Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 93–95 (2004) 211–216

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Effects of preparation method and precipitator on the propylene epoxidation over Ag/TS-1 in the gas phase

Xinwen Guo*, Ruipu Wang, Xiangsheng Wang, Jingquan Hao

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China

---

Abstract

The effects of preparation method and precipitator on the catalytic properties of Ag/TS-1 in the gas-phase epoxidation of propylene were investigated in a fixed bed, quartz reactor. The Ag/TS-1 catalysts were characterized by XRD, UV–vis, FT-IR and TEM. The results show that the catalysts prepared by both deposition-precipitation (DP) and impregnation (IMP) methods exhibit catalytic activity and selectivity in the reaction. 0.48% propylene conversion with 57.88% selectivity to PO is obtained over Ag/TS-1 catalyst prepared by IMP method. However, DP method is optimum. Alkaline metal carbonate is a suitable precipitator. Using K_2CO_3 as the precipitator, the catalyst exhibits high activity and selectivity; using Cs_2CO_3 as the precipitator, the stability of the catalyst is improved; the propylene conversion and the selectivity to PO are 1.28% and 84.12%, 1.11% and 85.41% at 31 and 54 min, respectively. Besides the dispersion of silver particles, pH value of precipitators as well as the interaction between silver species and the support are the key factors for the gas-phase epoxidation of propylene.

Keywords: Propylene oxide; Propylene; Ag/TS-1; Oxygen; IMP; IE; Precipitator

---

1. Introduction

Propylene oxide (PO) is one of the most important chemical feedstocks for the production of polyether polyol polymers, such as polyurethane. Commercially, PO is manufactured either by chlorohydrin or the co-production (Halcon) routes, which has many disadvantages [1,2]. The invention of titanium silicalite (TS-1) [3,4] opened a new route for the selective oxidation of olefins using dilute H_2O_2 as an oxidant, but the cost of H_2O_2 is quite high. Ethylene epoxidation using oxygen as an oxidant has been commercialized for many years, but many critical issues related to propylene epoxidation have not yet been solved.

In analogy to ethylene epoxidation, researchers have paid more attention to the direct synthesis of PO by oxygen or air in the gas phase. This is mainly focused on supported [5–15] and non-supported catalysts [16–18]. For the supported catalysts reacted at ambient pressure, it mainly focused on Au [5–10] and Ag catalysts [11]. Using these two supported catalysts, researchers reported that only DP method could get selective catalyst; while using IMP [10,11] or sol–gel method [11], no PO was detected in the gas-phase epoxidation of propylene. It is noteworthy that all the catalysts were prepared by using NaOH or Na_2CO_3 as the precipitator, when DP method was adopted. Haruta and coworkers [8,9] investigated the effect of precipitator on the propylene epoxidation, and found that NaOH was the best depositing agent to prepare the catalysts. On a TS-1-supported Au catalyst, the propylene conversion and the PO selectivity were 0.71% and 93%, respectively [5]. When Au/Ti–MCM-48 was used as the catalyst, about 5% propylene conversion with higher than 90% PO selectivity was obtained [9]. However, de Oliveira et al. [11] reported that both NaOH and Na_2CO_3 could be used for the preparation of Ag/TiO_2. Over Ag/TiO_2 catalyst prepared with Na_2CO_3 as the precipitator, 0.4% propylene conversion with about 90% selectivity to PO was obtained. It is reported that on the modified Ag catalysts, potassium is usually used to improve the catalytic properties [19–22]. Some researchers explained that K^+ has stronger basicity that killed the acid sites of the catalyst surface, and thus increases the selectivity to PO. While Lambert and coworkers [23] reported that as a promoter, when K loading is 1.7%, the silver particle size distribution can be changed and achieved maximum selectivity and activity

---

* Corresponding author. Tel.: +86 411 88993908;
fax: +86 411 83689065.
E-mail address: guoxw@dlut.edu.cn (X. Guo).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.06.043

over K–Ag/$CaCO_3$ catalyst. The propylene conversion and the selectivity to PO are 6% and 15.2%, respectively.

