ELSEVIER

Catalysis Today 74 (2002) 77–84

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Selective hydrogenation of reformate oils over amorphous NiB/SiO_2 catalyst

Xiaoxin Zhang*, Aizeng Ma, Xuhong Mu, Enze Min

Research Institute of Petroleum Processing, Beijing 100083, China

Abstract

A supported NiB/SiO_2 amorphous catalyst was prepared by impregnation and chemical reduction by KBH_4. Its amorphous characteristics were determined by XRD and DSC methods. Its catalytic activity was measured during the selective hydrogenation of olefins in reformate oils. This new amorphous catalyst exhibits superior catalytic properties to the traditional post-hydrogenation catalyst, such as sulfide CoMo/Al_2O_3. However, significant deactivation of the catalyst was observed after reaction for 580 h. The structure of the used catalysts was determined using XRD, TEM, TG and XPS methods. Experimental results show that the deactivation is mainly caused by the surface oxidation of the active component, crystallite aggregation and carboneous species deposition. © 2002 Published by Elsevier Science B.V.

Keywords: Amorphous alloy; NiB/SiO_2; Reformate oils; Deactivation

1. Introduction

Amorphous alloys have properties that are of interest in catalysis: (a) the presence of a large number of surface coordinatively unsaturated sites; (b) the lack of surface segregation of alloying elements; and (c) the isotropic, single phase nature of the materials. Ever since the first report using amorphous alloy as catalysts by Smith et al. [1], numerous papers on this subject have been published [2–5]. However, most of the published data on hydrotreatment reactions were obtained using model compounds as a probe reaction; this makes it difficult to interpret the performance results and to correlate them to commercial operations. Therefore, it is our intention to describe the results obtained by using reformate oils as feedstock in a continuos fixed-bed reactor, which closely mimic a commercial operation.

Catalytic reforming is one of the most important processes to produce high grade motor gasolines. Besides isomerization and dehydrocyclization reactions, the formation of aromatics by dehydrogenation of naphthenes occurs. Thus, catalytic reformers within refineries are an important source of BTX, aromatics (benzene, toluene, xylenes). Frequently high purity aromatics are recovered from these streams using modern extractive distillation or liquid extraction processes. Reforming process normally produce a small amount of olefins which will impair the quality of the product aromatics and refinate. Due to the residual content in diolefins and some olefins the reformer streams as well as the benzene and toluene afterextractive distillation show a dark, yellowish color expressed by an acid wash color. Aromatics product specification, notably bromine number and acid wash color, have obligated producers to utilize clay treatment and selective hydrogenation to remove trace impurities of diolefins and olefins. The conventional clay treatment is a multiple vessel batch process

---

* Corresponding author.

PII: S0920-5861(01)00532-6

which periodically requires disposal of the spent clay in a suitable environmental manner, which is costly and environmentally unfriendly. Conventional sulfide CoMo or NiMo catalysts are used in the selective hydrogenation in commercial plants, however, these kinds of catalysts are only used at a high reaction temperature (300–340 °C) and low LHSV (2–3 h^{-1}) [6]. In this paper, a new amorphous NiB/SiO_2 catalyst has been developed, which is very efficient and environmentally compatible during the selective hydrogenation of reformate streams in liquid–solid phase.

2. Experimental

2.1. Catalyst preparation

The NiB/SiO_2 sample was prepared in the following procedures. Predried silica (20 mesh, 480 $m^2\,g^{-1}$) was impregnated with a desired amount of $Ni(CH_3COO)_2\cdot 4H_2O$ solution. After being dried at 120 °C, the above precursor was reduced by adding dropwise 0.20 M KBH_4 solution. The initial molar ratio of B/Ni was 2.5/1 to ensure that all the Ni^{2+} ions on the support were completely reduced. The resulting NiB/SiO_2 catalyst was washed thoroughly with distilled water and then with ethanol. No further treatment was attempted before it was used in the activity test.

2.2. Catalyst characterization

The Ni loading on the support was analyzed by ICP. X-ray diffraction (XRD) measurements were performed on a D5000D Siemens powder diffractometer with Cu Kα radiation source of 35 kV × 30 mA power. Electron diffraction was used for the identification of structure of the samples. Its crystallization process was followed by differential scanning calorimeter (DSC) under N_2 atmosphere at a heating rate of 10 K/min. X-ray photoelectron spectroscopy (XPS) was performed on a Microlab MK II PS system to determine its surface composition and the surface electronic states of the catalysts. All the binding energy (BE) values were calibrated by using Si 2p (BE = 103.3 eV) as a reference. For all those experiments, the samples were kept in ethanol solution to protect them from air oxidation.

