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Some characterization of β-zeolite for alkylation of benzene in near critical regions

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Abstract

Alkylation of benzene with ethylene to ethylbenzene over a β-zeolite catalyst is carried out in the five different near critical regions. With the application of X-ray diffraction (XRD) and scanning electron microscope (SEM), structures of the catalysts used under the five different near critical conditions are compared with those of the fresh catalyst. The results show that the high pressure operating conditions, including the supercritical fluid operation, may be harmful to the catalyst structure, and the operation in the vapor–liquid state near the critical point may cause heavy destruction to the catalyst. The coking mechanism of the catalysts is suggested based on element material analysis (EMA) and electron paramagnetic resonance (EPR) characterization. Supercritical and other near critical operations are compared. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Near critical region; Supercritical fluid; Alkylation; Reaction; Phase equilibria; β-Zeolite; Coking

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1. Introduction

Starting from Tiltscher [1], there has been a growing research interest in exploring special transport properties of supercritical fluids (SCF) as solvents for catalytic reactions [2]. However, reported applications of SCFs in catalytic reactions [3–7] cared much about indices such as reaction rate and selectivity, and their relations with the presumed influential effects, such as catalyst coking. In their papers, the authors did not pay much attention to changing of the catalyst structures tied to the operating conditions near the critical point. Understandably, those extreme conditions might impose some effects on the catalyst structure and lead to observed activity change. On the other hand, it is still not clear to which extent the catalyst structure is affected by the SCF, and how the non-SCF operating conditions adjacent to the critical point would affect the catalyst structure.

The work of Tiltscher and Hofmann [3] demonstrated the potential applications of SCFs as media to catalytic reactions through 1-hexene isomerization over low activity macroporous-Al_2O_3. They showed that the deposition of low volatility hexene oligomers could be prevented or eased when the fluid was in a supercritical state. In contrast to their report, Saim and Subramaniam [8,9] observed that the catalyst also deactivated obviously under supercritical conditions based on their work using a microporous Pt/γ-Al_2O_3 catalyst. Similar results were presented by Manos and Hofmann [10], who found that the loss of activity was not able to be recovered through in situ regeneration

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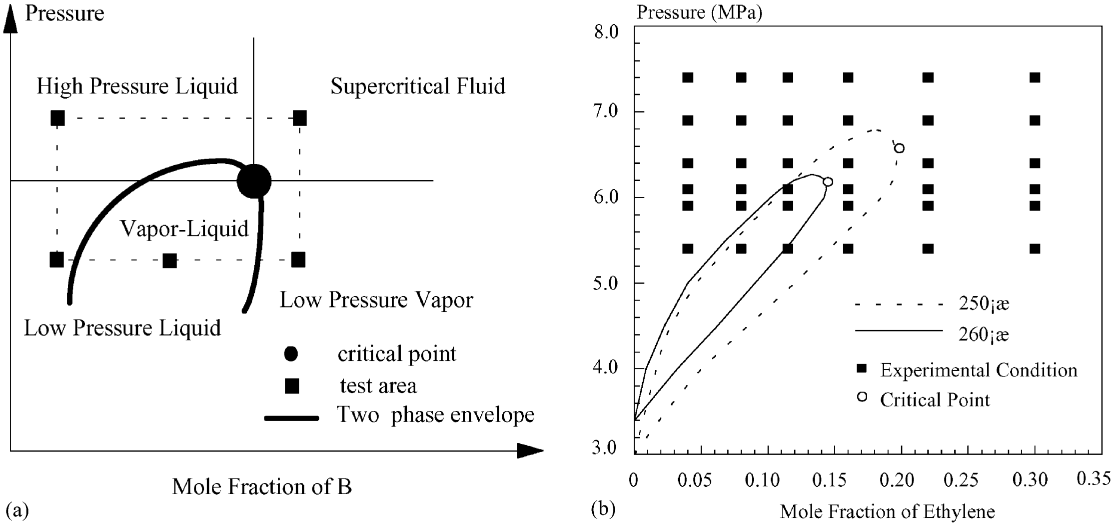