In this paper, the effects of preparation method of Ag/TS-1 catalysts, such as DP, IMP and ion-exchange (IE) methods and precipitators, such as Na_2CO_3, K_2CO_3 and Cs_2CO_3, on the propylene epoxidation in the gas phase are investigated.

2. Experimental

2.1. Catalyst preparation

TS-1 was synthesized according to the literature [24]. Ag/TS-1 was prepared by DP [25], IMP and IE method. In a typical preparation for the Ag/TS-1 catalyst by DP method, 1.5 g TS-1 was mixed with 200 mL of 0.05 mol/L Na_2CO_3 solution, and then 100 mL 2.8 mmol/L $AgNO_3$ solution was added drop by drop into the mixture. When the addition was finished, the mixture was continuously stirred for 1 h. Solid sample was separated by filtration, washed with distilled water, dried at 90 °C overnight and then calcined at a rate of 1 °C/min from room temperature to 450 °C, and maintained at 450 °C for 5 h in air. For the isovolumetric IMP method, 1.5 g TS-1 was added to the suitable amount of $AgNO_3$ solution, stayed at the room temperature for 10 h, and then dried, calcined at the same conditions as those used in DP method. For the IE method, 1.5 g TS-1 was added to 100 mL $AgNO_3$ solution, stirred at 70 °C for 2 h. Solid sample was separated by filtration, washed with distilled water, and then dried, calcined at the same conditions as those used in DP method. The same process was repeated for three times.

2.2. Catalyst characterization

X-ray powder diffraction patterns were collected on a D/max-2400 Diffractometer using Cu Kα radiation. UV–vis characterization was conducted on a Jasco V-550 by using the diffuse reflectance technique in the range of 190–800 nm. IR measurements were recorded on a Nicolet 20DXB FT-IR spectrometer. The sample was ground with KBr and pressed into thin wafers. The transmission electron microscopy (TEM) was obtained on a JEX-2000EX, accelerated voltage 100 kV. ICP analysis was performed on ICP 1014.

2.3. Catalytic test

The catalytic activity tests in the gas-phase epoxidation of propylene were carried out in a vertical fixed-bed quartz reactor with an inner diameter of 8 mm. About 0.6 g Ag/TS-1 catalyst was placed in the middle of the reactor with quartz beads support at each end. The typical reaction conditions were as follows—150 °C, atmospheric pressure, space velocity: 4000 h^{-1}, $V_{C_3H_6} : V_{O_2} : V_{H_2} : V_{N_2} = 1:2:3:12$. Analysis of the products was carried out by GC–MS (HP 6890 GC/5973 MSD) and GC (GC7890F, FID detector with 50 m × 0.25 mm × 0.4 μm PEG20M capillary column and GCSRI 8610C, TCD detector with 2.5 m × 3 mm GDX-101 packed column). The conversion of propylene ($X_{C_3H_6}$) and the selectivity to PO (S_{PO}) were calculated by the carbon balances [17].

3. Results and discussion

3.1. Effect of preparation method

The catalytic properties of Ag/TS-1 catalysts prepared by different methods are shown in Table 1. It can be seen from Table 1 that the catalyst prepared by IE method hardly has any activity. Among the three methods, the Ag/TS-1 catalyst prepared by DP method is optimum, 0.78% propylene conversion with 94.85% PO selectivity is obtained. However, on the catalyst prepared by IMP method, 0.48% propylene conversion and 57.88% PO selectivity are obtained. At the same conditions, over Ag/Ti–MCM-41 catalyst prepared by IMP method, it exhibited 0.14% propylene conversion with 20.86% selectivity to PO. Therefore, it can be concluded that the catalysts prepared by both DP method and IMP method can get selective catalyst for the gas-phase epoxidation of propylene.