Table 1
Main properties of different feedstocks

Feedstock	1	2	3
Properties			
Bromine number (g Br × $(100\,g)^{-1}$)	2.0	2.1	5
Aromatics (wt.%)	57	57	59
Existent gum (wt.%)	1.4	5	9
Boiling range (°C)	44–169	65–177	47–182

2.3. Feedstocks

The composition of the effluent of a catalytic refomer depends mainly on the feed as well as the processing parameters of the catalytic reformer. Thus, the aromatics content as well as the impurity level (olefins) can vary in wide ranges. Some of the properties of the reformate oil used in the present investigation are summarized in Table 1. It is well known that a small amount of olefins (express as bromine number) will impair the quality of the product aromatics and refinate. Generally, the bromine number of the product is less than 0.5 g Br × $(100\,g)^{-1}$ for the commercial specification. Simultaneously, the aromatic losses by ring hydrogenation should keep below 0.5%. The feedstock was kept under nitrogen atmosphere to protect it from oxygen dissolving.

2.4. Catalytic measurement

The activity of the catalysts was tested in a stainless steel trickel-bed reactor (10 cm i.d.) under continuous down-flow conditions. The weight of the catalyst was 10 g for each of the experiments. The bromine number was measured using microcoulomb method and the amormatics of products were analyzed by gas chromatography. The reaction was finished when the bromine number of the product exceeded 0.5 g Br × $(100\,g)^{-1}$. The deactivated catalyst was kept for further characterizations to determine if any sintering, crystallization or surface poisoning occurred after deactivation.

3. Results and discussion

3.1. Reactivity screening and analysis

The experimental results under different reaction conditions using reformate 1 as feedstocks are shown in Table 2. The experiments show that the bromine number of the product oil keeps nearly unchanged with the increase of temperature, decreases with the increase of pressure, and goes up with space velocity. The hydrogen-to-oil ratio has no significant effect on the quality of the product oil in this process. Considering both bromine number and aromatic, it is recommended that this process be operated at a temperature of 100 °C, pressure of 1.0 MPa, liquid hourly space velocity of 6.0 h^{-1}, and hydrogen-to-oil ratio of 50 (v/v). From all our experiments, it can be seen that the hydrogenation process using amorphous NiB/SiO_2 has the advantages of low temperature, large space velocity, low hydrogen rate and high selectivity of olefin hydrogenation compared with other commonly used hydrogenation catalysts, for example, sulfurized CoMo/Al_2O_3 as reported in [6].

Table 2
The influence of reaction conditions (temperature, pressure, LHSV) on the bromine number and aromatics content of products

	Bromine number (g Br × $(100\,g)^{-1}$)	Δ Aromatics (wt.%)
Temperature[a] (°C)		
80	0.14	0.2
100	0.09	0.1
150	0.10	0.1
200	0.12	0
250	0.12	−0.1
Pressure[b] (MPa)		
0.5	0.18	−0.1
0.8	0.14	−0.1
1.0	0.11	−0.1
1.5	0.10	−0.2
LHSV[c] (h^{-1})		
3	0.09	−0.1
6	0.10	0.1
12	0.20	0.3
20	0.33	0.2

[a] Other reaction conditions: pressure 1.0 MPa, LHSV 6.0 h^{-1}.
[b] Other reaction condition: temperature 100 °C, LHSV 6.0 h^{-1}.
[c] Other reaction condition: temperature 100 °C, pressure 1.0 MPa.

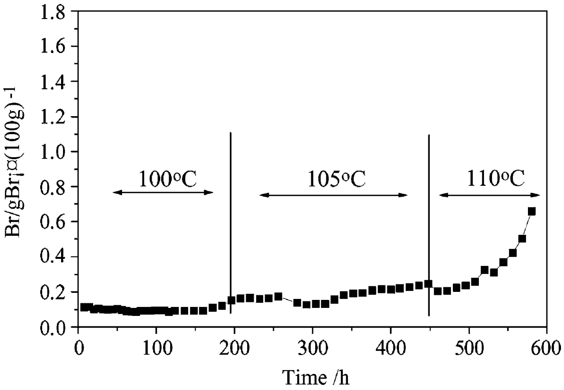

Fig. 1. The life test of NiB/SiO_2 catalyst. Reaction condition: catalyst 50 g, 100–110 °C, 1.0 MPa, 6 h^{-1}, H_2/oil = 50 (v/v).

