Catalysis Letters Vol. 105, Nos. 1–2, November 2005 (© 2005)
DOI: 10.1007/s10562-005-8001-5

Study of Mn-based catalysts for oxidative dehydrogenation of cyclohexane to cyclohexene

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Received 19 April 2005; accepted 6 August 2005

The gas-phase oxidative dehydrogenation (ODH) of cyclohexane to cyclohexene in the presence of molecular oxygen has been studied over various Mn-based catalysts. It is found that LiCl/MnO_x/PC (Portland cement) catalyst exhibits the highest catalytic performance, and a 42.8% cyclohexane conversion, 58.8% cyclohexene selectivity and 25.2% cyclohexene yield can be achieved under 600 °C, 20,000 h^{-1} and $C_6H_{12}/O_2/N_2 = 14/7/79$. There are good correlations between the selectivities to cyclohexene and the electrical conductivities of Li doped Mn-based catalysts, from which it is deduced that the non-fully reduced oxygen species (O_2^-, O_2^{2-}, O^-) involved in a new phase of $LiMn_2O_4$ might be responsible for the high selectivity toward cyclohexene, whereas the Mn_2O_3 crystal phase results in the CO_x formation. The selectivity to cyclohexene increases with increasing molar ratio of Li to Mn in LiCl/MnO_x/PC.

KEY WORDS: cyclohexane; cyclohexene; oxidative dehydrogenation; Mn-based catalysts.

1. Introduction

Cyclohexane oxidation is currently performed in industry in homogeneous phase to produce cyclohexanone and cyclohexanol, which are to be further converted into adipic acid and cyclohexanone oxime in the production way to Nylons [1]. The gas-phase oxidative dehydrogenation (ODH) of cyclohexane to cyclohexene is suggested as the first step of alternative ways to finally produce cyclohexanone or adipic acid [2,3]. Nowadays, gas-phase ODH of cyclohexane to cyclohexene has attracted much attention [4–8] and a wide variety of catalysts have been reported, such as nickel oxide [4,5],vanadate [7] and heteropolycompounds (HPA) [8]. The selectivity to cyclohexene, however, is still very low and the yield is not high (≤15%) due to the easier consequent dehydrogenation of cyclohexene to benzene. So how to control the deep dehydrogenation reaction becomes a challenging topic for ODH of cyclohexane. Zhu *et al.* [9] showed that the addition of acetic acid to the ODH process can completely forbid the deep dehydrogenation of cyclohexane, but this high cyclohexene selectivity (~100%) was at the expense of its catalytic activity and only a 6.9% cyclohexane conversion was obtained. Therefore, seeking a catalyst with high activity and cyclohexene selectivity seems much essential for ODH of cyclohexane to cyclohexene.

Our previous work [10–12] revealed that various p-type semiconductor catalysts, such as $CaTiO_3$ and Ni–V–O catalysts exhibit high catalytic performance in ODH of lower alkanes. Ge *et al.* [12] found that in ODH of ethane the p-type semiconductor catalyst, LiCl/MnO_x/PC can give a high ethylene selectivity of 87.4% at an ethane conversion of 66.1%; the non-fully reduced oxygen species $O^{\delta-}$ (O_2^{2-}, O^-, O_2^-) in the catalyst was supposed to play an important role for its high selectivity to ethylene, while the synergistic effect between the Cl, Li and the PC components of LiCl/MnO_x/PC was responsible for its high low-temperature activity. Based on the distinctive oxidation ability of $O^{\delta-}$ [11], this mobile oxygen species is expected to be also effective in the partial dehydrogenation of cyclohexane to cyclohexene. In this paper, various Mn-based catalysts were tested in ODH of cyclohexane and a high cyclohexene yield (25.2%) was found over LiCl/MnO_x/PC catalyst. The relationship of the catalytic performances with the physicochemical properties of the catalysts was also discussed.