3.2. Effect of precipitator

Table 2 shows the effect of precipitator on the propylene epoxidation over Ag/TS-1 catalysts in the gas phase. It can be seen from Table 2 that precipitator has an important influence on the catalytic properties of the catalyst. The Ag/TS-1 samples prepared by using alkali metal carbonate as the

Table 1
Effect of preparation method of Ag/TS-1 on the gas-phase epoxidation of propylene

Preparation method	Actual Ag loading (%)	$X_{C_3H_6}$ (%)	Selectivity for products (%)			
			Aldehyde	PO	Propanal	Acetone
IMP	1.56	0.48	9.12	57.88	28.88	4.12
IE	1.35	0.03	41.39	0	0	58.61
DP	0.37	0.78	1.98	94.85	3.16	0

The Ag content in Ag/TS-1, 2 wt.%; Ag/TS-1 calcined at 450 °C in air, 0.6 g; 150 °C; atmospheric pressure; $V_{C_3H_6}:V_{O_2}:V_{H_2}:V_{N_2}$, 1:2:3:12; space velocity, 4000 h^{-1}; n_{Si}/n_{Ti}, 33; reaction time, 70 min.

Table 2
Effect of precipitator on the propylene epoxidation over Ag/TS-1 in the gas phase

Precipitator	$X_{C_3H_6}$ (%)	Selectivity for products (%)			
		Aldehyde	PO	Propanal	CO_2
Na_2CO_3	0.78	1.98	94.85	3.16	0
K_2CO_3	0.69	3.27	96.73	0	0
NaOH	1.29	10.60	0	19.73	58.15
KOH	1.29	8.69	0.64	9.47	78.08
NH_4OH	0.34	12.55	4.09	70.73	0
TPAOH	0	0	0	0	0

2 wt.% Ag/TS-1 calcined at 450 °C in air, 0.6 g; 150 °C; atmospheric pressure; space velocity, 4000 h^{-1}; $V_{C_3H_6}$:V_{O_2}:V_{H_2}:V_{N_2}, 1:2:3:12; the initial pH value for DP, 11.7; n_{Si}/n_{Ti} is 33; reaction time, 70 min.

precipitator are superior to those prepared by using alkali metal hydoxides as the precipitator. Although TPAOH and NaOH have similar basicity, the activities of Ag/TS-1 samples prepared by using these two precipitators are clearly different. Using TPAOH as the precipitator, the prepared Ag/TS-1 does not show any catalytic activity. Moreover, it is noteworthy that the existence of K^+ benefits the formation of PO both for the alkali metal carbonate and the alkali metal hydroxide precipitators, which is not in agreement with Haruta and coworkers' observation [7].

From the results it can be seen that the precipitators containing CO_3^{2-} are better than that containing OH^-. 0.07 mol/L $(NH_4)_2CO_3$ was then used to prepare the catalyst, which result is shown in Table 3. It can be seen that both the activity and the selectivity are quite poor. It is proposed that besides the anion ions, the basicity of the precipitator also has an important effect on the catalytic properties. Therefore different precipitator concentrations of Na_2CO_3 and K_2CO_3 were investigated, and found that 0.07 mol/L K_2CO_3 is optimum.

Using K_2CO_3 or $(NH_4)_2CO_3$ as the precipitator, Ag_2CO_3, KNO_3 and Ag_2CO_3, NH_4NO_3 are formed in the mixture, respectively. In order to further identify the effect of the pH value (or the cations), 0.07 mol/L K_2CO_3 + a little NH_4NO_3 (the same mole amount as that of $AgNO_3$ used in the preparation) and 0.07 mol/L $(NH_4)_2CO_3$ + a little KNO_3 (the same mole amount as that of $AgNO_3$ used in the preparation) were then used to prepare Ag/TS-1 catalysts. The results are shown in Table 3.

It can be seen from Table 3 that the difference of the catalytic properties with K_2CO_3 or $(NH_4)_2CO_3$ as the precipitator is not due to the existence of KNO_3 or NH_4NO_3, but would be the effect of cations or the pH value of the solution. Compared with that using K_2CO_3 as the precipitator, the stability of Ag/TS-1 prepared with Cs_2CO_3 has been improved, while the PO selectivity decreases slightly. It can be seen that the catalytic activity decreases gradually with time on stream. The results related to the catalyst deactivation and regeneration have been reported in literature [26].

