Catalytic Isomerization

DOI: 10.1002/ange.200600377

A Highly Active and Selective Nanocomposite Catalyst for C_{7+} Paraffin Isomerization**

*Jinsuo Xu and Jackie Y. Ying**

Due to the increasingly stringent regulation by the EPA of toxic aromatics in motor fuel, there has been a sharp rise in the demand for processes that can boost the octane value of non-aromatic hydrocarbons.[1] This is particularly true for C_{7+} paraffins (i.e. n-C_7 and higher paraffins), whose straight-chain counterparts have very low octane values. Skeletal isomerization of these hydrocarbons into high-octane branched paraffins has been found to be the most effective route to compensate for the octane value loss associated with removal of aromatics.[1–4] However, the isomerization of C_{7+} paraffins is very different from the isomerization of light paraffins (i.e. n-C_4 and n-C_5) as cracking becomes increasingly competitive with isomerization as the carbon chain length increases.[2,5] Furthermore, the yield of multibranched paraffins is more critical for the economics of the process than the yield of total branched paraffins since the monobranched C_{7+} paraffins do not have high enough octane numbers to be blended directly into the octane pool. Thus, minimizing cracking while achieving high yields of multibranched paraffins has been a

---

[*] Prof. J. Y. Ying
Institute of Bioengineering and Nanotechnology
31 Biopolis Way
The Nanos, Singapore 138669 (Singapore)
Fax: (+65) 6478-9020
E-mail: jyying@ibn.a-star.edu.sg
Homepage: www.ibn.a-star.edu.sg

Dr. J. Xu, Prof. J. Y. Ying
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139-4307 (USA)

[**] We thank Dr. Frits Dautzenberg and Dr. Philip Angevine (ABB Lummus Global, Inc.) for helpful discussions, and Michael Frongillo (MIT-NSF CMSE) for assistance with HR-TEM studies. This work was supported by ABB Lummus Global, Inc.

Supporting Information for this article is available on the WWW under http://www.angewandte.org or from the author.

major challenge for the development of C_{7+} isomerization catalysts.[2,4,6–12]

Here we report the development of a highly active and selective multicomponent nanocomposite catalyst, Pt/WO_3/M-ZrO_x. This system involves highly dispersed WO_3 domains and Pt clusters supported on heteroatom-substituted ZrO_2 nanocrystals (M-ZrO_x). This nanocomposite material enables the efficient isomerization of C_{7+} paraffins at a remarkably low temperature of 125 °C. This highly active catalyst is very selective for branched paraffins, especially multibranched paraffins, and demonstrates long-term stability and excellent tolerance to feed impurities. Unlike conventional isomerization catalysts, which are designed as strong solid acids, the superior catalytic performance of Pt/WO_3/M-ZrO_x is associated with an unusually high surface density of spilt-over H_2 and a facile reverse process of H_2 spillover.[13–15]

Nanocomposite processing can be used to develop unique catalysts with superior surface areas, ultrahigh dispersion of components, and excellent stability.[16,17] In this study, an easier method of simultaneously precipitating different metal cations, such as Al^{3+} with Zr^{4+}, under controlled pH conditions is employed to obtain metal hydroxides that are mixed at an atomic level. Ultrahigh dispersions of WO_3 and Pt on the M-ZrO_x support are then obtained by sequential impregnation. The resulting Pt/WO_3/M-ZrO_x nanocomposite catalyst exhibits significantly greater activity than the benchmark Pt/WO_3/ZrO_2 and Pt/Beta catalysts and is able to successfully convert various paraffins with boiling points close to that of *n*-C_7 at a relatively low temperature with superb isomerization selectivity.

n-Heptane isomerization was chosen as a model reaction to evaluate the catalyst performance. Figure 1 shows that Pt/WO_3/Al-ZrO_x is about six times as active as Pt/WO_3/ZrO_2 and twice as active as Pt/Beta at 200 °C after about 2 h. The dopant also improves the catalyst's isomerization selectivity substantially. At 80 % conversion of *n*-heptane, an isomerization selectivity of 86 % was maintained over Pt/WO_3/Al-ZrO_x, whereas selectivities of 81 % and 76 % were obtained with Pt/WO_3/ZrO_2 and Pt/Beta, respectively.

