Catalytic partial oxidation of *n*-heptane for hydrogen production

Ran Ran[a], Guoxing Xiong[a,*], Shishan Sheng[a], Weishen Yang[a], Norbert Stroh[b], and Herwig Brunner[b]

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, China*
[b] *Fraunhofer Institute for Interfacial Engineering and Biotechnology, Nobelstrasse 12, D-70569 Stuttgart, Germany*

Received 24 September 2002; accepted 6 March 2003

Partial oxidation of *n*-heptane (POH) for hydrogen generation was studied over several catalysts between 700 and 850 °C. Modified Ni-based/γ-Al_2O_3 catalyst exhibited not only good catalytic activity but also good carbon deposition resistance ability. Under the modified reaction conditions, 100% *n*-heptane conversion and 93% hydrogen selectivity can be obtained.

KEY WORDS: partial oxidation; *n*-heptane; Ni-based catalyst; hydrogen production; carbon deposition.

1. Introduction

Nowadays, there is considerable interest in hydrogen fuel cell technology for stationary power supply and transportation. The hydrogen fuel cell is favored for its high fuel-to-electricity conversion efficiency (40–60%+) and environmental compatibility [1]. Liquid fuels are preferred as hydrogen sources for on-board mobile application, and gasoline is favored not only for the higher energy density and H/C ratio compared with other liquid fuels but also for its commercial availability. Many efforts have been made to apply steam reforming of gasoline for hydrogen production [2–5], but very few via partial oxidation (POX) processes. Partial oxidation of octane and surrogate fuel to syngas has been reported recently [6], where the processes were carried out at 1100 °C with an Rh (7 wt%) catalyst to suppress the deactivation caused by carbon deposition and sulfide. Although only a few reports have referred to catalytic POX of gasoline for hydrogen generation, there are several obvious advantages of such a procedure: (1) it is more favorable for a fast response system owing to the short residence time with high product selectivity and (2) its exothermic nature [$C_7H_{16} + 3.5O_2 = 7CO + 8H_2$, $\Delta H_{298\,K} = -549.4$ kJ/mol] could greatly simplify the reactor system as compared with the strong endothermic process of steam reforming [$C_7H_{16} + 7H_2O = 7CO + 15H_2$, $\Delta H_{298\,K} = 1451.4$ kJ/mol]. Moreover, the products of such a process could be used directly for molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC), since both CO and H_2 can be electrochemically oxidized at the anodes. Nevertheless, since the dissociative adsorption of higher hydrocarbons is much faster than that of methane [7], the rate of carbon accumulation on the surface would be expected to be faster. This could lead to serious coke formation. Hence a stable and active catalyst for the realization of such a process seems to be the key issue.

Ni-based catalysts are now frequently employed during the steam reforming of hydrocarbons to syngas in the chemical industry [8]. Further, Ni-based catalysts are also the preferred catalysts for the partial oxidation of natural gas or methane (POM) to syngas [9]. In our previous work, it was demonstrated that the Ni-based catalysts have good activity in the POX of ethane, propane, and their mixtures to syngas [10–12]. Here we report a study of the partial oxidation of *n*-heptane (as a typical component of gasoline) (POH) to $CO + H_2$ over supported Ni-based and lower-loading noble metal catalysts at 700–900 °C. Good catalytic activity of the Ni-based catalysts was found under the conditions of 800–900 °C, GHSV of 3.8×10^4 l/kg/h and O/C ratio of 1.08. Good carbon deposition resistance ability of the modified Ni-based/γ-Al_2O_3 catalyst was also established.

2. Experimental

The catalysts used in the present study were prepared by the following impregnation method. The NiLiLa/γ-Al_2O_3 catalysts were prepared as follows: first, commercially supplied supports were impregnated with a mixed solution of $LiNO_3$ and $La(NO_3)_3$, calcined in air at 550 °C for 1 h, and then impregnated with a stoichiometric amount of $Ni(NO_3)_2$ for 24 h, dried at 120 °C for 12 h and calcined in air at 850 °C for 4 h. The preparation procedures for supported Ni and noble metal catalysts were similar to the second step of the above preparation procedure. $RhCl_3$ and $PdCl_2$ solutions were used for Rh/γ-Al_2O_3 and Pd/γ-Al_2O_3 catalyst, respectively. Chemicals used in the preparations were of AR grade.