3.3. Characterization of Ag/TS-1 prepared by different methods

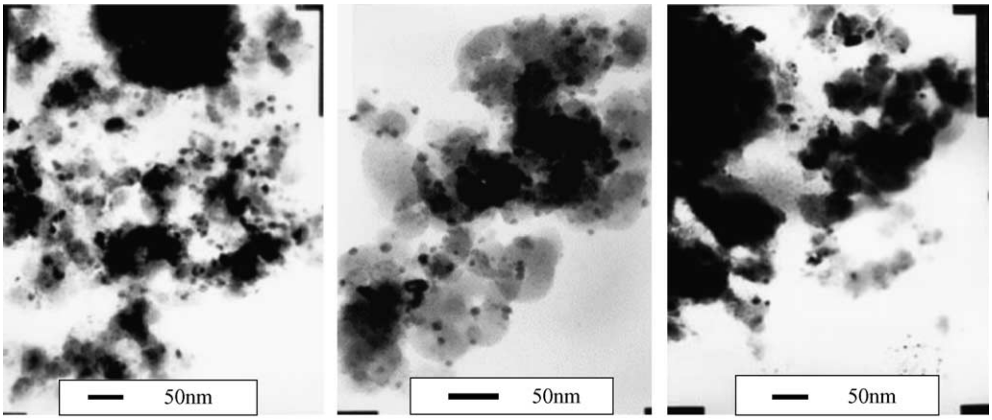
XRD patterns of Ag/TS-1 prepared by different methods do not show obvious difference. TEM photographs of Ag/TS-1 prepared by different methods are shown in Fig. 1. It can be seen that the silver particles are much uniform prepared by IMP method (Fig. 1(b)), while the catalyst prepared by IE method (Fig. 1(c)) shows an evident decrease in density and the silver particles are small and inhomogenous, which size are 1–2, 5–7 and 13–15 nm, respectively. The Ag particles prepared by IMP method are 1–3 nm smaller than that prepared by DP method, but their catalytic properties have an obvious difference.

During the preparation of Ag/TS-1 catalysts with IE, IMP and DP methods, different silver compounds were formed, which are $AgNO_3$ and Ag_2CO_3, respectively. When the catalysts were calcined at 450 °C in air, perhaps different

Table 3
Effect of precipitator on the gas-phase epoxidation of propylene over Ag/TS-1

Precipitator	*t* (min)	$X_{C_3H_6}$ (%)	Selectivity for products (%)			
			Aldehyde	PO	Propanal	CO_2
0.07 mol/L K_2CO_3	6	1.88	1.06	90.92	0	8.02
	24	0.77	0	90.22	0	9.78
	51	0.44	0	100	0	0
0.07 mol/L Cs_2CO_3	6	2.53	9.56	62.67	0	27.78
	31	1.28	5.17	84.12	0	10.71
	54	1.11	4.02	85.41	0	10.57
0.07 mol/L K_2CO_3 + a little NH_4NO_3	6	1.39	2.41	68.38	0	29.22
	30	1.29	1.84	86.99	1.57	9.60
	54	1.05	1.47	88.57	1.14	8.82
0.07 mol/L $(NH_4)_2CO_3$ + a little KNO_3	30	0.39	13.03	5.21	51.77	19.72
	53	0.30	7.82	5.15	58.41	14.06
	6	0.50	17.11	26.53	5.44	35.20
0.07 mol/L $(NH_4)_2CO_3$	27	0.29	8.88	5.46	54.81	17.92
	50	0.26	9.12	3.72	52.64	20.35

Notes are the same as in Table 2 except without maintaining the same initial pH value.



(a) DP (b) IMP (c) IE

Fig. 1. TEM photographs of Ag/TS-1 prepared by different methods.

structures, states and some different interaction between silver species and TS-1 support were formed.