2. Experiments

2.1. Catalyst preparation

$MnCO_3$ was dried at 120 °C for 4 h, and then calcined at 600 °C for 3 h and 800 °C for 3 h to form $MnOx$. MnO_x/PC was prepared in this course: 90 wt% $MnCO_3$ and 10 wt% PC (Portland cement, mainly containing 64.0% CaO, 20.3% SiO_2, 5.8% Al_2O_3 and 4.9% Fe_2O_3, BET surface area of 5.1 m^2/g, produced in Dalian) were fully mixed by grinding, dried at 120 °C for 4 h, then calcined at 600 °C for 3 h and 800 °C for 3 h.

LiCl/MnO_x/PC, Li_2SO_4/MnO_x/PC and $CaCl_2$/MnO_x/PC were prepared by impregnation of $MnCO_3$/PC (particle size of 20–40 mesh) with a corresponding volume of LiCl, Li_2SO_4 or $CaCl_2$ solution at room temperature,

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respectively. The soaked samples were dried at 120 °C for 4 h, and calcined at 600 °C for 3 h and 800 °C for 3 h. In catalyst samples, the molar ratio of Li (or Ca) to Mn is 1/3 if not specially mentioned.

2.2. Catalyst characterization

The physicochemical properties of catalysts were dertermined by X-ray powder diffraction (XRD, D-MAX, Rigaku), N_2 adsorption (ASAP2000) and electrical conductivity measurement. The electrical conductivity was measured as following: 0.2 g of sample was compressed and placed between two platinum electrodes. The electrical resistances were measured with a fluke 8840A Multi-meter under different atmospheres and temperatures. The electrical conductivity σ ($s{\cdot}m^{-1}$) was then determined by the formula:

$$\sigma = L/(R \cdot A)$$

where R is the measured electrical resistance (Ω), A is the cross sectional area of the electrodes (m^2), L is the thickness of the sample (m).

2.3. Catalytic test

The reactions were carried out at atmospheric pressure with 0.2 g of catalyst (20–40 mesh) being placed in a fixed-bed quartz reactor (i.d. = 6 mm). Quartz grains (20–40 mesh) were employed to fill both sides of catalyst bed to minimize the homogeneous gas-phase reactions. The reactor was placed in an electrical furnace, and the reaction temperature was monitored using a thermocouple located in the reactor center. The reaction temperature was ranging from 500 to 600 °C at 20 °C intervals. Flow rates of O_2 and N_2 were controlled by mass flow controllers; cyclohexane was introduced with a syringe pump, vaporized and premixed with the above gases serially. The products were analyzed by two online Gas Chromatographs (Varian 3800), one used a 100 m PONA capillary column with a flame ionization detector (FID) as the detector, and the other used a 1.8 m HAYESEP C packed column that was connected serially with a 1.2 m MOLESIEVE 13X packed column, with a thermal conductivity detector (TCD) as the detector. The product selectivities (fractions of cyclohexane converted to different product molecules) were calculated on a carbon atom basis. For the variation of C_6H_{12}/O_2 molar ratio, the flow rate of O_2 was changing at a constant C_6H_{12} flow rate of 14 ml/min, and N_2 was used to balance the total flow rate of 100 ml/min; whereas for the variation of gas-hourly space velocity (GHSV), the catalyst mass was varied at a fixed total flow rate of 100 ml/min.

3. Results and discussion

The results of ODH of cyclohexane over various Mn-based catalysts are shown in table 1. The overall products are cyclohexene, benzene, carbon monoxide, carbon dioxide, water, and other cracking products (methane, ethylene, etc.); Oxygenates such as cyclohexanone, cyclohexanol and partially dehydrogenated cyclohexadiene are not observed. As shown in table 1, a blank test loaded with only quartz sand shows that the non-catalytic contribution for cyclohexane conversion at 600 °C is negligible. It is found over MnO_x that CO_x ($x = 1, 2$) especially CO_2 is the main product, while the selectivities to cyclohexene is 29.3% at 11.5% conversion of cyclohexane. The addition of PC, an adhesive, does not alter the catalytic performance of MnO_x though the specific BET surface area was increased from 1.7 m^2/g of MnO_x to 3.6 m^2/g of MnO_x/PC [12]. When salts ($CaCl_2$, Li_2SO_4 and LiCl) introduced into MnO_x/PC sample, the selectivities to cyclohexene are obviously enhanced. The introduction of $CaCl_2$ to MnO_x/PC slightly increases the cyclohexene selectivity from 28.4% to 33.8% and reduces the CO_x formation from 47.4% to 41.6%, whereas the introduction of Li_2SO_4 greatly improves the cyclohexene selectivity to 50.5% and decreases the CO_x formation to 24.7%. It should be noted that in the case of LiCl addition to MnO_x/PC, both the cyclohexene selectivity and the cyclohexane conversion greatly increase, reaching 64.3% and 30.7%, respectively; the CO_x formation is only 2.6%.