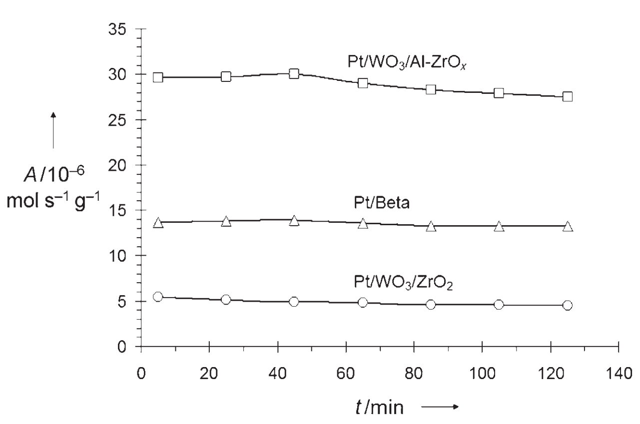

Figure 1. *n*-Heptane isomerization activities (*A*) over Pt/WO_3/Al-ZrO_x, Pt/Beta, and Pt/WO_3/ZrO_2 at 200 °C and atmospheric pressure; *t* = reaction time, H_2/*n*-C_7 feed molar ratio = 16. The contact time was adjusted to obtain *n*-C_7 conversions of 15–30 %.

The superior activity of Pt/WO_3/Al-ZrO_x allows this nanocomposite catalyst to operate at a lower reaction temperature, which is favorable for greater isomerization selectivity. As shown in Figure 2, an isomerization selectivity of more than 80 % is attained even at 90 % conversion of *n*-heptane at 150 °C. Remarkably, multibranched heptanes account for over 45 % of the isomers obtained, thus providing an unprecedented boost in octane value. At 150 °C, the Pt/WO_3/Al-ZrO_x nanocomposite catalyst also efficiently converts other paraffins that are typically present with *n*-C_7 in the refinery stream, such as *n*-hexane (0.22 $\mu mol\,s^{-1}g^{-1}$) and *n*-octane (9.9 $\mu mol\,s^{-1}g^{-1}$), again with excellent isomerization selectivities. At 80 % conversions of *n*-hexane and *n*-octane, isomerization selectivities of 98 % and 82 %, respectively, were attained (see Supporting Information).

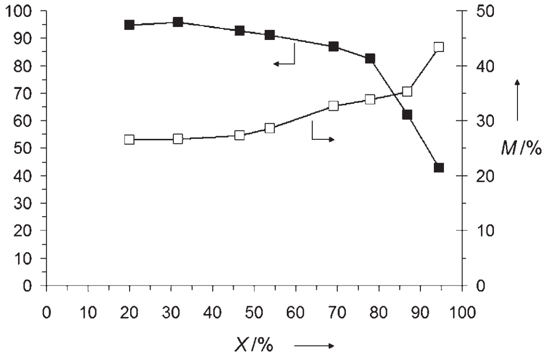

Figure 2. Isomerization selectivity (*S*; ■) and percentage of multibranched paraffins in total isomers (*M*; □) versus *n*-C_7 conversion (*X*) over Pt/WO_3/Al-ZrO_x at 150 °C and atmospheric pressure; H_2/*n*-C_7 feed molar ratio = 16. The contact time was adjusted to obtain the different levels of *n*-C_7 conversions noted.

The reaction temperature over Pt/WO_3/Al-ZrO_x could be lowered further at elevated pressures, as commonly practiced in commercial processes. For example, at a total pressure of 100 psig, a H_2/*n*-C_7 feed molar ratio of 1.0, and a volume hour space velocity of 1 h^{-1}, 30 % conversion of *n*-C_7 with greater than 99 % isomerization selectivity was obtained over this nanocomposite catalyst at 125 °C under trickle-bed conditions. Such a low reaction temperature would further boost the formation of highly branched isomers while simultaneously reducing cracking.

Pt/WO_3/Al-ZrO_x also demonstrates good tolerance against feed impurities and excellent long-term stability. Pt/chlorided-alumina catalysts can be rapidly deactivated by trace amounts of aromatics or cyclohexane in the feedstock due to the strong adsorption of these electron-rich molecules at acidic sites.[5] Pt/zeolite catalysts are also sensitive to aromatics and cyclohexane; additionally, they cannot isomerize *n*-hexane effectively without significantly cracking the heavier paraffins present in the feed stream.[2] Thus, complicated separation and purification processes are needed for the isomerization of light reformate over traditional bifunctional catalysts. The performance of Pt/WO_3/Al-ZrO_x under realistic conditions was examined using a simulated feedstock of light reformate, which contained 19.4 mol % of *n*-pentane, 28.0 mol% of *n*-hexane, 37.8 mol% of cyclohexane, 13.1 mol% of *n*-heptane, and 1.7 mol% of benzene. The nanocomposite catalyst successfully converted all the different components in a single process at 150 °C without substantial deactivation (Figure 3). *n*-Heptane and *n*-hexane were efficiently converted into their branched isomers, while a lower conversion of *n*-pentane was obtained. Cyclohexane was isomerized to methylcyclopentane, which has a higher octane value than cyclohexane. Benzene was completely hydrogenated to cyclohexane, followed by partial isomerization to methylcyclopentane. The overall octane number of the light reformate feedstock was increased by about 13 (from 54 to 67), with less than 0.85% mass loss due to cracking. This significant upgrade in octane value is very attractive considering that current premium gasoline with an octane number of 89 is generally US$ 0.10–0.20 more expensive per gallon than regular gasoline with an octane number of 87.