The active metal loading and the specific surface areas of catalysts are as follows: Ni loading of 9 wt% for

---

[*] To whom correspondence should be addressed.
E-mail: gxxiong@dicp.ac.cn

1011-372X/03/0500-0055/0

NiLiLa/γ-Al_2O_3 (surface area 93.1 m^2/g), 13 wt% for Ni/γ-Al_2O_3 (surface area 101.2 m^2/g), Ni/MgO (surface area 19.7 m^2/g) and Ni/SiO_2 (surface area 147.5 m^2/g). The noble metal loading of Rh/γ-Al_2O_3 and Pd/γ-Al_2O_3 was 1 wt%.

Catalytic performances were investigated in a quartz micro-reactor with an internal diameter of 4 mm and at atmospheric pressure. Amounts of 50 or 100 mg of catalyst were employed during the catalytic tests. A thermocouple was placed at the exit of the catalyst bed to control and indicate the reaction temperatures. The effluents of the reaction were analyzed using an on-line HP4890 gas chromatograph with a thermal conductivity detector. Standard gases were used to calibrate the concentrations of product gases. The purity of *n*-heptane was >98.5% and the impurities were alkanes with different carbon numbers. *n*-Heptane was premixed with oxygen and helium (diluted gas) before reaching the reactor, the ratio of helium to *n*-heptane being about 5.8 : 1.

Surface areas of the catalysts were obtained from the nitrogen adsorption and desorption isotherm at 77 K using a Brunauer–Emmet–Teller (BET) surface analyzer (Coulter 100CX, USA).

X-ray diffraction analysis of the catalysts was carried out with a Riguku D/Max-RB X-ray diffractometer using a copper target at 40 kV and 100 mA and a scanning speed of 10°/min at room temperature. The different phases were identified using the JCPDS Powder Diffraction Files [13].

The temperature-programmed reduction (TPR) experiment was performed as follows. The catalysts were placed in the quartz reactor, which was inserted into an electronically controlled furnace. The oven was heated at a rate of 10 °C/min from 50 to 1050 °C, while a 5% H_2–Ar mixture gas was swept over the catalyst at a constant flow-rate of 30 ml/min. The hydrogen consumption was determined by an *in situ* thermal conductivity detector interfaced with a computer data acquisition system.

X-ray photoelectron spectroscopy was performed at room temperature on a VG ESCALAB Mk II spectrometer. The instrument typically operated at pressures below 1.33×10^{-7} Pa with monochromatized Al exciting radiation. The relative atomic ratio of the surface of catalyst was calculated according to the intensities of the spectral lines.

3. Results and discussion

A series of Ni-based catalysts on different supports were prepared first following the above-mentioned preparation procedures. The X-ray diffraction patterns of the catalysts are shown in figure 1. No characteristic diffraction peaks of NiO phases appeared in the patterns of Ni/MgO and Ni/γ-Al_2O_3 calcined at 850 °C. The results imply very small NiO crystallite sizes or a strong interaction between Ni and supports. However, in the pattern of Ni/SiO_2, the relative I/I_0 values and the peaks appearing at 2θ of about 37, 43, 63, 76 and 80° for (111), (200), (220), (311) and (222) faces, respectively, imply the existence of NiO crystals [13].

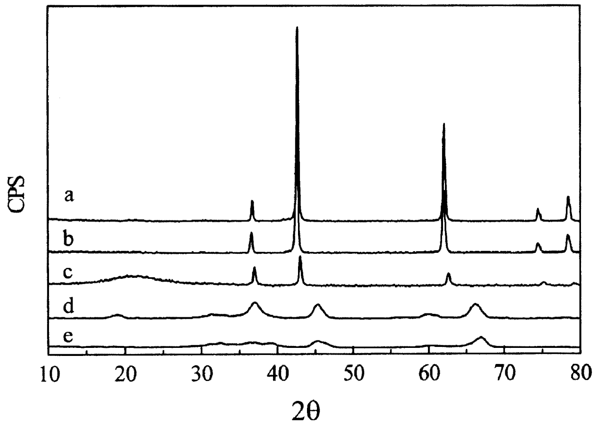

Figure 1. X-ray diffraction patterns of the catalysts and supports calcined at 850 °C. (a) MgO; (b) Ni/MgO; (c) Ni/SiO; (d) Ni/γ-Al_2O_3; (e) γ-Al_2O_3.