Figure 1 shows the variation in product selectivity, cyclohexane conversion and cyclohexene yield with the reaction temperature over LiCl/MnO_x/PC catalyst. The conversion of cyclohexane increases gradually as the increasing temperature. At 620 °C, the conversion of

Table 1
The results of ODH of cyclohexane over various Mn-based catalysts (600 °C, $C_6H_{12}/O_2/N_2 = 14/7/79$ ml/min, STP)

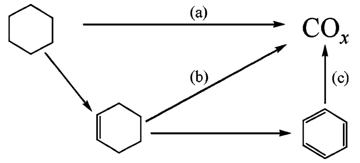
Catalyst	Conversion (%)	Product selectivity (%)						Yield C_6H_{10} (%)
		C_6H_{10}	C_6H_6	Alkanes[a]	Lower alkenes[b]	CO	CO_2	
Quartz sand	0.0	–	–	–	–	–	–	–
MnO_x	11.5	29.3	12.3	2.4	5.8	2.6	47.6	3.4
MnO_x/PC	12.2	28.4	14.3	2.8	7.1	3.3	44.1	3.5
$CaCl_2$/MnO_x/PC	13.2	33.8	12.3	2.1	10.2	1.8	39.8	4.5
Li_2SO_4/MnO_x/PC	11.2	50.5	12.0	6.8	6.0	4.1	20.6	5.7
LiCl/MnO_x/PC	30.7	64.3	23.1	7.9	2.1	0.8	1.8	19.7

[a] Methane, ethane, propane, and butane.

[b] Ethylene, propylene, butylenes and 1,3-butadiene.

cyclohexane reaches ~41%, about 57% selectivity and a maximum yield of cyclohexene ~23% can be obtained though the cyclohexene selectivity continually decreases with the temperature. Meantime, benzene selectivity increases to 24%, while the selectivities to lower alkenes and CO_x nearly unchanged. Above 620 °C, dehydrogenation products cyclohexene and benzene reduce abruptly, CO_x and lower alkene formations greatly increase. This is mainly due to the unavoidable gas-phase oxidative cracking (GOC) of cyclohexane at high temperature [13]. Considering that the cyclohexane conversion and cyclohexene yield are only 7.9% and 2.9%, respectively, in pure GOC process without the existence of catalyst at 620 °C (not shown here), the excellent performance observed over LiCl/MnO_x/PC is therefore an evidence of real catalysis phenomena. Compared with some previous studies [4–8,14–16] on ODH of cyclohexane, for example, over nickel contained structured egg-shell catalyst [14] the cyclohexene selectivity decreased gradually from 90% to 60% when cyclohexane conversion increased from 3% to 15% (the maximum cyclohexene yield is 9%, which is much lower than that of 12% over LiCl/MnO_x/PC within the same conversion range). Also over V–Mg–O and V–Nd–O catalysts [15], the cyclohexene selectivity reduced gradually from 75% to 30% when cyclohexane conversion increased from 2% to 20% (the maximum cyclohexene yield is less than 7%).