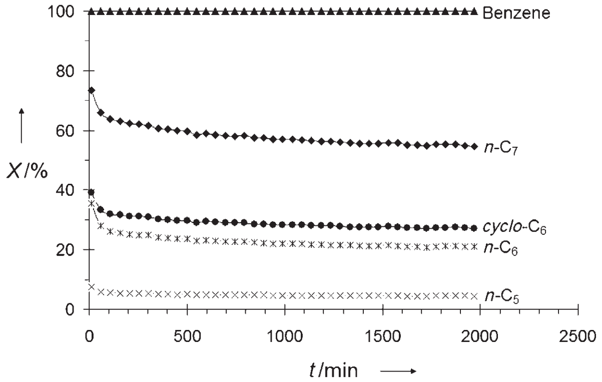

Figure 3. Isomerization of simulated light reformate feedstock over Pt/WO_3/Al-ZrO_x at 150 °C and atmospheric pressure; X = conversion, t = time on stream. Reaction conditions: infuse rate of the mixed feed = 0.44 mL h^{-1}; H_2 flow rate = 21.1 mL min^{-1}; WHSV = 3.1 h^{-1}; catalyst loading = 1.0 g.

The catalytic performance of Pt/WO_3/M-ZrO_x nanocomposite is critically related to the doping of the support, unlike other doped oxide catalysts, where the support's surface area or crystal phase play a more important role.[11,18,19] In our nanocomposite system, the heteroatom is truly substituted as a dopant for Zr^{4+} in the ZrO_2 crystal lattice instead of forming a separate phase. This was confirmed by changes in the ZrO_2 unit cell volume (Figure 4) produced by the introduction of dopants of different ionic radii. The most significant increases in catalytic activity were observed when Al^{3+} and Ga^{3+} were used as the dopants; these trivalent cations also lead to substantial decreases in the ZrO_2 unit cell volume. In contrast, a lower reduction in the ZrO_2 unit cell volume was observed when Si^{4+} was introduced. This is because only part of the Si^{4+} is incorporated in the ZrO_2 lattice—most of the Si^{4+} introduced is segregated into a separate silica phase on the zirconia surface. This could weaken the interaction between WO_3 and the zirconia support and give rise to the severe reduction in catalyst activity observed in Figure 4.

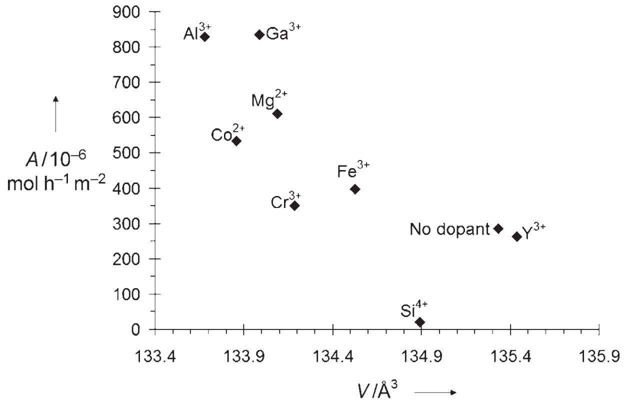

Figure 4. Catalytic activity of Pt/WO_3/M-ZrO_x (A) versus the unit cell volume of M-ZrO_x (V), where M represents the cation introduced (M/Zr cation ratio = 0.05). Reaction conditions: 200 °C, 1 atm, H_2/*n*-C_7 feed molar ratio = 16. The contact time was adjusted to obtain *n*-C_7 conversions of 15–30%.