Fig. 1. Experimental conditions of the alkylation: (a) phase states in near critical regions of a binary system; (b) experimental condition distribution for the ethylene–benzene system.

using SCFs. They considered that the coke which led to catalyst deactivation was created by further reaction of some larger molecules called coke precursors. SCFs could only dissolve the newly formed coke precursors, but not those formed earlier. The results of Saim and Subramaniam [8,9] and Manos and Hofmann [10] were drawn from reduction of reaction rates, or the analysis of reaction products, but not from the catalyst itself. While the present authors would believe it is necessary to characterize the used catalysts under different operation conditions. Meanwhile, the coking mechanism of alkylation of benzene with ethylene to ethylbenzene was studied under low pressure conditions [11]. It was shown that there might exist two kinds of coke: low temperature coke and high temperature coke, depending on the temperature under which the coke forms. It is intended to extend the operating conditions to the near critical regions of which different coking mechanisms may exist.

In this paper, a β-zeolite catalyst supplied by the Research Institute of Petroleum Processing (RIPP) is used in alkylation of benzene to ethylbenzene. Operating conditions of the reaction are deliberately chosen based on the high pressure fluid phase equilibria of all five near critical regions, including those of SCF, high pressure liquid (HPL), low pressure liquid (LPL), vapor–liquid (VL) and low pressure vapor (LPV), as schematically shown in Fig. 1(a). Fig. 1(b) shows the experimental condition distribution for the alkylation based on the authors' phase equilibrium experiments [12].

With the application of X-ray diffraction (XRD) and scanning electron microscope (SEM), structures of the catalysts used under the five near critical conditions are studied and then compared with those of the fresh catalyst.

Also have been characterized are the catalysts having been operated in all the five regions using element material analysis (EMA) and electron paramagnetic resonance (EPR) to study the coking mechanisms. Thus, the results obtained under different conditions can be compared so as to explore the coking mechanism of the reaction.

2. Experimental

The experimental setup for this catalytic reaction is shown in Fig. 2. Preliminary experiments have been completed to determine the minimum flow rate which guarantees that the external mass transfer resistance is eliminated, and the maximum pellet size which makes the internal diffusion resistance to be neglected [13]. The β-zeolite catalyst pellets of 60–80 mesh

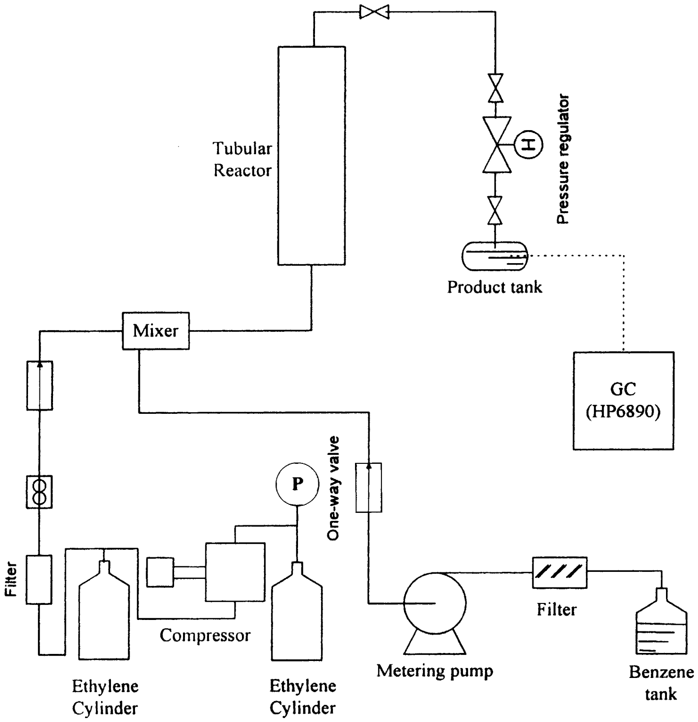

Fig. 2. Experimental setup.

