Available online at www.sciencedirect.com

Catalysis Today 98 (2004) 601–605

www.elsevier.com/locate/cattod

Reforming of methane and coalbed methane over nanocomposite Ni/ZrO_2 catalyst

Qin-Hui Zhang, Yan Li, Bo-Qing Xu*

Innovative Catalysis Program, Key Laboratory of Organic Optoeletronics and Molecular Engineering,
Department of Chemistry, Tsinghua University, Beijing 100084, China

Abstract

Nanocomposite Ni/ZrO_2-AN catalyst consisting of comparably sized Ni metal and ZrO_2 nanoparticles is studied in comparison with zirconia- and alumina-supported Ni catalysts (Ni/ZrO_2-CP and commercial Ni/Al_2O_3-C) for steam reforming of methane (SRM) and for combined steam and CO_2 reforming of methane (CSCRM). The reactions are performed under atmospheric pressure with stoichiometric amounts of H_2O and CH_4 or ($H_2O + CO_2$) and CH_4 at 1073 K. Under a wide range of methane space velocity (gas hourly space velocity of methane $GHSV_{CH_4}$ = 12,000–96,000 ml/(h $g_{cat.}$), the nanocomposite Ni/ZrO_2-AN catalyst always shows higher activity and stability for both SRM and CSCRM reactions. The two supported Ni catalysts (Ni/ZrO_2-CP and Ni/Al_2O_3-C) exhibit fairly stable catalysis under low $GHSV_{CH_4}$ but they are easily deactivated under high $GHSV_{CH_4}$ and become completely inactive when they are reacted for ca.100 h at $GHSV_{CH_4}$ = 48,000 ml/(h $g_{cat.}$). The CSCRM reaction is carried out with different H_2O/CO_2 ratios in the reaction feed while keeping the molar ratio $(H_2O + CO_2)/CH_4 = 1.0$, the results prove that the nanocomposite Ni/ZrO_2-AN catalyst can be highly promising in enabling a catalytic technology for the production of syngas with flexible H_2/CO ratios (ca. H_2/CO = 1.0–3.0) to meet the requirements of various downstream chemical syntheses.

Keywords: Metal/oxide nanocomposite; Ni catalyst; Natural gas; Syngas; Coalbed methane; Steam reforming of methane

1. Introduction

One of the most attractive chemical approaches for the utilization of CO_2 and methane, which are the main components of some natural gas resources including coalbed gases, could be the catalytic CO_2 reforming of methane (CRM) to produce syngas (a mixture of H_2 and CO). CO_2 molecules in CRM function as a cheap and clean oxidant for methane molecules [1]. In some other natural resources, the CO_2/CH_4 molar ratio can be below the stoichiometry of the CRM reaction ($CO_2/CH_4 = 1.0$). A simple and convenient technological solution for the utilization of such resources is thus, to add water (steam) as a compensation for CO_2 since catalytic steam reforming of methane (SRM) produces the same product, which means a combined steam and CO_2 reforming of methane (CSCRM). Since the product H_2/CO ratio of the CRM reaction ($H_2/CO = 1.0$) is different from that of the SRM reaction ($H_2/CO = 3.0$), depending on the ratio of $H_2O/CO_2/CH_4$ in the reaction feed, the catalytic CSCRM technology can be applied to adjust the H_2/CO ratio in the product syngas to meet the requirements of downstream chemical synthesis.

Supported Ni catalysts have been extensively used in the industrial steam reforming of methane (SRM) process [2–4], however, deactivation by carbon deposition makes them unsuitable for CRM as well as for combined steam and CO_2 reforming of methane (CSCRM). Recent work in this laboratory exploring the use of oxide nanoparticles for catalysts has led to the discovery that the Ni catalyst ‘supported’ by small nanoparticles of ZrO_2 (7–25 nm) [5–8] or MgO (10–12 nm) [9] can be highly active and extremely stable for the CRM reaction with a stoichiometric mixture of methane and CO_2 ($CO_2/CH_4 = 1.0$) at 700–800 °C. In contrast to conventional oxide-supported metal catalyst having discrete metal nanocrystals (1–20 nm) supported on

---

* Corresponding author. Fax: +86 10 62792122.
E-mail address: bqxu@mail.tsinghua.edu.cn (B.-Q. Xu).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.09.015

oxide particles that are often one to several orders of magnitude larger than the metal nanocrystals, the stable Ni/ZrO_2 catalysts appear as nanocomposites of comparably sized Ni-metal (10–15 nm) and zirconia nanocrystals (7–25 nm). Ni catalysts supported on conventional oxide supports are not able to avoid coking and deactivate rapidly under the same conditions of the CRM reaction [10,11]. Attempts in reducing the particle sizes of support oxides to approach metal/oxide nanocomposites have also resulted in significant performance improvement of Au catalysts 'supported' on TiO_2 [12] and ZrO_2 [13].