3.2. Catalyst stability

Lifetime tests for hydrofining of reformate oils over NiB/SiO_2 catalyst were carried out in a continuous fixed bed reaction system with the same parameters as the above temperature, pressure, LHSV and H_2/oil, all with 50 g of catalyst. The results of service life test for amorphous NiB/SiO_2 during hydrogenation of reformate oil are shown in Fig. 1. The results indicate that the NiB/SiO_2 catalyst maintains a constant activity during the first 200 h. Some degree of deactivation is observed after 200 h, but the activity can be maintained by raising the temperature to 105 °C. However, continued deactivation over 450 h is found and the temperature can not be raised sufficiently to keep up with deactivation, so that the test has to be terminated at 580 h.

3.3. Catalyst characterization

To achieve a better understanding on the hydrogenation and deactivation processes, the amorphous NiB/SiO_2 catalysts were charaterized by XRD, DSC, SAED, XPS and TG measurements.

Table 3 shows some properties of the fresh amorphous NiB/SiO_2 catalyst, and the corresponding deactivated catalyst after reaction 580 h. ICP analysis shows that no significant changes in bulk composition of the Ni alloy. However, a significant *decrease* of the top surface Ni atoms and *increase* of the top surface B atoms is observed from XPS analysis; that is, there is enrichment in B on the surface.

Table 3
Some properties of the amorphous NiB/SiO_2 catalysts

Sample	S_{BET} ($m^2\,g^{-1}$)	Ni loading (wt.%)	Composition atom ratio	Ni/Si atom	B/Si atom
SiO_2	480	–	–	–	–
Fresh NiB/SiO_2	410	4.6	$Ni_{75}B_{25}$	0.018	0.026
Used NiB/SiO_2	360	4.5	$Ni_{76}B_{24}$	0.015	0.032

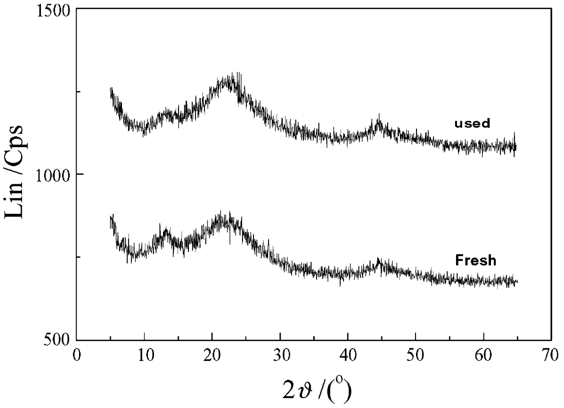

Fig. 2. XRD patterns of NiB/SiO_2 sample fresh and used for 580 h.

The XRD patterns of both the fresh and the used NiB/SiO_2 samples are presented in Fig. 2. It is found that the amorphous structure of NiB/SiO_2 is destroyed slightly after reaction, except for a broad peak around $2\theta \approx 22^\circ$ owing to the silica gel, only one broad peak around $2\theta \approx 45^\circ$ is observed, indicating typical amorphous characteristics.

Further evidence for this conclusion is provided by the electron-diffraction image of selected areas of the samples (SAED), as shown in Fig. 3. The broad and diffuse Debye rings correspond to a typical amorphous structure can be seen in the fresh sample, as shown in Fig. 3(a). A few crystallite NiO appear in used samples, as shown in Fig. 3(b), indicating oxidation of nickel.

Fig. 4 shows the results of DSC measurement. Compared with that of the original NiB/SiO_2 catalyst (Fig. 4(1)), it can be seen that the patterns of the used sample are nearly the same as in Fig. 4(2), which further reveals that the amorphous structure remained after 580 h of hydrogenation. The DSC experiments show that the crystallization of the fresh NiB/SiO_2 occurred at about 360 °C, but at 410 °C for the used sample. This result suggests the used catalyst has a more stable structure. SEM pictures show that some Ni aggregation occurs after reaction.