It is evident that the relationships plotted in figure 1 are characteristic of a sequential reaction mechanism where cyclohexane is dehydrogenated stepwise to benzene via cyclohexene as a semi-stable intermediate. Combustion occurs at all degrees of conversion and CO_x may be formed in three ways, where the CO_x would be produced from the oxidation of cyclohexane, cyclohexene and benzene in the way (a), (b) and (c), respectively. Just as illustrated in figure 1, the selective formation of CO_x is steady with the increasing temperature, and is somewhat independent of the formation of cyclohexene and benzene. This implies that the generation of CO_x occurs principally from the direct combustion of cyclohexane rather than from the oxidation of cyclohexene or benzene, which is consistent with the report on ODH of cyclohexane over MOVS catalyst [6]. Therefore, it is deduced that there are two main independent reactions existing over this Mn-based catalysts in ODH of cyclohexane, one is the dehydrogenation reaction of cyclohexane to cyclohexene or benzene, and the other is the oxidation of cyclohexane to CO_x.



It is well known that Mn_2O_3 is a typical catalyst for total oxidation of hydrocarbons to produce CO_2 [17]. Just as displayed by XRD patterns in figure 2, a typical phase of Mn_2O_3 is detected over the catalysts MnO_x/PC and $CaCl_2$/MnO_x/PC, while a new crystal phase of $LiMn_2O_4$ appears over LiCl/MnO_x/PC and Li_2SO_4/MnO_x/PC. According to the results of the catalytic performances (table 1) and the XRD patterns (figure 2), it can be concluded that the catalysts having Mn_2O_3 crystal phase always give a rather high selectivity to CO_x of 40%; and over the catalysts LiCl/MnO_x/PC and Li_2SO_4/MnO_x/PC containing a new $LiMn_2O_4$ phase, the CO_x formation is greatly decreased; especially for LiCl/MnO_x/PC, only a 2.6% selectivity to CO_x is produced (table 1).

Due to the formation of $LiMn_2O_4$ phase by Li doping of Mn_2O_3 crystal lattice, more oxygen vacancies (Vö) would be created, which, as electron donors, prefer to give electrons to gaseous oxygen molecules and form non-fully reduced oxygen species ($O^{\delta-}$) in the following way [12,18]:

$$\text{Vö} + 1/2\ O_2 \leftrightarrow O^{\delta-} + h^{\cdot}$$

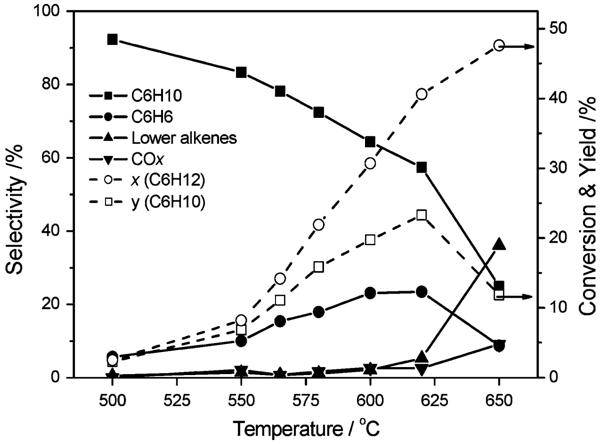


Figure 1. Variation in the product selectivity, cyclohexane conversion and cyclohexene yield with reaction temperature over LiCl/MnO_x/PC catalyst. (C_6H_{12}/O_2/N_2 = 14/7/79 ml/min, STP)

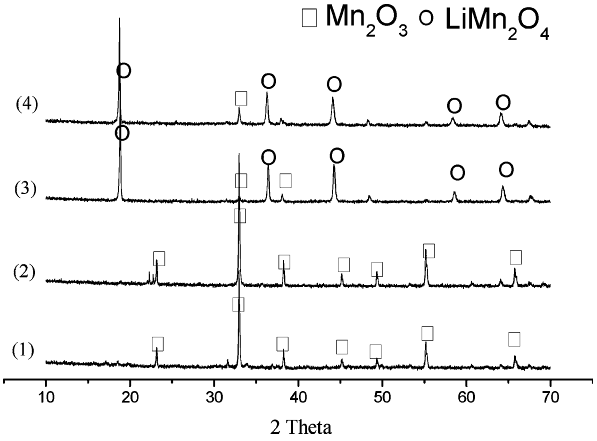


Figure 2. XRD patterns of various Mn-based catalysts. (1) MnO_x/PC; (2) $CaCl_2$/MnO_x/PC; (3) Li_2SO_4/MnO_x/PC; (4) LiCl/MnO_x/PC.