In the present work, we first test our nanocomposite Ni/ZrO_2-AN catalyst [5,6,8] for the SRM reaction with a stoichiometric mixture of steam and methane in a wide range of feed space velocities. We prove that the nanocomposite catalyst is superior to Ni catalysts supported on bigger particles of conventional oxides (Ni/ZrO_2-CP and Ni/Al_2O_3) for the SRM reaction. We then attempt to extend the use of the nanocomposite catalyst Ni/ZrO_2-AN for CSCRM reactions to explore the feasibility of a catalytic technology for the production of syngas with flexible H_2/CO ratios.

2. Experimental

To prepare the nanocomposite Ni/ZrO_2-AN catalyst, a $ZrO(OH)_2$ alcogel was first obtained by completely washing a conventional $ZrO(OH)_2$ hydrogel with anhydrous ethanol. The alcogel was then dried at 270 °C in flowing-nitrogen under atmospheric pressure and was further calcined at 650 °C for 5 h. Impregnation with aqueous $Ni(NO_3)_2$ followed by drying at 110 °C and calcination in air at 650 °C gave the oxidized Ni/ZrO_2-AN catalyst. A similar procedure with conventional zirconia (ZrO_2-CP), obtained by calcination of the $ZrO(OH)_2$ hydrogel at 650 °C, resulted in an oxidized Ni/ZrO_2-CP catalyst. After reduction in hydrogen, the weight content of Ni in Ni/ZrO_2-AN and Ni/ZrO_2-CP catalysts was 12.1 and 12.9%, respectively, according to XRF measurement. Further details for the catalyst preparation can be found in refs. [5–8]. For the comparison purpose, a commercial SRM catalyst Z107 (13.0 wt.% Ni/Al_2O_3-C) was also adopted in the present study. The catalysts were used earlier for the CRM reaction and were characterized with a number of physicochemical methods [5–8].

The catalytic reaction was conducted with 100 mg catalyst at 800 °C in a vertical fixed-bed U-shape quartz reactor (10 mm i.d.) under atmospheric pressure as described previously [5–8]. A specially designed chamber, heated to 300 °C to ensure no condensation of the steam feed, was placed ahead of the reactor inlet and used to make the required mixture of CH_4 with steam or CO_2 or steam and CO_2. The steam and/or CO_2 were well mixed with methane in the chamber according to the reaction stoichiometry of SRM ($H_2O/CH_4 = 1.0$), CRM ($CO_2/CH_4 = 1.0$) or CSCRM ($(H_2O + CO_2)/CH_4 = 1.0$) reactions. The reaction temperature was measured and controlled by a thermal couple inserted into the catalyst bed. Before reaction, the catalyst was reduced in situ with flowing hydrogen (40 ml/min) at 700 °C for 3 h. The effluent gases from the reactor were removed from water by passing through a cold trap cooled to -16 °C with a salt-ice bath and then analyzed with an on-line GC (SQ206) equipped with a TCD. An 1.5 m carbon molecular sieve (80–100 mesh size) column was used for the separation of the reaction products.

Although it is difficult to avoid temperature and concentration gradient, special attention was paid to detect any temperature fluctuation in the catalyst bed. Our record showed that any temperature fluctuation during the reaction was within ± 1 °C from the temperature specified for the reaction. In a set of reaction tests with different pellet sizes (20–40, 40–60 and 140–160 meshes), the nanocomposite catalyst produced basically the same conversions for the reactants, suggesting that any diffusion effect on the catalytic reactions could reasonably be ignored.