The reducibility of the catalyst was investigated by means of TPR. The results are shown in figure 2. For the catalysts which were calcined at 850 °C for 4 h, Ni/γ-Al_2O_3 and NiLiLa/γ-Al_2O_3 both give a sharp reduction peak at around 900 °C whereas Ni/SiO_2 exhibits a wide reduction peak at about 550 °C. At all the investigated temperatures (50–1030 °C), no obvious reduction peak appears for the Ni/MgO catalyst. Although the TPR result for Ni/MgO corresponds to that reported by Xu *et al.* [14] and Hu and Ruckenstein [15], we performed another TPR for Ni/MgO which had been calcined at only 550 °C for 4 h, for further investigation of the reducibility of the catalyst. A lower calcination temperature usually leads to lower interaction between the active metal and the support

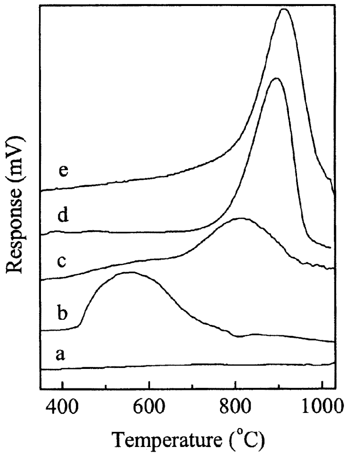

Figure 2. TPR profiles of different nickel-based catalysts. (a) Ni/MgO calcined at 850 °C; (b) Ni/SiO_2 calcined at 850 °C; (c) Ni/MgO calcined at 550 °C; (d) Ni/γ-Al_2O_3, 850 °C; (e) NiLiLa/γ-Al_2O_3, 850 °C.

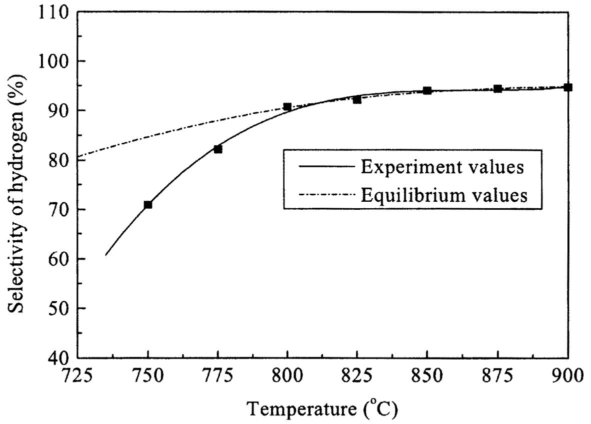

Figure 3. Influence of temperature on H_2 selectivity over Ni/γ-Al_2O_3 with O/C = 1.08, GHSV = 3.8×10^4 l/kg/h, and helium/*n*-heptane = 5.8.

[14,16,17]. Two H_2-TPR reduction peaks are observed for the 550 °C-calcined Ni/MgO, a larger peak at around 810 °C and a smaller at around 550 °C. The TPR results imply that stronger interactions occurred between nickel oxide with alumina and magnesium oxide. It has been reported that a solid solution of NiO–MgO [14,18,19] or a spinel structure $NiAl_2O_4$ [16] could form during calcination at certain temperature. The results of TPR and XRD imply a good interaction between Ni and the support. As a result, NiO phase could not be detected in the XRD patterns. It is believed that a suitable interaction between active components and support is helpful for keeping the catalyst stable during the reactions [20–22].

The POH performance was investigated first with the 13 wt% Ni-based catalysts; 100% conversion of oxygen was obtained in all of the reactions mentioned below. When the operating temperatures were higher than 800 °C, 100% *n*-heptane conversion to CO_x (the sum of $CO + CO_2$) + CH_4 was also obtained.

The effects of temperature (750–900 °C) on the reactions over Ni/γ-Al_2O_3 are shown in figures 3 and 4. The reactions were carried out at a space velocity of 3.8×10^4 l/kg/h, an O/C molar ratio of 1.08 and a ratio of helium to *n*-heptane of 5.8. The figures show increasing selectivity of CO and H_2 and decreasing selectivity of CO_2 and CH_4 with increase in temperature. An equilibrium result for the hydrogen selectivity is also shown in figure 3 as the dash-dotted line calculated via the HSC software package (Outokumpu Research Oy, 1991) by the GIBBS program using the so-called Gibbs Energy Minimization Method [23]. The hydrogen selectivity increased with increase in temperature and reached the equilibrium values when the temperature was higher than 800 °C. However, the experimental values were much lower than the equilibrium values below 800 °C. Moreover, C_2^+ and rapid deactivation were observed when the temperature was lower than 750 °C, and only CO, CO_2, CH_4 and H_2 could be detected above 750 °C. The deviation between the equilibrium values and experimental values in figure 3 is assumed to be due to the lower catalytic activity at lower operating temperatures. Additionally, partial active sites would be covered since coke is favored at lower temperatures. However, this aspect will be studied in detail in our further investigations.