Fig. 2 shows the UV–vis spectra of Ag/TS-1 prepared by different methods, respectively. Due to the absorbance of titanium species in the range of 190∼400 nm [27], it is difficult to identify the absorbance of silver species in this region. Therefore the absorbance of silver species is mainly studied at 400–800 nm. It can be seen from Fig. 2 that the absorbance between 400 and 800 nm has an obvious difference and is gradually shifted to high wavelength with DP, IMP and IE methods. Moreover, the absorbance of Ag/TS-1 prepared by IE method is lower than that of the other two, that is to say, due to the basic nature of TS-1, few amount of silver ions were exchanged on it. The ICP analysis showed that the actual Ag loading is only 0.37% (Table 1). This may be another reason for the low activity.

Fig. 3 exhibits the FT-IR spectra of Ag/TS-1 prepared by different methods. In FT-IR spectra, the peak centered at 960 cm^{-1} is ascribed to the framework titanium species and its intensity shows the relative amount of the species [27]. It can be seen from Fig. 3 that the intensity of the framework titanium decreases in the order of IE, DP and IMP, due to the silver species covering, which result is in agreement with that of ICP analysis and UV–vis spectra. Therefore, it can be concluded that besides the dispersion of silver particles, the interaction between silver species and TS-1 plays an important role in the gas-phase epoxidation of propylene.

3.4. Characterization of Ag/TS-1 prepared with different precipitators

The aim of using alkaline material is to deposit Ag^+ on TS-1 during the preparation of the catalyst. With various anions (CO_3^{2-} or OH^-) in the precipitators, different precipitates, Ag_2CO_3 or AgOH (usually existed as Ag_2O), would be formed on the support. Because these precipitates decompose via various routes during the following calcination in air, there would be difference in the interaction between silver species and TS-1 support. The difference may be the source of the different catalytic properties of Ag/TS-1 catalysts.

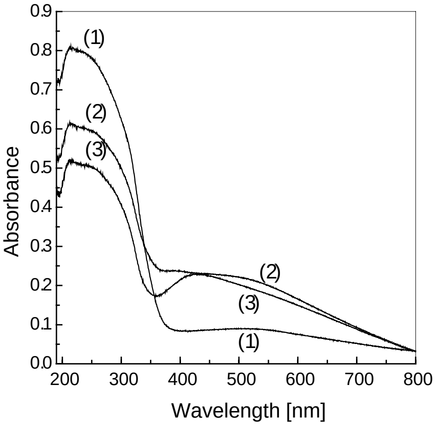


Fig. 2. UV–vis spectra of Ag/TS-1 prepared by different methods: (1) IE; (2) IMP; (3) DP.

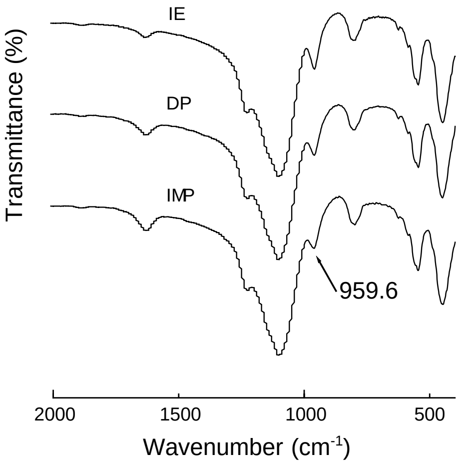


Fig. 3. FT-IR spectra of Ag/TS-1 prepared by different methods.

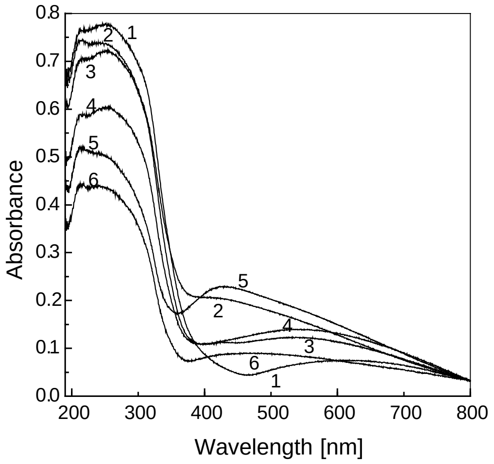


Fig. 4. UV–vis spectra of Ag/TS-1 prepared by different precipitators with the same pH value: (1) TPAOH; (2) K_2CO_3; (3) KOH; (4) NaOH; (5) Na_2CO_3; (6) NH_4OH.