3. Results and discussion

3.1. Morphological structure of the catalysts

The physicochemical properties of the reduced catalysts are presented in Table 1. The loaded nickel ions were found completely reducible in the temperature-programmed reduction (TPR) measurement [5–9], as indicated by the reducibility data in the table. It should be realized that the particle sizes of Ni-metal estimated from the Ni-dispersion

Table 1
Physicochemical properties of the catalysts reduced at 700 °C

Sample	Ni-load[a] (wt.%)	BET surface (m^2/g)	Ni-red.[b] (Ni %)	Oxide-phase[c] (%)	Ni-disp.[d] (%)	Ni-size[e] (nm)	Oxide-size[f] (nm)
Ni/ZrO_2-AN	12.1	38	95.2	M41/T59	9.4	10.6	18–25
Ni/ZrO_2-CP	12.9	18	98.5	M5/T95	5.8	17.8	40–200
Ni/Al_2O_3-C	13.0	23	92.0	Gamma	5.3	18.9	50–300

[a] Measured from X-ray fluorescence analysis.

[b] Reducibility of nickel measured from temperature-programmed reduction (TPR) with 5% H_2/Ar.

[c] M and T represent monoclinic and tetragonal phase, respectively.

[d] Dispersion of nickel obtained from temperature-programmed desorption (TPD) of hydrogen after the TPR measurement.

[e] Particle size of Ni-metal (d) calculated with the assumption $d = 1/\text{dispersion}$.

[f] Particle size of the oxide 'support' measured by TEM.

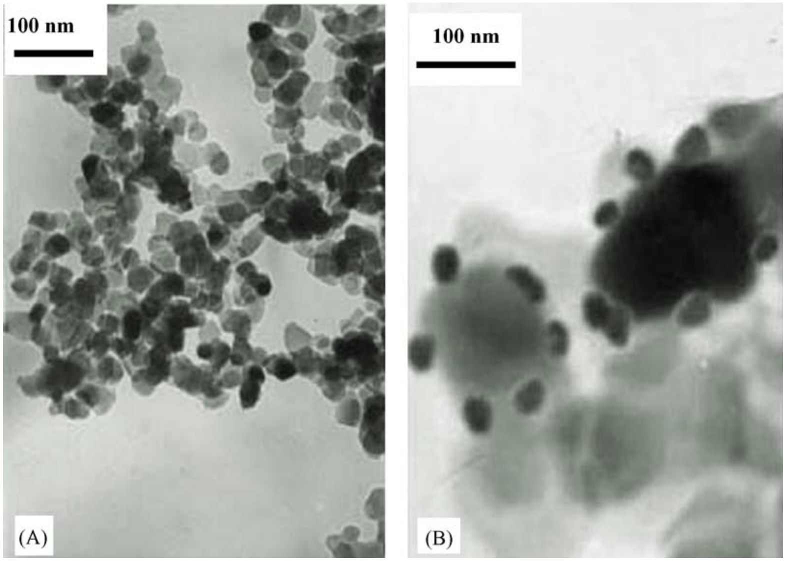

Fig. 1. Representative TEM micrograms of the reduced Ni/ZrO_2-AN (A) and Ni/ZrO_2-CP (B) catalysts.

data of the reduced Ni/ZrO_2-AN catalyst are comparable to the sizes of zirconia 'support' particles in the same samples, as shown in the last two columns of Table 1. The comparably sized Ni-metal and ZrO_2-AN nanoparticles are further evidenced in the TEM microgram of the reduced Ni/ZrO_2-AN sample (Fig. 1A), demonstrating the nanocomposite nature of this Ni/ZrO_2-AN catalyst.

The TEM micrograms of the reduced Ni/ZrO_2-AN and Ni/ZrO_2-CP samples are compared in Fig. 1. A significant difference exists apparently between the structure of Ni/ZrO_2-AN and Ni/ZrO_2-CP. The comparably sized nanocrystals of metallic Ni (10–15 nm) and ZrO_2 (18–25 nm) in the nanocomposite catalyst (Fig. 1A) is in clear contrast to the easily distinguishable metallic Ni nanocrystals (14–30 nm) supported on large particles of ZrO_2 up to 200 nm in the conventional zirconia-supported Ni catalyst (Ni/ZrO_2-CP in Fig. 1B). The commercial Ni/Al_2O_3-C catalyst showed similar TEM microgram to that of the Ni/ZrO_2-CP catalyst in Fig. 1B and can conventionally be classified as an alumina-supported Ni catalyst.

