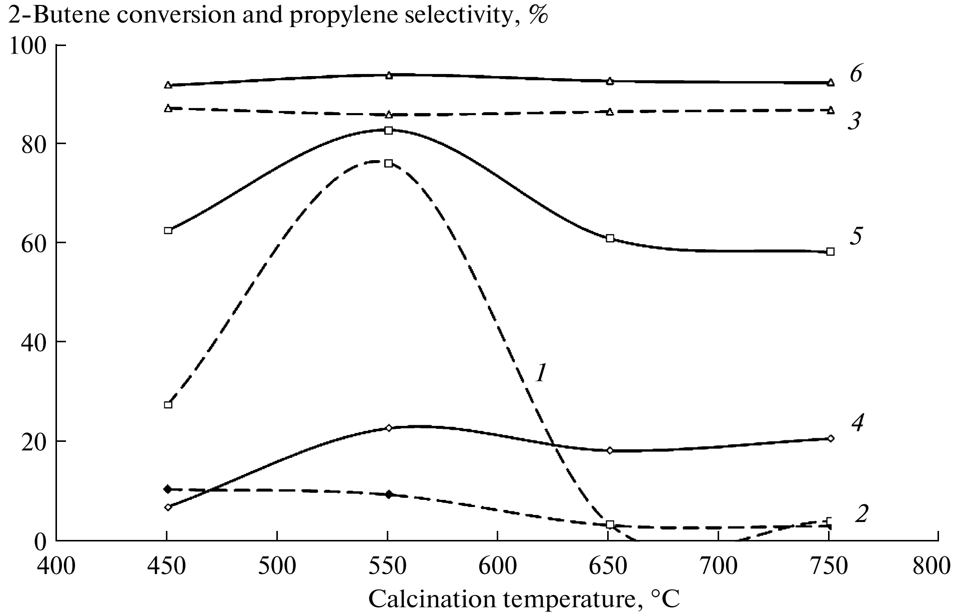

Fig. 5. Metathesis activity of tungsten catalysts as a function of calcination temperature : *1–3*—2-butene conversion at 300 (*1*), 400 (*2*) and 500°C (*3*); *4–6*—propylene selectivity at 300 (*4*), 400 (*5*) and 500°C (*6*).

widely suggested that the surface tetrahedral tungsten oxide species are the active sites for the formation of metathesis product. The catalyst W(550), exhibiting the highest yield of propylene contains the surface tetrahedral tungsten species as confirmed by Raman peak at 970 cm^{-1} (Fig. 3). Moreover, the W(550) catalyst showed a high metal–support interaction as indicated by the shift to higher temperature of TPR-H_2 spectrum (Fig. 4). Thus, the active sites for propylene formation in metathesis reaction appear to be the surface tetrahedral tungsten oxide species capable to a strong metal–support interaction.

It has been reported [4] that the Brønsted acidity favors the formation of propylene in metathesis reaction; however, in our study a reduction in acidity was observed at higher calcination temperatures. As the Brønsted acidity decreases and Lewis acidity increases at enhanced temperatures, the high propylene yield obtained on the catalyst calcinated at 550°C seems to be not affected by the decrease in Brønsted acidity. On the other hand, the increased formation of 1-butene and *cis*-2-butene as by-products obtained on the catalyst calcinated at temperatures above 550°C was accompanied by an increase in Lewis acidity. Thus, the Lewis acidity may *inter alia* contribute to the formation of such by-products. The possible formation of crystalline or polytungstate at calcination temperatures above 550°C may be responsible for the appearance of sites which promote the yield of products of side reactions (1-butene and *cis*-2-butene) favored by the presence of Lewis acidity.

The existence of surface tetrahedral tungsten species in the W(550) catalyst markedly promotes both 2-butene conversion and propylene selectivity in metathesis reaction particularly at 400°C (Fig. 5). However, such influence was less dominant for the reaction at 300°C, and almost no significant effect of calcination temperature was observed for the reaction at 500°C. It can be suggested that in addition to the availability of surface tetrahedral tungsten species the metalcarbene effect [12] also plays an important role for metathesis activity. The reaction temperature of

Table 3. Products distribution for metathesis reaction between ethylene and 2-butene at 400°C on catalysts calcinated at different temperatures