(0.131–0.180 mm) are packed in a tubular reactor, which is 6 mm in diameter and 0.6 m in height. The mixture of ethylene and benzene, whose compositions are chosen based on the authors' high pressure fluid phase equilibria [12], is charged to the reactor and the reactions are carried out under the operating conditions as shown in Table 1. For each experiment, catalyst quantity is fixed at 0.18 g. The ethylene flow rate keeps unchanged at 1.0 g/min, with a varying benzene fraction. Certainly the external mass transfer resistance can by all means be ignored even at the lowest benzene concentration. For all the experiments, ethylene conversion is kept lower than 5% so that the reactor is under a differential operation mode and that no side reactions need to be considered.

Table 1
Operating conditions of correspondent phase states ($T = 260\,^{\circ}\mathrm{C}$, $t = 2.5\,\mathrm{h}$)

	Phase				
	LPL	HPL	VL	LPV	SCF
Pressure (MPa)	5.9	6.4	5.9	5.9	6.4
Mole fraction of ethylene	0.08	0.08	0.115	0.16	0.16

Table 2
Materials used in the reaction

Materials	Sources	Purity (%)
Ethylene	Shanghai Chemical Industry Research Institute	99.95
Benzene	Shanghai Feida Corporation	99.5[a]

[a] After purification.

Each experiment lasts for 2.5 h. After the reaction is completed, the catalysts are collected for characterization. Here, the XRD and SEM are applied. Besides, EMA and EPR are also used.

The chemicals used in the reaction are presented in Table 2, together with their suppliers and purities.

3. Results and discussions

Typical XRD spectra of the fresh catalyst and catalysts used under the five near critical conditions are

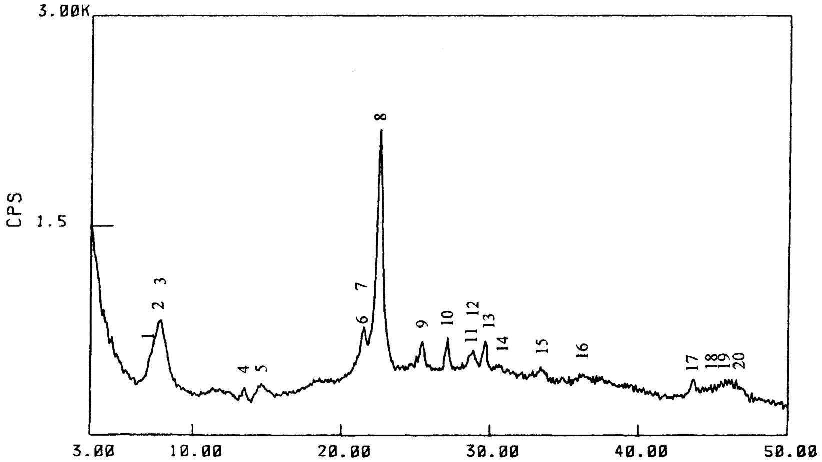

Fig. 3. XRD spectrum of unused catalyst.

shown from Figs. 3–8. It is shown from these figures that the five of them (Figs. 3–7) give more or less similar spectra, implying that the crystallinity of the catalysts does not seem to undergo an evident change. The only difference appears in Fig. 8, where the spectrum looks obviously different from the others. The peak is obviously lower. This means that, probably due to the repeated VL shifting, catalyst run in the VL two phase region tends to cause some amorphous structure. The reaction rate is lower, comparing with those of the other regions, as has also been verified by our reaction kinetic experiments [13].

The values of *d* and *I* of the main peaks, representing the crystal grain size [14] are shown in Fig. 9.