The B 1s XPS spectra of both the fresh and the used NiB/SiO_2 sample are presented in Fig. 5. According to Fig. 5(a), both the elemental (188.5 eV) and oxidative (192.2 eV) states of the boron species can be observed in the fresh sample, while on the used catalyst, oxidation of boron occurs leaving no detectable elemental boron. After 13.5 min of Ar^+ etching, oxidized boron is still the main species. These results suggest that oxygen causes the formation of oxidation of B during the reaction, which inevitably exists in the

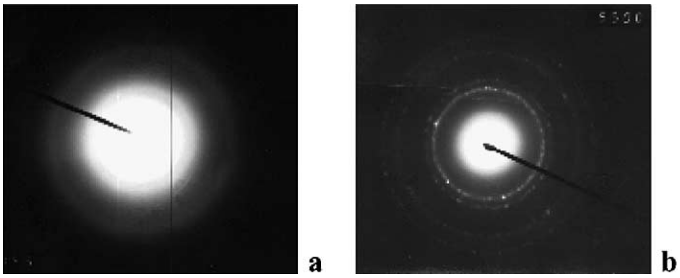

Fig. 3. SAED pictures of NiB/SiO_2 samples: (a) fresh catalyst; (b) used for 580 h.

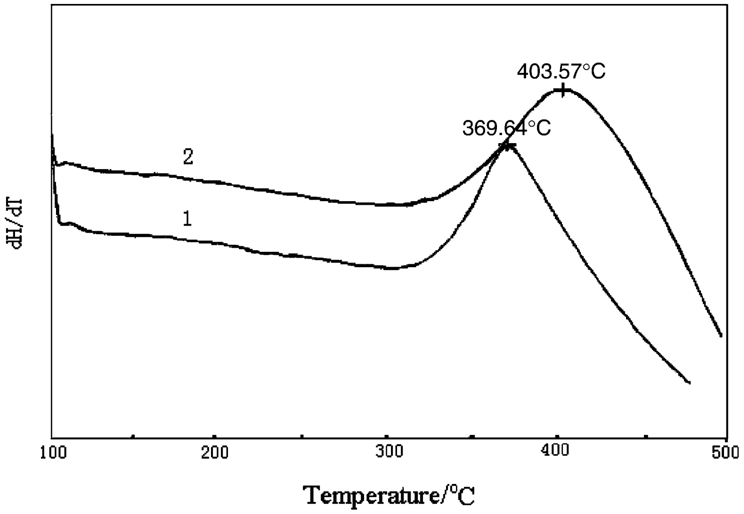

Fig. 4. DSC curve of NiB/SiO_2 samples: (1) fresh; (2) used for 580 h.

liquid feedstock, concomitant with a decomposition of the NiB alloy.

The TG curve for used NiB/SiO_2 is presented in Fig. 6. The thermal behavior of catalyst is generally characterized by two transition: (1) the first one at low temperature is endothermic and corresponds to the loss of interlayer water; (2) the second thermal transition at higher temperature is also endothermic and is due to the loss of polymer and gum present in this system. It could be seen that there is a 1 wt.% loss at the first transition from 100 to 190 °C, and a 2.4 wt.% loss at the second from 230 to 429 °C. These results are consistent with carbon accumulation during the reaction.

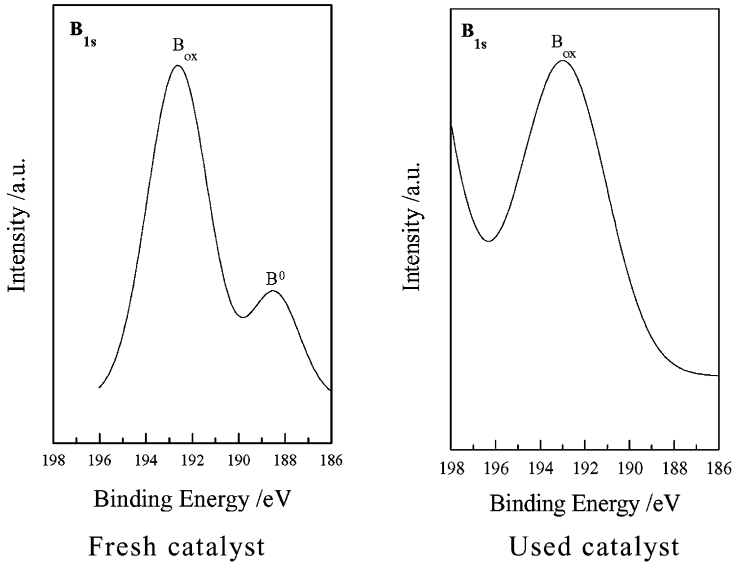

Fig. 5. B 1s spectra of amorphous NiB/SiO_2 catalyst: (a) fresh catalyst; (b) used catalyst.