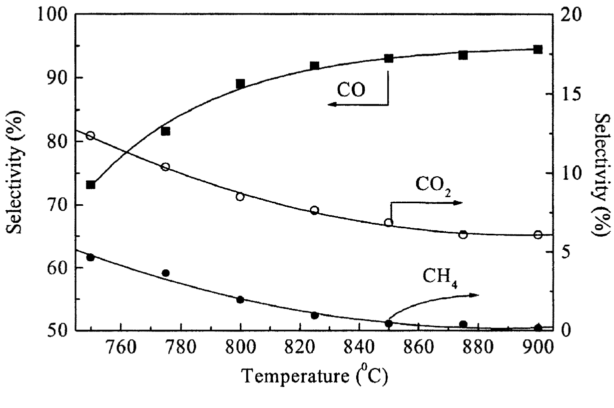

Figure 4. Relationship between reaction temperature and the selectivity of the products over Ni/γ-Al_2O_3 catalysts with O/C = 1.08, helium/*n*-heptane = 5.8, GHSV = 3.8×10^4 l/kg/h.

The effects of support, catalyst modification, and active metal element on the POH performance were then investigated. Table 1 shows the different hydrogen selectivities over different catalysts at 800 and 850 °C. Higher hydrogen selectivity was obtained over Ni/MgO, Ni/γ-Al_2O_3, NiLiLa/γ-Al_2O_3 and Rh/γ-Al_2O_3 and much lower selectivity over Ni/SiO_2 and Pd/γ-Al_2O_3. Further, rapid deactivation was found during the POH reaction over Ni/SiO_2 catalyst. Ni-based/γ-Al_2O_3 catalysts exhibited very similar hydrogen selectivity to that of Rh/γ-Al_2O_3 whereas the selectivity of hydrogen over Ni/MgO catalyst was slightly lower. It was identified that γ-Al_2O_3 and MgO are superior to SiO_2 as the support for POH, and Rh and Ni seem to be the preferred active metal components, as expected.

The differences in hydrogen selectivity of 13 wt% Ni/support catalysts are believed to be related to the interaction between the active component and the support. At least two advantages of the interaction between active metal with support can be identified: increased dispersion of metal particles and decreased amounts of Ni^0 particles on the catalyst surface. These two advantages could not only improve the ability of sintering resistance but also decrease the possibility of carbon deposition [19]. In contrast, Ni^{2+} could be reduced easily to Ni^0 over SiO_2 and Ni^0 could then segregate into large particles, which is more favorable for carbon deposition. As a result, rapidly deactivation could then be observed [19]. The reason for the lower activity of 1 wt% Pd/γ-Al_2O_3 was assumed to be the lower efficiency of the active component than that of 1 wt% Rh/γ-Al_2O_3, which needs further identification, but a higher loading of Pd is not economically attractive.

Table 1

H_2 selectivity (%) comparison of different catalysts for POH to syngas under reaction conditions of O/C = 1.08, GHSV = 3.8×10^4 l/kg/h

Temperature (°C)	13 wt% Ni/MgO	13 wt% Ni/SiO_2	13 wt% $Ni/\gamma\text{-}Al_2O_3$	9 wt% $NiLiLa/\gamma\text{-}Al_2O_3$	1 wt% $Rh/\gamma\text{-}Al_2O_3$	1 wt% $Pd/\gamma\text{-}Al_2O_3$
850	93.6	—	94.5	94.3	94.5	69.7
800	87.9	76.8[a]	90.0	90.6	91.0	—

[a] This value was recorded after 1 h of reaction whereas all the others were recorded when the reaction became stable.