The increase of *d* shows that a negative effect on reaction exists besides the catalyst deactivation caused by coke formation. This is because the larger is the value of *d*, the smaller is the specific surface area of the crystal grain, and hence lower is the reaction rate [15]. Thus reduction of reaction rate may not be caused directly from the loss of catalyst activity. If the operation is long enough for the changing of crystal grain size, the reaction rate also tends to descend even though coke formation is well prevented. In other words, the

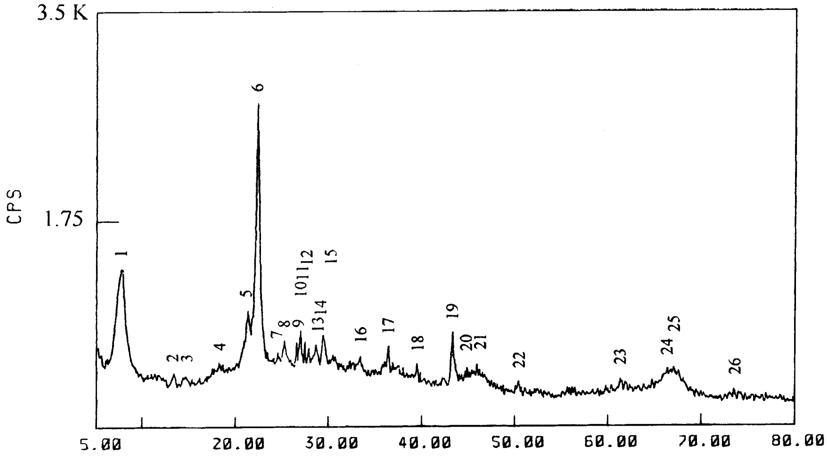

Fig. 4. XRD spectrum of catalyst operated at LPL condition.

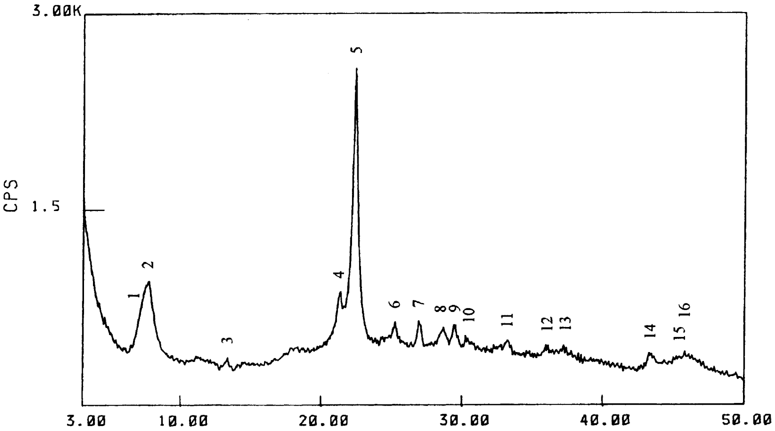

Fig. 5. XRD spectrum of catalyst operated at HPL condition.

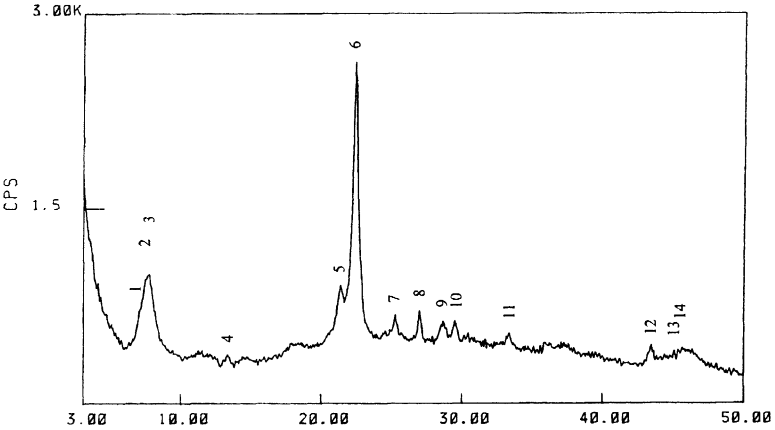

Fig. 6. XRD spectrum of catalyst operated at LPV condition.