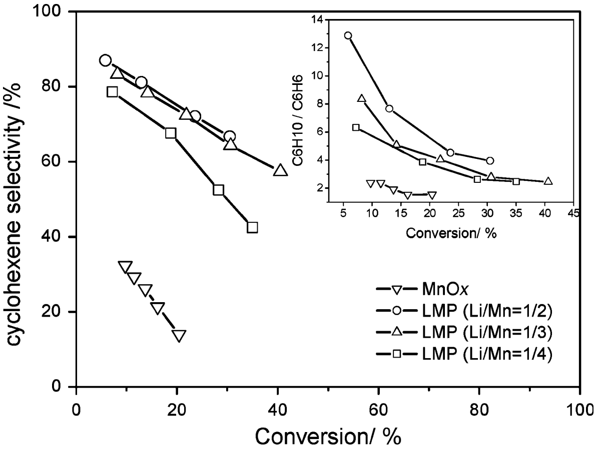


Figure 3. Variation in cyclohexene selectivity with increasing conversion of cyclohexane over MnO_x and LiCl/MnO_x/PC (LMP) with various Li/Mn molar ratios. Inset: the effect of cyclohexane conversion on the product C_6H_{10}/C_6H_6 ratio. (C_6H_{12}/ O_2/ N_2 = 14/7/79 ml/min, STP)

where $h^{\cdot}$ is the positive hole (or electron vacancy). Such $O^{\delta-}$ (O_2^-, O_2^{2-}, O^-) is thought to be the main factor of influencing the alkene selectivity in ODH of ethane and propane over the Mn-based catalysts at 500–600 °C [12, 19]. The electrical conductivities of various Mn-based catalysts were determined under oxidative atmosphere. The results are shown in table 2. Those listed samples were all proved to be p-type semiconductors. Sample MnO_x/PC has the lowest electrical conductivity while Li_2SO_4/MnO_x/PC possesses an electrical conductivity two times as high as that of $CaCl_2$/MnO_x/PC. The introduction of LiCl to MnO_x/PC greatly improves the electrical conductivity by an order of magnitude, and the value slightly increases with the increasing molar ratio of Li to Mn (Li/Mn) in LiCl/MnO_x/PC. Considering that the inclusion of halide ions in perovskite catalysts can promote the mobility of oxygen species by weakening the coulombic force between oxygen atoms and surrounding framework atoms [20,21], the presence of Cl in LiCl/MnO_x/PC (Cl content is 2.03 wt% [19]) must have the same effect and also enhances the mobility of $O^{\delta-}$, thus resulting in the increase of the electrical conductivity. This could be revealed by table 2 that the electrical conductivity for LiCl/MnO_x/PC is two times higher than that for Li_2SO_4/MnO_x/PC. According to tables 1 and 2, it is concluded that there are good correlations between the electrical conductivities of Mn-based catalysts and the selectivities to cyclohexene. The higher electrical conductivity, the higher selectivity to cyclohexene.

Figure 3 shows the variation in cyclohexene selectivity with increasing cyclohexane conversion over MnO_x and LiCl/MnO_x/PC catalysts. The molar ratio of Li/Mn in LiCl/MnO_x/PC plays an important role in the cyclohexene selectivity, which gradually decreases with the increasing conversion of cyclohexane. As the increase of Li/Mn ratio from 1/4 to 1/2, the higher cyclohexene selectivity at any given cyclohexane conversion is achieved. According to figure 3 and table 2, it can be known that the progressing introduction of LiCl to MnO_x/PC enhances the electrical conductivity, and therefore improves the selectivity to cyclohexene. Usually, cyclohexene is more reactive than cyclohexane and tends to further conversion to benzene in ODH of cyclohexane; however, over LiCl/MnO_x/PC catalyst cyclohexene other than benzene is more ready to be produced. Just as illustrated in the inset to figure 3, the higher Li/Mn ratio, the higher cyclohexene/Benzene ratio in the product. This implies that the non-fully reduced oxygen species $O^{\delta-}$ prefers to promote the partial dehydrogenation rather than the deep dehydrogenation of cyclohexane. This may attribute to the distinctive oxidation ability of $O^{\delta-}$ [11,18], whose potential energy might be more suitable for ODH of cyclohexane to cyclohexene.