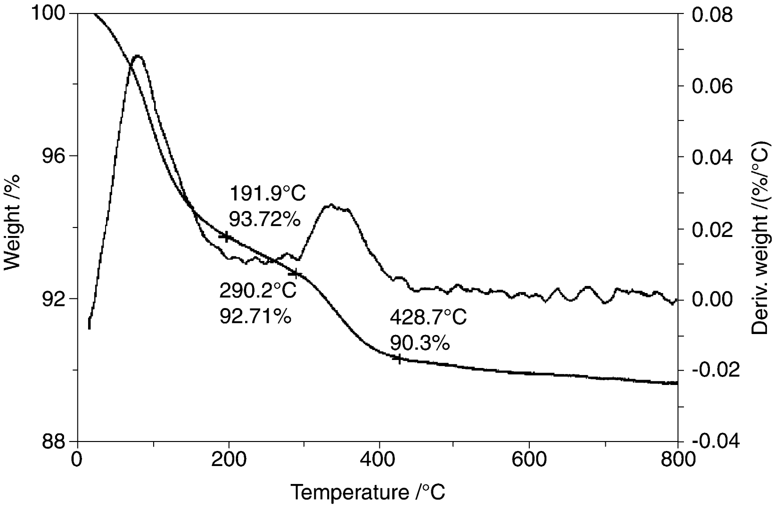

Fig. 6. TG–DTA diagrams of used NiB/SiO$_2$.

3.4. Investigation of water and feedstock factors

Generally, oxygen, sulfur and water are considered as the possible poisons of amorphous NiB/SiO$_2$ catalyst in the hydrogenation process [7]. Besides these, carboneous overlayers are considered as unfavorable factor for reformates such as existent gum. Therefore, the effect of these substances on the hydrogenation activity is investigated.

3.4.1. The influence of water

The catalytic activity of the fresh NiB/SiO$_2$ sample is used as a reference. Different amounts of water are added into the feedstock, and its resultant catalytic activities are recorded. The experiment results show that the influence of water on the activity is *dramatic*. When the water content is 50 ppm, the bromine number of the product is 0.6 g Br × $(100\,\mathrm{g})^{-1}$, while the reference is 0.1 g Br × $(100\,\mathrm{g})^{-1}$. The Ni 2p$_{3/2}$ XPS spectrum shows that Ni(OH)$_2$ is the main nickel species on the surface of the used catalyst. The same phenomenon has been described in [7]. From XPS analysis results on the surface atoms as listed in Table 4, it could be suggested that a trace amount of water could aid in transport of top surface nickel.

Table 4
The influence of water on the surface atoms of NiB/SiO$_2$ catalyst

	Ni/Si atom	B/Si atom
Fresh	0.018	0.026
Used	0.015	0.026

3.4.2. The effect of feedstocks

In commercial operation, hydroprocessing catalysts invariably undergo some degree of deactivation depending on the feed source. The experimental results with different feeds (shown in Table 1, having a higher soluble oxygen) at a reaction temperature of 100 °C are shown in Fig. 7. It can be seen that, for relatively light feed 1#, deactivation of the catalyst is minimal, and the process operates for long periods of time. However, for feed 3# having more gum, deactivation of the catalyst is severe. Thermogravimetric analysis on samples used in different feedstock gives the TG curves shown in Fig. 8. The TG curves are characterized by a well-defined weight loss in the temperature of 200–450 °C (the collections of numerical values is shown in Table 5). According to the TG results, we

Table 5
The data corresponding to TG curves in Fig. 8

Feedstock	Temperature range (°C)	Loss (wt.%)
1	247–435	1.1
2	279–418	2.2
3	223–442	5.0