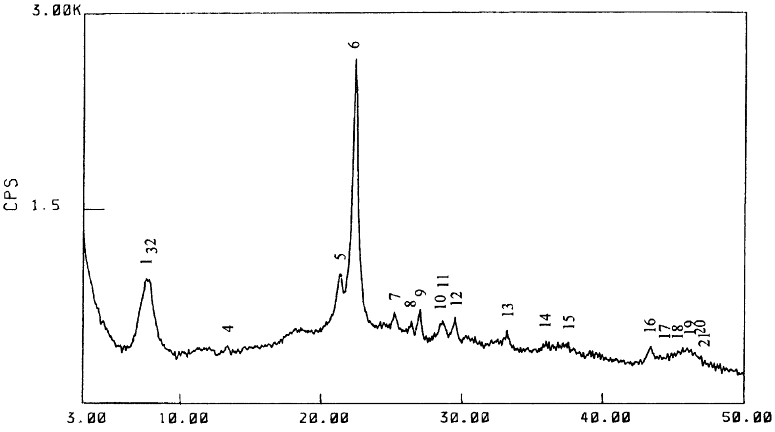

Fig. 7. XRD spectrum of catalyst operated at SCF condition.

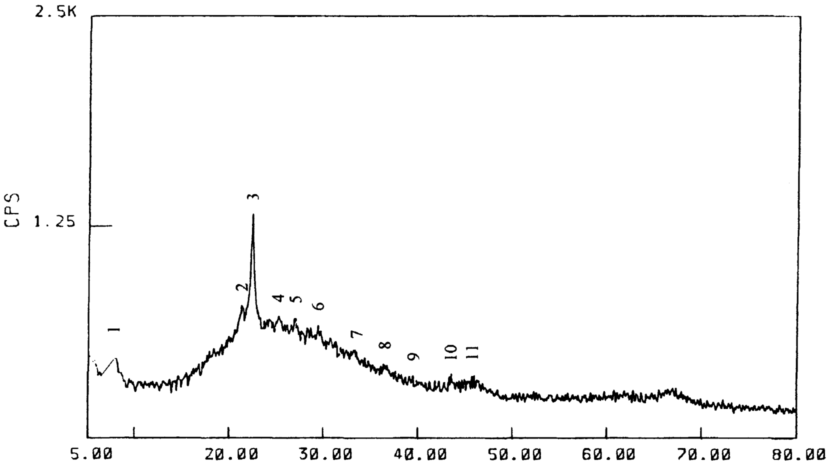

Fig. 8. XRD spectrum of catalyst operated at VL condition.

reaction rate as an index of catalyst activity may not be reliable unless some evidence is shown that other effects on the reaction rate can be neglected. Besides, the value of *d* increases with the increase of ethylene or operating pressure, which shows that the operation under high pressure or supercritical state may harm the catalyst.

The value of *I* for catalyst used under the VL condition is much smaller than those of others. This means that the catalyst, unlike the others, is not in a good state of integrity [16]. Looking back to the operating conditions, the only significant difference between the catalyst operated under the VL condition and the others is that the former is operated under a near critical two phase conditions, while the other four are under single phase conditions. The VL phase in the near critical region is highly unstable and the phase repeatedly shifts from vapor to liquid, or vice versa. Thus, we suppose a frequent shock force exists and acts on the catalyst. This force may destroy

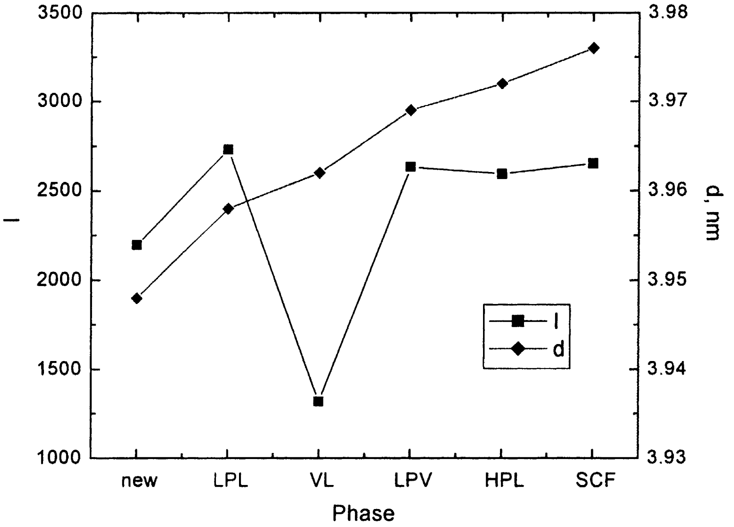

Fig. 9. The *d* value and *I* value after running under various operating conditions.