The method of introducing dopants into ZrO_2 has a significant impact on the successful heteroatom substitution in the ZrO_2 lattice, and consequently on the catalyst performance. Straightforward co-precipitation by adding the base solution to a mixed solution containing both dopant and Zr^{4+} salts has frequently been used in the preparation of doped oxide catalysts.[18,20,21] However, this method has serious drawbacks when an ultrahigh dispersion of dopants is required because the dopant and Zr^{4+} might precipitate at different points and different rates under a variable pH environment. An Al^{3+}-doped catalyst prepared by this direct method also consists of irregularly shaped oxide particles with a broad size distribution of 5–25 nm (see Supporting Information). This limitation of Al^{3+} substitution and the poor control of nanoparticle precipitation lead to an Al^{3+}-doped catalyst that is only slightly more active than the undoped catalyst.[20] In contrast, our Al^{3+}-doped zirconia nanocrystals were prepared at a constant pH of 9, whereby the Zr^{4+} and Al^{3+} cations are simultaneously precipitated from their mixed salt solution. This constant-pH precipitation ensures an ultrahigh dispersion of Al^{3+} and Zr^{4+}, and a high level of Al^{3+} substitution in the ZrO_2 lattice. It also leads to spherical oxide particles with a very narrow size distribution of 10–12 nm (see Supporting Information).

Generally, the increase in activity in conventional isomerization catalysts can be correlated to changes in their acidic properties.[11,18,21] In our case, the distribution of Brønsted and Lewis acid sites in the Pt/WO_3/Al-ZrO_x nanocomposite was found to be very similar to that in Pt/WO_3/ZrO_2, according to the IR spectra of samples subjected to pyridine chemisorption. The total acid amount is actually slightly lower in Pt/WO_3/Al-ZrO_x (0.13 mmol NH_3 per gram) than in Pt/WO_3/ZrO_2 (0.15 mmol NH_3 per gram). Thus, factors other than acidity must be responsible for the superior catalytic performance of Pt/WO_3/Al-ZrO_x. As the H_2 atmosphere is important and necessary for the isomerization reaction, the amount of H_2 adsorbed on the different catalysts under a flowing stream of H_2 was measured by thermogravimetric analysis (TGA). All samples were reduced at 350 °C in H_2 prior to H_2 adsorption at room temperature. It was found that the H_2 uptake by Pt/WO_3/Al-ZrO_x is more than twice that of Pt/

WO_3/ZrO_2 (Figure 5a). The remarkably high H_2/Pt molar ratio over both catalysts indicates that H_2 is adsorbed not only by Pt but also by WO_3 and/or Al-ZrO_x through H_2 spillover.[14] It has been reported that H_2 spillover takes place very readily in the Pt/WO_3 system.[15] However, the large difference in H_2 uptake between Pt/WO_3/Al-ZrO_x and Pt/WO_3/ZrO_2 can be best explained by the role of Al-ZrO_x in H_2 storage, which would typically occur only at very high temperatures in undoped ZrO_2.[22]

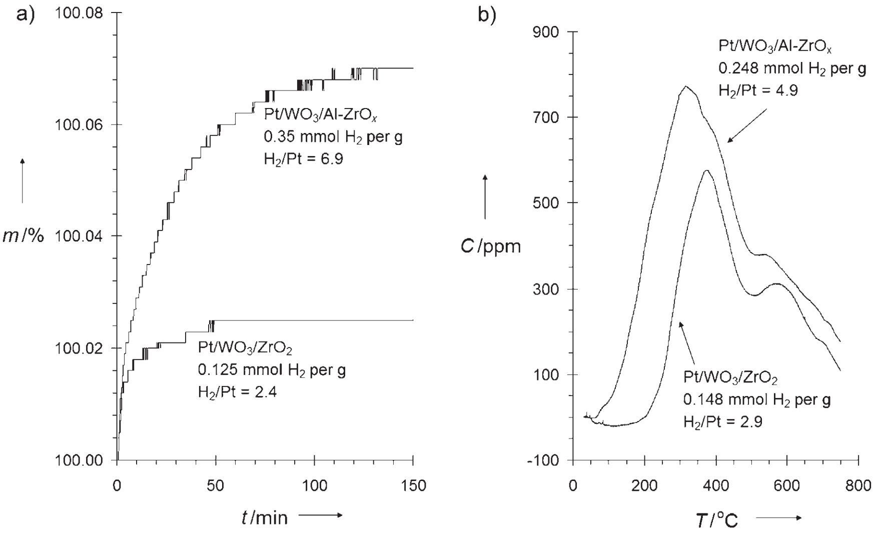

Figure 5. a) Uptake and b) TPD of H_2 over Pt/WO_3/Al-ZrO_x and Pt/WO_3/ZrO_2. m = weight; t = adsorption time; C = H_2 desorbed; T = desorption temperature.