In addition, the synergistic effect, existing in Cl, Li and PC components in LiCl/MnO_x/PC, makes great contributions to the activation of ethane molecules and therefore results in a high ethane conversion in ODH of ethane [12]. In ODE of cyclohexane, the much higher conversion observed over LiCl/MnO_x/PC may also attribute to this synergistic effect, in which the Cl, Li and

Table 2

The electrical conductivities of Mn-based catalysts under oxidative atmosphere (600 °C, O_2/N_2 = 20/180 ml/min, STP)

Sample	MnO_x/PC	$CaCl_2$/MnO_x/PC	Li_2SO_4/MnO_x/PC	LiCl/MnO_x/PC (Li/Mn = 1/4)	LiCl/MnO_x/PC (Li/Mn = 1/3)	LiCl/MnO_x/PC (Li/Mn = 1/2)
σ (S/m)	0.05	0.11	0.22	0.40	0.43	0.44

Table 3
Conversions and selectivities for ODH of cyclohexane over LiCl/MnO$_x$/PC under various reaction conditions

Entry	Temperature (°C)	GHSV (h^{-1})	C_6H_{12}/O_2	Conversion (%)	Product selectivity (%)						Yield C_6H_{10} (%)
					C_6H_{10}	C_6H_6	Alkanes	Lower alkenes	CO	CO_2	
1	600	30,000	∞	3.0	92.9	5.8	0.0	1.3	0.0	0.0	2.8
2	600	30,000	2.8	20.7	68.7	12.5	8.8	5.1	1.8	3.1	14.2
3	600	30,000	2.3	27.9	68.9	20.0	7.9	1.9	0.5	0.8	19.2
4	600	30,000	2.0	30.7	64.3	23.1	7.9	2.1	0.8	1.8	19.7
5	600	30,000	1.4	43.8	54.1	29.4	9.9	3.2	1.1	2.3	23.7
6	600	70,000	2.0	12.8	79.1	13.8	4.9	2.2	0.0	0.0	10.1
7	600	45,000	2.0	21.3	71.9	17.7	7.4	1.8	0.4	0.8	15.3
8	600	20,000	2.0	42.8	58.8	27.9	8.2	2.2	0.7	2.2	25.2
9	500	30,000	2.0	2.5	92.3	5.7	1.5	0.5	0.0	0.0	2.3
10	620	30,000	2.0	40.6	57.4	23.4	11.3	5.3	0.7	1.9	23.3
11	650	30,000	2.0	47.6	24.9	8.7	21.2	36.1	2.9	6.2	11.9

PC all play important roles in improving the catalytic performance. This effect may include the promotion by PC components for activating cyclohexane molecules, inhibiting the loss of Cl in the catalyst, and etc., the reasons of which will be further investigated.

Table 3 shows the variation in the conversion and selectivity in ODH of cyclohexane over LiCl/MnO$_x$/PC catalyst with various reaction conditions. It could be seen that: (1) as the molar ratio of C_6H_{12}/O_2 decreases from ∞ to 1.4 (table 3, entries 1–5) and the GHSV drops from 70,000 to 20,000 h^{-1} (entries 3 and 6–8), the cyclohexane conversion remarkably increases while cyclohexene selectivity gradually decreases; (2) the cyclohexane conversion and cyclohexene yield rise as the reaction temperature boosts from 500 to 620 °C (entries 3 and 9–10), above 650 °C (entry 11) cyclohexene yield declines. (3) a 42.8% cyclohexane conversion, 58.8% cyclohexene selectivity and 25.2% cyclohexene yield could be achieved (entry 8) at 600 °C, 20,000 h^{-1} and $C_6H_{12}/O_2/N_2 = 14/7/79$ (ml/min, STP).