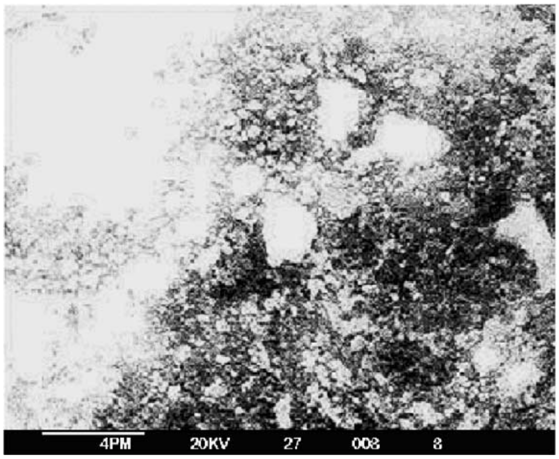

Fig. 10. SEM of the unused catalyst.

the crystallinity of catalyst and lead to a sharp drop of *I*.

In addition, obvious difference between the catalyst operated under the VL condition and other conditions is found when comparing the six SEM photos shown in Figs. 10–15. The figures near critical show that the surface of the catalyst operated under the VL condition is not as tight as that of other catalysts but loose. This could be regarded as a circumstantial evidence of the structure destruction by operation under the VL condition in the near critical region.

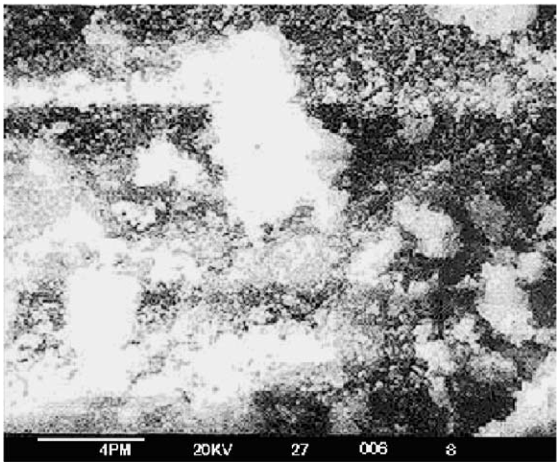

Fig. 11. SEM of catalyst in the LPL phase.

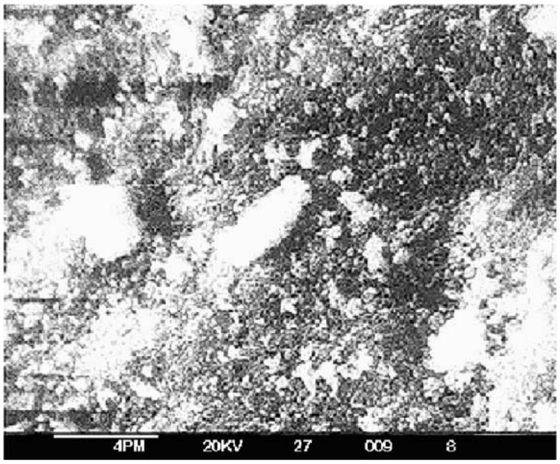

Fig. 12. SEM of catalyst in the HPL phase.

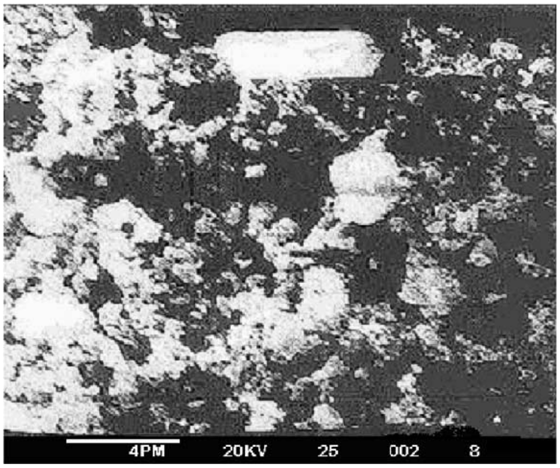

Fig. 13. SEM of catalyst in the VL phase.