Hydrogen desorption from the catalysts was measured in temperature-programmed desorption (TPD) studies. As shown in Figure 5b, H_2 desorption in Pt/WO_3/Al-ZrO_x occurs at a temperature about 150 °C lower than in Pt/WO_3/ZrO_2, and the amount of H_2 desorbed from Pt/WO_3/Al-ZrO_x is about 69 % higher than from Pt/WO_3/ZrO_2. Substitution of Zr^{4+} by a lower valence cation, such as Al^{3+}, would generate oxygen vacancies in the ZrO_2 crystal structure to preserve the electroneutrality. These oxygen vacancies could increase the ionic conductivity of ZrO_2 significantly.[23] As a result, the rate of reverse H_2 spillover could be increased in Pt/WO_3/Al-ZrO_x, thus allowing for a more facile H_2 desorption.[24] In an isomerization reaction, the higher surface density of spilt-over H_2, which might exist in the form of an H^+/H^- pair, and the rapid H^+/H^- migration in the catalyst could substantially facilitate the hydrocarbon conversion and inhibit the cracking of intermediates arising from long residence times at the acidic sites.[4,5]

In conclusion, our Pt/WO_3/Al-ZrO_x nanocomposite allows for the highly efficient and selective conversion of C_{7+} paraffins at a remarkably low temperature of 125 °C. This novel catalyst provides a competitive alternative to traditional zeolites and liquid acids in oil refinery and petrochemical production. The superior catalytic performance of Pt/WO_3/Al-ZrO_x is attributed to the much higher surface density of spilt-over H_2 and a more facile reverse process of H_2 spillover. The significant differences in H_2 adsorption and desorption behavior in Pt/WO_3/Al-ZrO_x compared to Pt/WO_3/ZrO_2 are related to the uniform and successful substitution of Zr^{4+} by Al^{3+} in ZrO_2, which produces a large number of oxygen vacancies and significantly increases the ionic conductivity of ZrO_2. This structure–property relationship might have a broad impact on the rational design of complex oxide catalysts and multifunctional nanocomposites.

Experimental Section

The incorporation of Al^{3+} into ZrO_2 was achieved by co-precipitation of Zr^{4+} and Al^{3+} salts (Al^{3+}/Zr^{4+} atomic ratio = 0.05) at a constant pH value of 9.0 by adding an aqueous solution of ammonium hydroxide. The precipitate was washed thoroughly with deionized water and dried at 120 °C. Ammonium metatungstate hydrate (99.9+ %, Strem Chemicals) was then loaded onto the precipitate by the incipient-wetness impregnation technique at a tungsten concentration of 20–25 wt % (based on the hydroxides). The resulting material was calcined at 800 °C for 3 h to yield WO_3/Al-ZrO_x with a surface area of 56 $m^2 g^{-1}$. It was then loaded with 1.0 wt % of Pt by impregnation with $[Pt(NH_3)_4](NO_3)_2$ (99 %, Strem Chemicals), and calcined at 450 °C for 1.5 h to yield the Pt/WO_3/Al-ZrO_x nanocomposite.

Pt/WO_3/ZrO_2 (containing 16 wt % W based on zirconium hydroxide) and Pt/Beta were prepared as benchmark catalysts. The former was synthesized according to the literature procedure;[4,10] WO_3/ZrO_2 was obtained with a surface area of 63 $m^2 g^{-1}$. Pt/Beta was obtained by calcining NH_4^+-Beta zeolite (Si/Al = 12.5, Zeolyst International) at 500 °C for 3 h to produce H^+-Beta, followed by loading with 1.0 wt % of Pt.

n-Heptane isomerization was conducted in a tubular reactor at atmospheric pressure. Prior to the reaction, the catalyst was treated in situ at 450 °C in air for 1.5 h to purge its surface, followed by reduction in H_2 at 350 °C for 1.5 h to reduce Pt^{II} to Pt metal. n-Heptane was introduced into the feed stream by flowing H_2 through an n-heptane saturator at 25 °C, which gave a H_2/n-heptane molar ratio of 16. The catalyst was tested at variable weight hour space velocities (WHSV) to obtain the desired n-C_7 conversion. For example, to compare the activities of different catalysts, the conversion was controlled from 15 % to 30 %. In the selectivity versus conversion studies, the conversion of n-C_7 was varied from 10 % to 90 % systematically by changing the WHSV.