4. Conclusions

LiCl/MnO$_x$/PC catalyst exhibits an excellent catalytic performance in ODH of cyclohexane to cyclohexene, which gives a 58.8% cyclohexene selectivity and 25.2% cyclohexene yield at a 42.8% cyclohexane conversion under 600 °C, 20,000 h^{-1} and $C_6H_{12}/O_2/N_2 = 14/7/79$. There are good correlations between the selectivities to cyclohexene and the electrical conductivities of Li doped Mn-based catalysts, from which it is deduced that the non-fully reduced oxygen species (O_2^-, O_2^{2-}, O^-) involved in a new phase of $LiMn_2O_4$ might be responsible for the high selectivity toward cyclohexene, whereas the Mn_2O_3 crystal phase results in the CO_x formation. The cyclohexene selectivity increases with increasing Li / Mn molar ratio in LiCl/MnO$_x$/PC from 1/4 to 1/2.

Acknowledgments

The authors thank SINOPEC for its financial support (X504012). And Qingjie Ge is grateful to the Ministry of Education (China) for the financial support.

References

[1] H. Nagahara, M. Ono, M. Konishi and Y Fukuoka, Appl. Surf. Sci 121/122 (1997) 448.
[2] U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R.S. da Cruz, M.C. Guerreiro, D. Mandelli, E.V. Spinacé and E.L Pires, Appl. Catal. A: Gen 211 (2001) 1.
[3] F. Patcas and D Honicke, Catal. Comm. 6 (2005) 23.
[4] F. Patcas, A. Akbas, F.C. Buciuman and D. Honicke, Chem. Technik 52(5/6) (2001) 224.
[5] F. Patcas, W. Krysmann, D. Honicke and F.C. Buciuman, Catal. Today 69 (2001) 379.
[6] E.C. Alyea and M.A. Keane, J. Catal. 164 (1996) 28.
[7] M.C. Kung and H.H. Kung, J. Catal. 128 (1991) 287.
[8] S. Hocine, C. Rabia, M.M. Bettahar and M. Fournier, Studies Surf. Sci. Catal. 130 (2000) 1895.
[9] Y.J. Zhu, J. Li, X.G. Yang and Y. Wu, Chem. Lett. 33 (2004) 822.
[10] T. Chen, Ph.D. Thesis, Dalian Institute of Chemistry Physics, Chinese (1997).
[11] B. Zhaorigetu, W.Z. Li, H.Y. Xu and R. Kieffer, Catal. Lett. 94 (2004) 125.
[12] Q.J. Ge, B. Zhaorigetu, C.Y. Yu, W.Z. Li and H.Y. Xu, Catal. Lett. 68 (2000) 59.
[13] X.B. Liu, W.Z. Li, H.Y. Xu and Y.X. Chen, Fuel Process. Technol. 86 (2004) 151.
[14] W. Krysmann, D. Honicke and F. Patcas, DE Patent 19852150.
[15] H.H. Kung, Adv. Catal. 40 (1994) 1.
[16] M. Panizza, C. Resini, G. Busca, E. Fernandez Lopez and V. Sanchez Escribano, Catal. Lett. 89 (2003) 199.
[17] M. Baldi, V. Sanchez Escribano, J.M. Gallardo Amores, J.M. Milella and G. Busca, Appl. Catal. B: Environ. 17 (1998) L175.
[18] A. Bielanski and J. Haber, Catal. Rev. Sci. Eng. 19 (1979) 1.
[19] Q.J. Ge, W.Z. Li, C.Y. Yu and H.Y. Xu, Chin. J. Chem. 19 (2001) 64.
[20] H.X. Dai, C.F. Ng and C.T. Au, J. Catal. 189 (2000) 52.
[21] H.X. Dai, C.F. Ng and C.T. Au, J. Catal. 193 (2000) 65.