The carbon deposition resistance ability of catalysts is very important for the POH process because a hydrocarbon with a higher C/H ratio favors carbon deposition on the surface of the catalyst [7]. The carbon deposition resistance capability of different catalysts was investigated further with a lower O/C ratio. The results are shown in figure 5. During the reaction, $Ni/\gamma\text{-}Al_2O_3$ catalyst lost its activity rapidly with decreasing hydrogen selectivity from 83 to 30% in only 4 h. After reaction, carbon black was found on the catalyst surface and the wall of the quartz reactor. However, Ni/MgO and $NiLiLa/\gamma\text{-}Al_2O_3$ exhibited much better stability. The results demonstrate that the deactivation of the POH reaction is more serious than that of the POM processes, since good stability of $Ni/\gamma\text{-}Al_2O_3$ has also been found during the POM reaction at lower O/C ratios [11,22,24].

It is believed that the existence of Lewis acid sites on the catalyst surface is favored over the cracking of C–C bonds and leads readily to carbon deposition [25,26] while the basic sites on the catalyst surface could prevent carbon formation. With respect to the nature of $\gamma\text{-}Al_2O_3$ and MgO, it seems that the acidic and basic properties of the supports are most likely responsible for the different stabilities of $Ni/\gamma\text{-}Al_2O_3$ and Ni/MgO catalysts. As it has been proved that the addition of Li_2O and La_2O_3 could greatly improve the carbon deposition resistance ability in our previous studies [24,27], good stability of $NiLiLa/\gamma\text{-}Al_2O_3$ is expected if the deactivation of the catalyst is caused by coke formation.

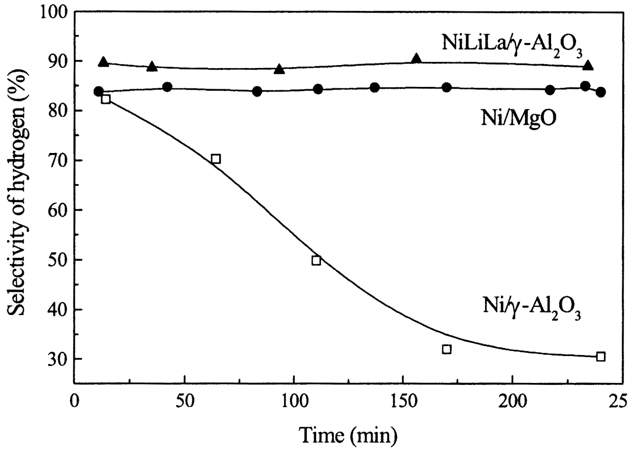

Figure 5. Hydrogen selectivity as a function of time over different catalysts. O/C = 1.00, GHSV = 3.5×10^4 l/kg/h, helium/*n*-heptane = 5.8, 850 °C.

X-ray photoelectron spectroscopic investigations further revealed the anti-carbon deposition ability of the catalysts. The relative atomic ratios of fresh and used catalysts are shown in table 2. The samples were obtained by the following method: the POH reaction was performed over the catalysts for 4 h under reaction conditions of 850 °C, O/C ratio of 1.05 and the ratio of helium to *n*-heptane of about 5.8 : 1. During the reaction, although there were no distinct changes in the catalyst activity, the amounts of carbon deposited over the three catalysts were obviously different. The results demonstrate that the Ni/MgO and $NiLiLa/\gamma\text{-}Al_2O_3$ catalysts exhibited a better carbon deposition resistance ability than the $Ni/\gamma\text{-}Al_2O_3$ catalyst, which is in accordance with the results in figure 5.

Moreover, thermal stability is also one of the most important parameters to evaluate catalysts, and much effort has been made to inhibit sintering and phase transformation of $\gamma\text{-}Al_2O_3$ during POM. Shaper *et al.* [28] believe that a lanthanum aluminate surface layer could format and improve the stability when introducing lanthanum. Oudet *et al.* [29] consider that the cubic $LaAlO_3$ structure on the surface of the support should be responsible for preventing sintering of active metal. Some investigators [30] consider that lithium could stabilize a spinel alumina by the formation of a mixed bulk phase. Additionally, the excellent thermal stability of the catalyst has also been proved in our previous work on the partial oxidation of lighter hydrocarbon (C_1–C_4) processes [10–12,24,27]. Consequently, it is reasonable to believe that $NiLiLa/\gamma\text{-}Al_2O_3$ catalyst possesses not only good carbon deposition resistance ability but also good thermal stability during the POH or similar processes.