3.2. Steam reforming of methane (SRM)

Fig. 2 shows the catalytic activity and stability of the Ni/ZrO_2-AN, Ni/ZrO_2-CP and Ni/Al_2O_3-C catalysts for the SRM reaction at 800 °C under atmospheric pressure (0.1 MPa). The gas hourly space velocity of methane ($GHSV_{CH_4}$) was 12,000 ml/(h $g_{cat.}$) and the H_2O/CH_4 ratio in the reaction feed was 1.0. All the three catalysts exhibited reasonably high and stable catalytic activities during the reaction up to 240 h; the methane conversions are 87–88%, 81–84% and 76–83% over Ni/ZrO_2-AN, Ni/Al_2O_3-C and Ni/ZrO_2-CP, respectively. The thermodynamic equilibrium conversion of methane at 800 °C is 90%. Apparently, the nanocomposite Ni/ZrO_2-AN catalyst showed higher activity as well as stability than the commercial Z107 (Ni/Al_2O_3-C) and the conventional zirconia-supported Ni (Ni/ZrO_2-CP) catalysts.

To further compare the catalyst stability at methane conversion far below its thermodynamic equilibrium, all the catalysts were subjected to stepwise increasing of the space velocity of methane by eight-fold up to 96,000 ml/(h $g_{cat.}$); the results are shown in Fig. 3. The data for the first 150 h are obtained with $GHSV_{CH_4}$ = 12,000 ml/(h $g_{cat.}$) and they are similar to those appearing in Fig. 2. The stability of the nanocomposite Ni/ZrO_2-AN catalyst is characterized by its ability to maintain very stable methane conversions every time after changing the reaction GHSVs. Also, the conversion at every specific GHSV was kept constant after switching between several GHSVs during 400 h reaction time-on-stream. In contrast, when the $GHSV_{CH_4}$ was increased to 48,000 ml/(h $g_{cat.}$), the conventional Ni/ZrO_2-CP and also the commercial Ni/Al_2O_3-C catalysts were seen to deactivate very rapidly and irreversibly; the two catalysts became completely inactive after they were reacted for ca. 100 h under $GHSV_{CH_4}$ = 48,000 ml/(h $g_{cat.}$).

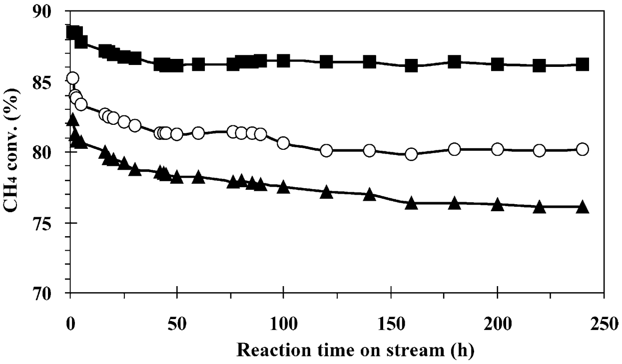

Fig. 2. Catalytic activity and stability of Ni/ZrO_2-AN (-■-), Ni/Al_2O_3-C (-○-) and Ni/ZrO_2-CP (-▲-) for atmospheric SRM reaction at 800 °C.

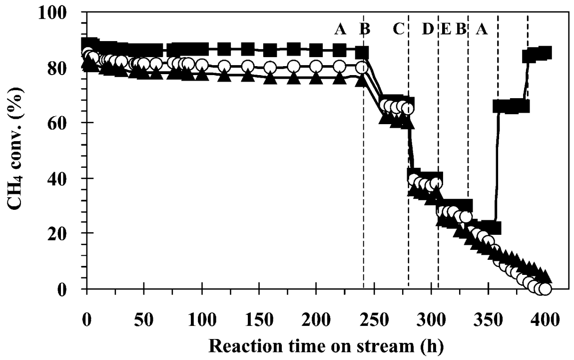

Fig. 3. Comparison of catalytic performance of Ni/ZrO_2-AN (-■-), Ni/Al_2O_3-C (-○-) and Ni/ZrO_2-CP (-▲-) for SRM reaction at 800 °C under different methane space velocities: $GHSV_{CH_4}$ = (A) 12,000; (B) 24,000; (C) 36,000, (D) 48,000 and (E) 96,000 ml/(h $g_{cat.}$).