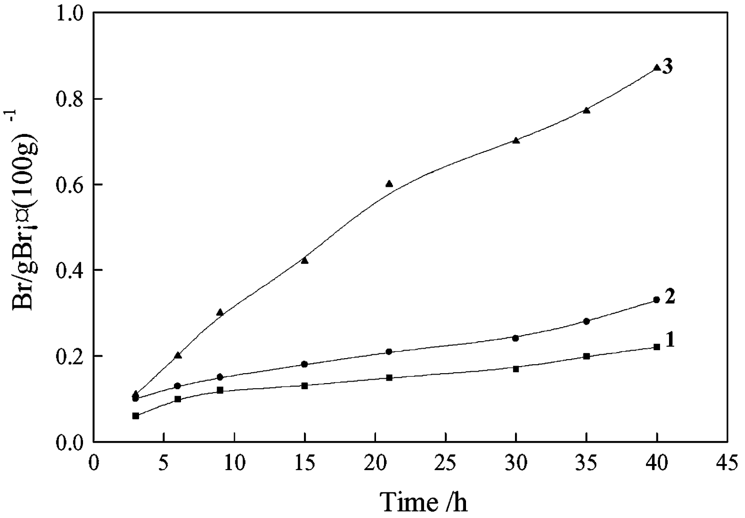

Fig. 7. The relation between activity and reaction time. Reaction condition: catalyst 10 g, 100 °C, 1.0 MPa, $6\,h^{-1}$, H_2/oil = 50 (v/v); (1) feed 1, (2) feed 2, (3) feed 3.

attribute the weight loss to the formation of a polymer with a low molecular weight. It could be obtained that continued deactvation over a longer time period is due to gum deposits whose rate of deactivation depends on the gum level in the feedstock.

In addition, the effect of oxygen on the catalyst is also investigated. It is found that soluble oxygen in oils has a negative effect. So, it is necessary to do a special treatment to the feedstock, for example, adding a removing oxygen process before hydrogenation unit.

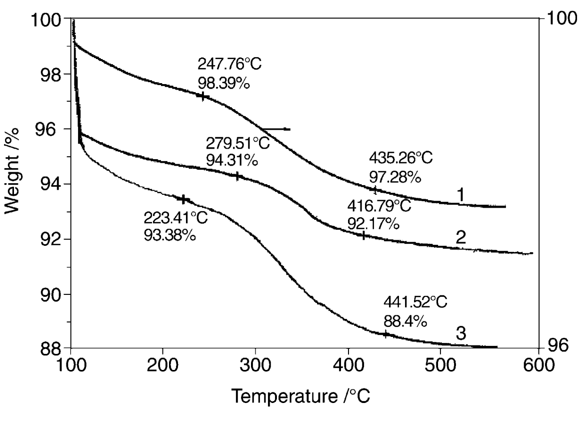

Fig. 8. TG curves of used NiB/SiO_2 using different feedstocks.

4. Conclusion

The results presented in this paper have shown that a new family of catalyst NiB/SiO_2 appears to be well suited for the selective hydrogenation of reformate oils. Compared with the conventional sulfide CoMo/Al_2O_3 catalysts, which are frequently used for selective hydrogenation of reformate, NiB/SiO_2 shows superior performance in terms of higher activity at less severe operating conditions, deeper conversion of olefins, and minimum aromatics losses. Although the deactivation of the catalyst is observed after reaction for 580 h, it is promising for NiB/SiO_2 catalyst to be applied in a commercial unit in which there is no gum and oxygen in the feedstock.

Acknowledgements

This work was supported by the National Natural Science Foundation of China under contract number 29792070.

References

[1] G.V. Smith, W.E. Brower, M.S. Matyjaszczyk, Stud. Surf. Sci. Catal. 7A (1981) 355.

[2] A. Molnar, G.V. Smith, M. Bartok, Adv. Catal. 36 (1989) 329.

[3] S. Yoshida, H. Yamashita, J. Chem. Soc., Faraday Trans. I 81 (1985) 2485.

[4] W.-J. Wang, M.-H. Qiao, J.-F. Deng, Appl. Catal. A: Gen. 163 (1997) 101.

[5] W.J. Wang, M.H. Qiao, J.F. Deng, Appl. Catal. A: Gen. 166 (1998) 243.

[6] X.-L. Hou, Petroleum Processing Technologies in China, China Petrochemical Press, Beijing, 1991, p. 176.

[7] W.J. Wang, M.H. Qiao, J.F. Deng, Appl. Catal. A: Gen. 168 (1998) 151.