H_2 uptake was measured by TGA. The catalyst was treated first in an air stream at 450 °C for 1.5 h, followed by reduction in 5.2 % H_2 in helium for 3 h. It was then flushed with pure helium at 450 °C for 12 h to remove the adsorbed H_2 and cooled to room temperature in helium. When the catalyst weight became stable, the gas flow was switched from pure helium to 5.2 % H_2 in helium, and the weight gain at room temperature due to H_2 adsorption was recorded as the amount of H_2 uptake.

TPD studies of H_2 was conducted in a tubular reactor. The catalyst was reduced at 350 °C in H_2 for 1.5 h and then cooled to room temperature in H_2. It was then flushed with argon to remove the weakly adsorbed H_2. H_2 desorption upon heating the catalyst bed from 30 °C to 750 °C at a rate of 5 K min^{-1} was analyzed with an HP 6890 GC equipped with a thermal conductivity detector (TCD).

Received: January 28, 2006
Revised: June 1, 2006

Keywords: alkanes · heterogeneous catalysis · hydrocarbons · isomerization · nanocomposites

---

[1] H. Weyda, E. Köhler, *Catal. Today* **2003**, *81*, 51.
[2] A. Chica, A. Corma, *J. Catal.* **1999**, *187*, 167.
[3] Z. B. Wang, A. Kamo, T. Yonedo, T. Komatsu, T. Yashima, *Appl. Catal. A* **1997**, *159*, 119.
[4] E. Iglesia, D. G. Barton, S. L. Soled, S. Miseo, J. E. Baumgartner, W. E. Gates, G. A. Fuentes, G. D. Meitzner, *Stud. Surf. Sci. Catal.* **1996**, *101*, 533.
[5] J. F. Kriz, T. D. Pope, M. Stanciulescu, J. Monnier, *Ind. Eng. Chem. Res.* **1998**, *37*, 4560.
[6] K. J. Chao, H. C. Wu, L. J. Leu, *Appl. Catal. A* **1996**, *143*, 223.
[7] S. Calero, M. Schenk, D. Dubbeldam, T. L. M. Maesen, B. J. Smit, *J. Catal.* **2004**, *228*, 121.
[8] E. A. Blekkan, C. Pham-Huu, M. J. Ledous, J. Guille, *Ind. Eng. Chem. Res.* **1994**, *33*, 1657.
[9] E. Iglesia, S. L. Soled, G. Kramer, *J. Catal.* **1993**, *144*, 238.
[10] M. Hino, K. Arata, *J. Chem. Soc. Chem. Commun.* **1988**, *18*, 1259.
[11] J. G. Santiesteban, J. C. Vartuli, S. Han, R. D. Bastian, C. D. Chang, *J. Catal.* **1997**, *168*, 431.
[12] E. Blomsma, J. A. Martens, P. A. Jacobs, *J. Catal.* **1997**, *165*, 241.
[13] H. Hattori, T. Shishido, *Catal. Surv. Jpn.* **1997**, *1*, 205.
[14] J. G. Santiesteban, D. C. Calabro, W. S. Borghard, C. D. Chang, J. C. Vartuli, Y. P. Tsao, M. A. Natal-Santiago, R. D. Bastian, *J. Catal.* **1999**, *183*, 314.
[15] P. A. Sermon, G. C. Bond, *J. Chem. Soc. Faraday Trans. 1* **1980**, *76*, 889.
[16] J. Y. Ying, T. Sun, *J. Electroceram.* **1997**, *1*, 219.
[17] A. J. Zarur, J. Y. Ying, *Nature* **2000**, *403*, 65.
[18] W. Hua, Y. Xia, Y. Yue, Z. Gao, *J. Catal.* **2000**, *196*, 104.
[19] M. Scheithauer, R. E. Jentoft, B. C. Gates, H. Knözinger, *J. Catal.* **2000**, *191*, 271.
[20] W. Hua, J. Sommer, *Appl. Catal. A* **2002**, *232*, 129.
[21] S. T. Wong, T. Li, S. Cheng, J. F. Lee, C. Y. Mou, *J. Catal.* **2003**, *215*, 45.
[22] D.-L. Hoang, H. Berndt, H. Lieske, *Catal. Lett.* **1995**, *31*, 165.
[23] D. K. Hohnke, *Solid State Ionics* **1981**, *5*, 531.
[24] H. Uchida, H. Yoshikawa, H. Iwahawa, *Solid State Ionics* **1989**, *35*, 229.