The amplitudes of the six EPR spectra of the fresh catalyst and the catalysts operated under the five near critical conditions are presented in Fig. 16.

The *g*-factors of the spectra for catalysts run under the five near critical conditions are shown in Table 3.

Table 3
g-Factors of EPR spectra of catalysts operated under different conditions ($h\nu = g\beta H$)

	LPL	VL	HPL	SCF	LPV
g-Factor	2.005096	2.005188	2.004818	2.005044	2.004951

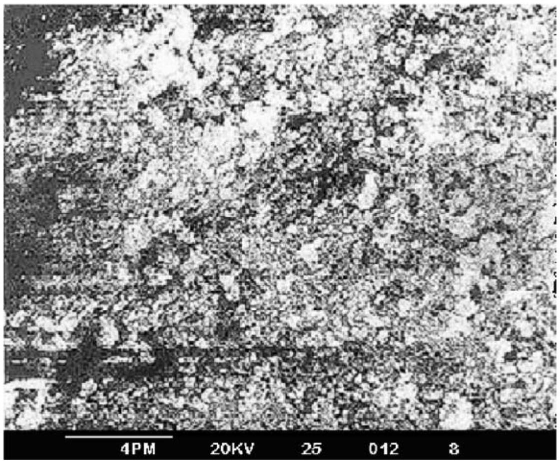

Fig. 14. SEM of catalyst in the LPV phase.

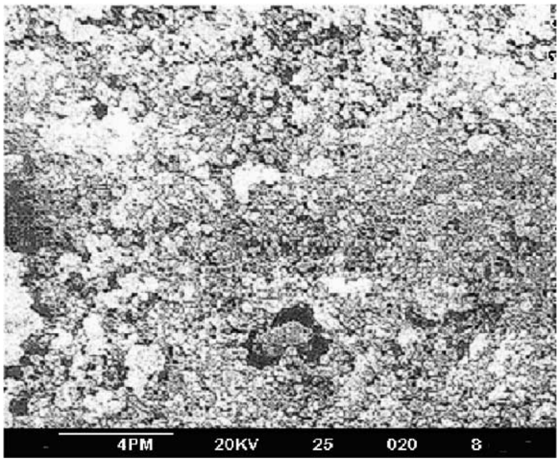

Fig. 15. SEM of catalyst in the SCF phase.

It is apparent that the g-factors, shown in Table 3, are very close to the spectrum split factor of the free electron ($g_e = 2.0023$). This implies that the source of the EPR signal is the free radical. The amplitudes of EPR signals, representing the amounts of free radicals, are shown in Fig. 16.

Fig. 17 presents the results of the EMA tests for the treated catalysts. The contents of carbon of these catalyst samples or the carbon–hydrogen ratios, represent some properties of the coke.

Fig. 18 depicts a plot of the amplitudes of the EPR spectra, representing the amounts of free radicals, against the carbon–hydrogen ratio, representing the coke formation. It reveals that the amount of free radicals is tightly related to the coke formation even though the reactions are carried out under different conditions.

On the other hand, the EPR spectra display that no hyperfine structure is observed from the catalysts used under these five operating conditions. This means that no middle free radicals appear in the reaction, which is different from the case of low pressure operations [11]. Ethylene plays no role in further reactions towards the coke formation under high pressure, and the type of coke is only the stable high temperature coke. The unique coking behavior in all the five regions