In earlier work of this laboratory, the advantage of nanocomposite Ni/ZrO_2 catalysts including Ni/ZrO_2-AN over the conventional zirconia-supported Ni catalyst (Ni/ZrO_2-CP) for the CRM reaction was studied with more details; the existence of high percentage metal-oxide boundary or perimeter in the nanocomposite catalysts, which can be crucial in keeping good balance between the rates of CH_4 decomposition and of CO_2 dissociation, was believed to be responsible for the excellent catalytic stability of the nanocomposite catalysts [5–7]. Since both SRM and CRM reactions may follow similar reaction mechanisms on the same catalyst, it is reasonable to believe that the high percentage of metal-oxide boundary or perimeter can also be crucial for the advanced catalytic performance of the nanocomposite Ni/ZrO_2-AN catalyst in the SRM reaction.

It should be mentioned that the SRM reaction in the present study was operated under high feed space velocity with a rather low water-to-gas molar ratio ($H_2O/CH_4 = 1.0$). Most commercial SRM processes are conducted with much higher water-to-gas ratios ($H_2O/CH_4 = 2.0$–5.0) [2,3] to avoid catalyst deactivation by carbon deposition. With high H_2O/CH_4 molar ratios (>2.0), the following drawbacks exist: (a) the water-gas shift reaction ($H_2O + CO = H_2 + CO_2$) would be favorable, thus the resultant H_2/CO ratio in product syngas would be high, making the syngas not preferable for the downstream methanol and Fischer–Tropsch syntheses; and (b) a large amount of energy would have to be consumed in the production of high temperature steam, thus energy efficiency and economy of the process would be low. Therefore, the advantage of the nanocomposite Ni/ZrO_2-AN over the commercial Ni/Al_2O_3-C catalyst in the SRM reaction with the stoichiometric feed mixture ($H_2O/CH_4 = 1.0$) can be promising for application in the future SRM process.

3.3. Combined steam and CO_2 reforming of methane (CSCRM)

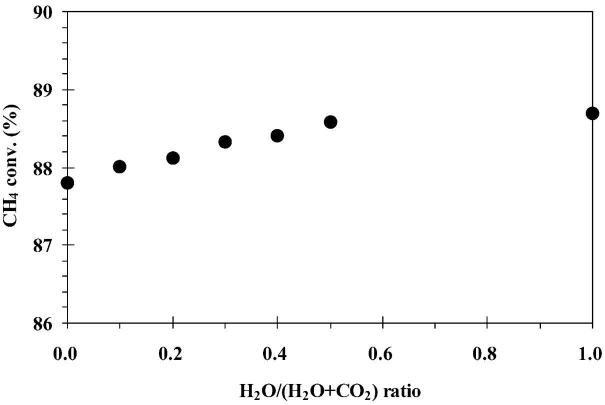

Fig. 4. Effect of the feed $H_2O/(H_2O + CO_2)$ ratio on methane conversion in the combined steam and CO_2 reforming of methane. Reaction temparature: 800 °C; $GHSV_{CH_4}$ = 12,000 ml/(h $g_{cat.}$); $(H_2O + CO_2)/CH_4 = 1.0$; reaction pressure: 0.1 MPa.

Due to its remarkable catalytic performance both in CRM [5–8] and the above SRM reactions, the nanocomposite Ni/ZrO_2-AN catalyst was further used for catalyzing the CSCRM reactions at 800 °C with the fixed ratio $(H_2O + CO_2)/CH_4 = 1.0$ in the reaction feed, the reaction feed space velocity was $GHSV_{CH_4}$ = 12,000 ml/(h $g_{cat.}$). Fig. 4 shows the effect of the feed $H_2O/(H_2O + CO_2)$ ratio on conversion of methane. It is seen that the CH_4 conversion changed only slightly in between 87.8% of a pure CRM and 88.8% of a pure SRM reaction; these conversion values are very close to the equilibrium methane conversions from the specified feed compositions. Whatever was the $H_2O/(H_2O + CO_2)$ ratio, the nanocomposite catalyst showed always-stable catalysis for the CSCRM reaction.

The effect of the feed $H_2O/(H_2O + CO_2)$ ratio on the composition (H_2/CO ratio) of the product syngas is shown in Fig. 5. Theoretically, with increasing concentration of steam or with reducing concentration of CO_2 in the reaction feed, the H_2/CO ratio in the product syngas could be changed in between 1.0 and 3.0. In practice, the H_2/CO ratio in the