Catalyst	Conversion of 2-butene, %	Products distribution, %			
		propylene	1-butene	1,3-butadiene	*cis*-2-butene
W(450)	63	28	32	2	38
W(550)	83	77	11	1	11
W(650)	61	4	42	2	52
W(750)	59	5	43	1	51

300°C may be too low for the appearance of the metalcarbene effect, and thus a relatively low conversions and selectivity were observed for all the catalyst samples irrespective of the calcination temperature. On the other hand, the reaction temperature of 500°C is high enough for the metalcarbene effect to appear, and therefore a considerably high metathesis activity was observed for ail the catalyst samples regardless of the effect expected from a high temperature treatment. It is also noteworthy that the formation of 1-butene and *cis*-2-butene was in inverse relation to yields of propylene, while the formation of 1,3-butadiene was almost independent of the presence of propylene. Thus, it is conceivable that the sites for 1-butene and *cis*-2-butene formation may be of another nature than the active sites for propylene formation that involve tetrahedral tungsten. A possible formation of crystalline or polytungstate at calcination temperatures in excess of 550°C may be responsible for the appearance of sites favorable for the formation of such by-products. The sites responsible for 1,3-butadiene formation, however, should be different from the sites some of which promote the formation of propylene and some favor the formation of 1-butene and *cis*-2-butene. This problem will be the subject of further investigation.

It can be concluded that the calcination temperature markedly affects physico-chemical properties of the catalysts investigated, particularly the active species of WO_3/SiO_2 catalysts. An array of characterization results provides evidence that the surface tetrahedral tungsten species capable to a strong metal–support interaction are the active site for propylene production. This suggestion is in accordance with the interpretation of Raman and TPR-H_2 spectra obtained for the W(550) catalyst. Moreover, in the presence of the W(550) catalyst as much as 85.6% of 2-butene was converted with 80.6% selectivity for propylene. The sites for 1-butene and *cis*-2-butene formation seem to be different from the active sites involving tetrahedral tungsten because the yields of the butenes were in the inverse relation with the propylene formation.

The authors would like to express their deep appreciation to the Thailand Research Fund (TRF) and SCG Chemical Co., Ltd. for their financial support. The special thanks also go to the Office of Higher Education Commission for its support on the National Research University Program (CC557A).

REFERENCES

1. Mol, J.C., *J. Mol. Catal. A: Chem.*, 2004, vol. 213, p. 39.
2. Van Roosmalen, A.J. and Mol, J.C., *J. Catal.*, 1982, vol. 78, p. 17.
3. Huang, S., Liu, S., Zhu, Q., Zhu, X., Xin, W., Liu, H., Feng, Z., Li, C., Xie, S., Wang, Q.X., and Xu, L., *Appl. Catal., A,* 2007, vol. 323, p. 94.
4. Huang, S., Chen, F., Liu, S., Zhu, Q., Zhu, X., Xin, W., Feng, Z., Li, C., Wang, Q.X., and Xu, L., *J. Mol. Catal. A: Chem.*, 2007, vol. 267, p. 224.
5. Huang, S., Liu, S., Xin, W., Bai, J., Xie, S., Wang, Q.X., and Xu, L., *J. Mol. Catal. A: Chem.*, 2005, vol. 226, p. 61.
6. Liu, H., Huang, S., Zhang, L., Liu, S., Xin, W., and Xu, L., *Catal. Commun.*, 2009, vol. 10, p. 544.
7. Spamer, A., Dube, T.I., Moodley, D.J., Van Schalkwyk, C., and Botha, J.M., *Appl. Catal., A*, 2003, vol. 255, p. 153.
8. Chen, J.Q., Bozzano, A., Glover, B., Fuglerud, T., and Kvisle, S., *Catal. Today*, 2005, vol. 106, p. 103.
9. Horsely, J.A., Wachs, I.E., Brown, J.M., Via, G.H., and Hardcastle, F.D., *J. Phys. Chem.,* 1987, vol. 91, p. 4014.
10. Lee, E.L. and Wachs, I.E., *J. Phys. Chem.*, 2008, vol. 112, p. 6487.
11. Chan, S.S., Wachs, I.E., and Murrell, L.L., *J. Catal.*, 1984, vol. 90, p. 150.
12. Andreini, A. and Mol, J.C., *J. Chem. Soc., Faraday Trans. 1*, 1985, vol. 81, p. 1705.