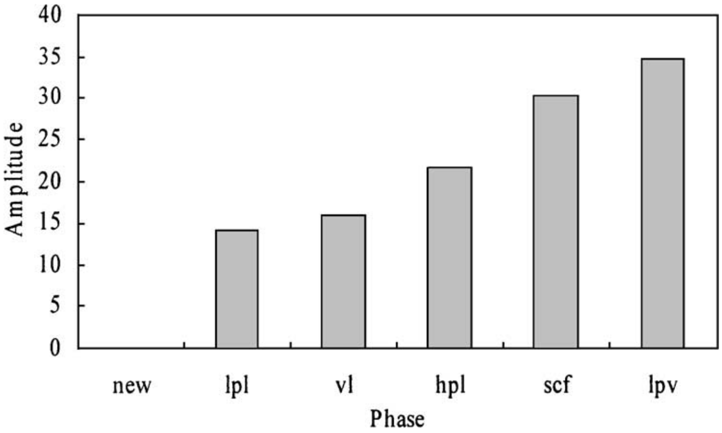

Fig. 16. Amplitudes of EPR spectra.

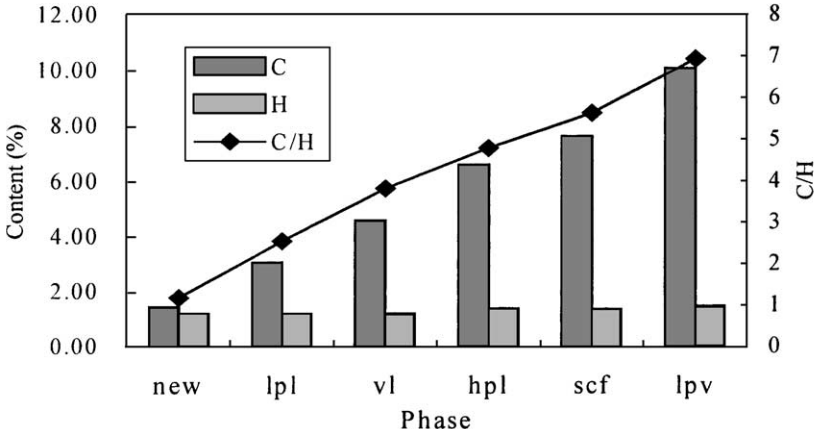

Fig. 17. Result of EMA tests.

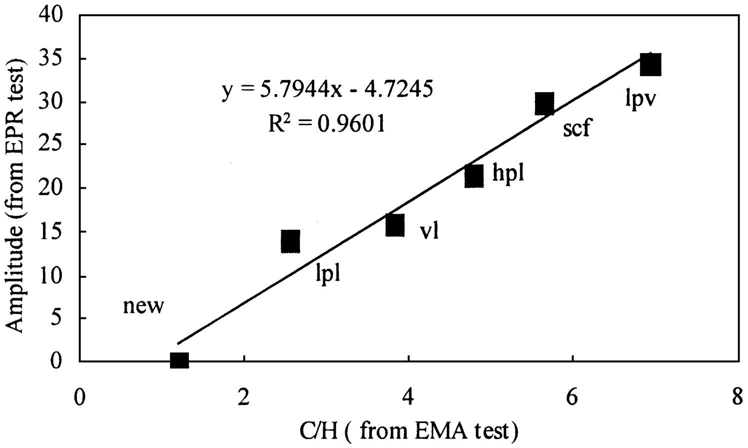

Fig. 18. Carbon–hydrogen ratio and amplitude of EPR.

implies that although the reaction behavior is strongly influenced by the phase state, the coking mechanism likely remains unchanged.

4. Conclusions

The conclusions can be drawn as follows:

1. In studying the reaction behaviors, it is believed that the measured reaction rate and product selectivity may not be regarded as the unique basis for catalyst evaluation, unless otherwise supported, since catalyst crystallinity and structure could change rapidly in the near critical regions.
2. High pressure operating conditions, including the SCF state operation, may be harmful to the catalyst structure.
3. Operation under the VL conditions in the near critical region may cause heavy destruction to the catalyst structure.
4. Ethylene does not take part in the further reaction towards coke formation under high pressure.
5. The formed coke is a stable high temperature coke. The coking mechanism does not change with the phase state in the near critical regions.

Acknowledgements

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