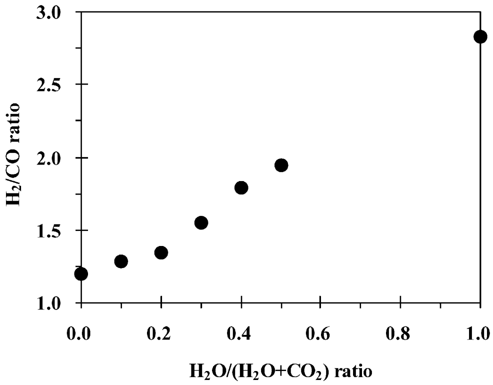

Fig. 5. Effect of the feed $H_2O/(H_2O + CO_2)$ ratio on the H_2/CO ratio of the product syngas in the combined steam and CO_2 reforming of methane. Reaction temparature: 800 °C; $GHSV_{CH_4}$ = 12,000 ml/(h $g_{cat.}$); $(H_2O + CO_2)/CH_4 = 1.0$; reaction pressure: 0.1 MPa.

produced syngas can be affected by possible side reactions, of which the water-gas shift reaction (WGS: $H_2O + CO = CO_2 + H_2$) and its reverse (RWGS: $CO_2 + H_2 = H_2O + CO$) are of the highest possibilities. Since the conversion of water/steam during the reaction was not quantified, accurate estimation of the side reactions on the product composition was not feasible in this work. However, the data of Fig. 5 reveal that with changing the feed $H_2O/(H_2O + CO_2)$ ratio, it is possible to enable a catalytic technology in methane reforming to produce syngas with the H_2/CO molar ratio being adjustable in between 1.2 and 2.9. The excellent catalytic performance of the nanocomposite Ni/ZrO_2-AN catalyst for the reforming of methane and coalbed methane in CRM, SRM and CSCRM reactions can be essential in enabling such flexible catalytic technology to meet the requirements of different downstream chemical synthesis.

4. Conclusions

This work proves that the nanocomposite Ni/ZrO_2-AN catalyst is highly active and extremely stable for both the steam reforming and the combined steam and CO_2 reforming of methane. In comparison with commercial Ni/Al_2O_3 catalyst, the high performance of the nanocomposite Ni/ZrO_2-AN catalyst allows the use of stoichiometric reactants for the reactions and can withstand much higher feed space velocity.

Acknowledgments

The authors wish to thank the financial support of this work from NSF China (Grant: 20125310) and National Basic Research Program of China (Grant: 2003CB615804).

References

[1] S.M. Stagg-Willimas, F.B. Noronha, G. Fendley, D.E. Resasco, J. Catal. 194 (2000) 240.
[2] J.P. Van Hook, Catal. Rev.-Sci. Eng. 21 (1980) 1.
[3] G. Ertl, H. Knoezinger, J. Weitkamp, Handbook of Heterogeneous Catalysis Part B: Catalytic Process, Wiley-VCH, 1997 p. 1819.
[4] I. Astrup, B.S. Clausan, J.R. Rostrup-Nielsen, Stud. Surf. Sci. Catal. 119 (1998) 5.
[5] B.-Q. Xu, J.-M. Wei, Y.-T. Yu, Y. Li, J.-L. Li, Q.-M. Zhu, J. Phys. Chem. B 107 (2003) 5203.
[6] B.-Q. Xu, J.-M. Wei, Y.-T. Yu, Y. Li, J.-L. Li, Q.-M. Zhu, Top. Catal. 22 (2003) 77.
[7] J.-M. Wei, B.-Q. Xu, K.-Q. Sun, J.-L. Li, Q.-M. Zhu, Chem. J. Chin. Univ. 23 (2002) 2106.
[8] Y. Li, Q. Ye, J.-M. Wei, B.-Q. Xu, Chin. J. Catal. 25 (2004) 326.
[9] J.-M. Wei, B.-Q. Xu, J.-L. Li, Z.-X. Cheng, Q.-M. Zhu, Catal. Today 68 (2001) 217.
[10] J.-M. Wei, B.-Q. Xu, Z.-X. Cheng, J.-L. Li, Q.-M. Zhu, Stud. Surf. Sci. Catal. 130 (2000) 3687.
[11] J.-M. Wei, B.-Q. Xu, J.-L. Li, Z.-X. Cheng, Y.-Q. Wang, Q.-M. Zhu, Chem. J. Chin. Univ. 23 (2002) 92.
[12] J.J. Pietron, R.M. Stroud, D.R. Rolison, Nano Lett. 2 (2002) 545.
[13] X. Zhang, H. Wang, B.-Q. Xu, Oral Presentation at 13th ICC, Paris, France, July 11–16, 2004, pp. O4–O19.