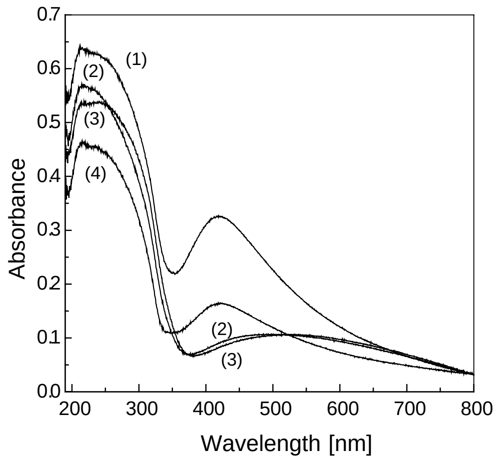


Fig. 5. UV–vis spectra of Ag/TS-1 prepared with different precipitators: (1) 0.07 M K_2CO_3; (2) 0.07 M $(NH_4)_2CO_3 + KNO_3$; (3) 0.07 M $(NH_4)_2CO_3$; (4) 0.07 M $K_2CO_3 + NH_4NO_3$.

Fig. 4 shows the UV–vis spectra of Ag/TS-1 prepared with different precipitators with the same pH value of the solution. It can be seen that there is a big difference among the spectra. Using Na_2CO_3 or K_2CO_3 as a reference, it can be seen that the absorbance of silver species on Ag/TS-1 prepared by using NH_4OH, NaOH, KOH or TPAOH as the precipitator is shifted to a higher wavelength in UV–vis spectra. When using K_2CO_3 as the precipitator, the absorbance of silver species has a little shift to high wavelength, compared with the Ag/TS-1 catalyst deposited by Na_2CO_3. This indicates that the interaction between silver species and the support is different. The ICP analysis indicates that the amount of K^+ or Na^+ is 1.23% and 0.22% in Ag/TS-1 catalysts, respectively, when using K_2CO_3 or Na_2CO_3 as the precipitator. When the catalyst was calcined at 450 °C in air, perhaps due to the existence of K^+ remained in the catalyst, K_2O was formed. The interaction between K_2O and silver species may decrease the transferring energy of electrons from silver surface, thus makes a shift of the wavelength and increases the catalytic activity. In addition, that the silver particle size of Ag/TS-1 prepared with K_2CO_3 is a little smaller than that prepared with Na_2CO_3 can increase the PO selectivity [26]. More basic nature of potassium than sodium may also be another reason for higher PO selectivity.

The UV–vis spectra of Ag/TS-1 prepared with K_2CO_3, $(NH_4)_2CO_3$ + a little KNO_3, $(NH_4)_2CO_3$, K_2CO_3 + a little NH_4NO_3 as the precipitators are shown in Fig. 5. It can be seen that the addition of KNO_3 or NH_4NO_3 to the solution does not affect the shape of UV–vis spectra. The silver species' absorbance of Ag/TS-1 prepared with $(NH_4)_2CO_3$ as the precipitator is shifted to a higher wavelength than that prepared with K_2CO_3 as the precipitator, which absorbance is higher than 500 nm. That is to say, although the precipitators contain the same anions, the silver species of the prepared Ag/TS-1 catalysts can be existed in different form. Combined with the above results, it can be concluded that the interaction between silver species and TS-1 support plays an important role in the reaction.