Table 2

C 1s relative atomic ratio of fresh and used catalysts after 4 h of reaction

Catalyst	Fresh			Used		
	C 1s	Al 2p	Mg 1s	C 1s	Al 2p	Mg 1s
Ni/MgO	0.27		1	1.15		1
$Ni/\gamma\text{-}Al_2O_3$	0.23	1		1.36	1	
$NiLiLa/\gamma\text{-}Al_2O_3$	0.12	1		0.76	1	

4. Conclusion

The performances in terms of *n*-heptane conversion and hydrogen selectivity indicate not only that the stable operation of partial oxidation to hydrogen is possible under harsh conditions, but also that the modified nickel-based/γ-Al_2O_3 would be a candidate to be used in the partial oxidation of gasoline process for hydrogen production. A detailed investigation is in progress into the further optimization of the catalyst formulations, the preparation method and decreasing the reaction operating temperature.

Acknowledgment

This work was supported by the Ministry of Science and Technology, China (Grant No. G1999022401).

References

[1] B.C.H. Steele and A. Heinzel, Nature (London) 414 (2001) 345.

[2] A.K. Avc1, Z.Il. Önsan and D.L. Trimm, Appl. Catal. A 216 (2001) 243.

[3] D.J. Moon, K. Sreekumar, S.D. Lee, B.G. Lee and H.S. Kim, Appl. Catal. A 215 (2001) 1.

[4] Y.H. Wang and D.Y. Wu, Int. J. Hydrogen Energy 26 (2001) 795.

[5] I.W. Carpenter, World Patent WO 9948805 (1999).

[6] A. Anumakonda, J. Yamanis and J. Ferrall, US Patent 6,221,280 (2001).

[7] D.L. Trimm, Catal. Today 49 (1999) 3.

[8] J.R. Rostrup-Nielsen and J.H. Hansen, J. Catal. 144 (1993) 38.

[9] A.T. Ashcroft, A.K. Cheetham, J.S. Foord, M.L.H. Green, C.P. Grey, A.J. Murrell and P.D.F. Vernon, Nature (London) 344 (1990) 319.

[10] Q. Miao, G. Xiong, Sh. Sheng, W. Chu, L. Xu and X. Guo, Appl. Catal. A 154 (1997) 17.

[11] S. Liu, G. Xiong, S. Sheng and W. Yang, Appl. Catal. A 198 (2000) 261.

[12] R. Ran, G. Xiong and W. Yang, J. Mater. Chem. 12 (2002) 1854.

[13] JCPDS Powder Diffraction Files, JCPDS, Swarthmore, PA.

[14] Z. Xu, Y. Li, J. Zhang, L. Chang, R. Zhou and Z. Duan, Appl. Catal. A 210 (2001) 45.

[15] Y.H. Hu and E. Ruckenstein, J. Catal. 184 (1999) 298.

[16] J.M. Rynkowski, T. Paryjczak and M. Lenik, Appl. Catal. A 106 (1993) 73.

[17] L. Zhang, J. Lin and Y. Chen, J. Chem. Soc., Faraday Trans. 88 (1992) 497.

[18] K. Tomishige, Y.G. Chen and K. Fujimoto, J. Catal. 181 (1999) 91.

[19] H.Y. Wang and E. Ruckenstein, J. Catal. 186 (1999) 181.

[20] M. Montes, C. Penneman de Bosscheyde, B.K. Hodnett, F. Delannay, P. Grange and B. Delmon, Appl. Catal. 12 (1984) 309.

[21] M.A. Keane and P.M. Patterson, J. Chem. Soc., Faraday Trans. 92 (1996) 1413.

[22] Y. Zhang, G. Xiong, S. Sheng and W. Yang, Catal. Today 63 (2000) 517.

[23] W.B. White, S.M. Johnson and G.B. Dantzig, J. Chem. Phys. 28 (1958) 751.

[24] S. Liu, G. Xiong, W. Yang, L. Xu, G. Xiong and C. Li, Catal. Lett. 63 (1999) 167

[25] J.H. Bitter, J. Catal. 183 (1999) 336.

[26] S. Tang, F. Qiu and S. Lu, Catal. Today 24 (1995) 253.

[27] Q. Miao, G. Xiong, X. Li, S. Sheng and Z. Guo, Catal. Lett. 41 (1996) 165

[28] H. Shaper, D.J. Amesz, E.B.M. Doesburg and L.L. Van Reijen, Appl. Catal. 9 (1984) 129.

[29] F. Oudet, P. Courtine and A. Vejux, J. Catal. 114 (1988) 112.

[30] R.M. Levy and D.J. Bauer, J. Catal. 9 (1967) 76.