4. Conclusions

The gas-phase epoxidation of propylene was carried out in the presence of hydrogen and oxygen. The effects of preparation method and precipitators were investigated. Among the catalyst preparation method, not only DP method but also IMP methods can prepare selective catalyst. However, DP method is optimum. Alkaline metal carbonate is a suitable precipitator. Besides the dispersion of silver particles, cations of precipitators as well as the interaction between silver species and the support are the key factors for the gas-phase epoxidation of propylene.

Acknowledgements

The project was sponsored by the Ministry of Education for the Scientific Research (99150) and the National Key Basic Research Project of China (G 2000048009).

References

[1] R.O. Kirk, T.J. Dempsey, in: M. Grayson, D. Eckroth, H.F. Mark, D.F. Othmer, C.G. Overberger, G.T. Seaborg (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, vol. 19, Wiley, New York, 1982, p. 246.
[2] H.P. Wulff, F. Wattimenu, US Patent 4 021 454 (1977).
[3] M. Taramasso, G. Perego, B. Notari, US Patent 4 410 501 (1983).
[4] M. Taramasso, G. Manara, V. Fattore, B. Notari, US Patent 4 666 692 (1987).
[5] B.S. Uphade, S. Tsubota, T. Hayashi, M. Haruta, Chem. Lett. 12 (1998) 1277.
[6] B.S. Uphade, T. Akita, T. Nakamura, M. Haruta, J. Catal. 209 (2002) 331.

[7] B.S. Uphade, Y. Yamada, T. Akita, T. Nakamura, M. Haruta, Appl. Catal. A: Gen. 215 (2001) 137.
[8] B.S. Uphade, M. Okumura, N. Yamada, S. Tsubota, M. Haruta, Stud. Surf. Sci. Catal. 130 (2000) 833.
[9] B.S. Uphade, T. Akita, T. Nakamura, M. Haruta, J. Catal. 209 (2002) 331.
[10] M. Haruta, B.S. Uphade, S. Tsubota, A. Miyamoto, Res. Chem. Intermed. 24 (1998) 329.
[11] A.L. de Oliveira, A. Wolf, F. Schüth, Catal. Lett. 73 (2001) 157.
[12] F.W. Zemichael, A. Palermo, M.S. Tikhov, R.M. Lambert, Catal. Lett. 80 (2002) 93.
[13] G.J. Jin, G.Zh. Lu, X.H. Wang, Chin. J. Catal. 23 (2002) 405.
[14] R. Meiers, U. Dingerdissen, W.F. Hölderich, J. Catal. 176 (1998) 376.
[15] G. Jenzer, T. Mallat, M. Maciejewski, F. Eigenmann, A. Baiker, Appl. Catal. A 208 (2001) 125.
[16] G.Zh. Lu, X.B. Zuo, Catal. Lett. 58 (1999) 67.
[17] J.Q. Lu, M.F. Luo, H. Lei, C. Li, Appl. Catal. A 237 (2002) 11.
[18] M.F. Luo, J.Q. Lu, C. Li, Catal. Lett. 86 (2003) 43.
[19] B. Cooker, A.M. Gaffney, J.D. Jewson, W.H. Onimus, US 5 780 657 (1998).
[20] A.M. Gaffney, WO 9 845 280 (1998).
[21] A.P. Kahn, A.M. Gaffney, US 5 861 519 (1999).
[22] A.P. Kahn, WO 9 906 385 (1999).
[23] F.W. Zemichael, A. Palermo, M.S. Tikhov, R.M. Lambert, Catal. Lett. 80 (2002) 93.
[24] G. Li, X.W. Guo, X.Sh. Wang, Q. Zhao, X.H. Bao, X.W. Han, L.W. Lin, Appl. Catal. A: Gen. 185 (1999) 11.
[25] S. Tsubota, D.A.H. Cunningham, Y. Bando, M. Haruta, Stud. Surf. Sci. Catal. 91 (1995) 227.
[26] R.P. Wang, X.W. Guo, X.Sh. Wang, J.Q. Hao, Catal. Lett. 90 (2003) 57.
[27] G.N. Vayssilov, Catal. Rev. 20 (1997) 55.