

# Effect of Pd on the stability improvement of Cu/H-MFI for NO removal under hydrothermal pretreatment conditions

Piyasan Prasertthdram\*, Suphot Phatanasri, Jakrit Rungsimanop,  
Pornsawan Kanchanawanichkun

*Petrochemical Engineering Laboratory, Department of Chemical Engineering, Faculty of Engineering,  
Chulalongkorn University, Bangkok 10330, Thailand*

Received 6 June 2000; received in revised form 18 September 2000; accepted 5 October 2000

## Abstract

The effect of Pd-modification of Cu ion-exchanged H-MFI (Pd/Cu/H-MFI) on its performance for NO removal was studied. The stability of the catalysts subjected to hydrothermal treatment with a He stream containing 10% steam at 800°C was investigated. The Cu/H-MFI catalyst markedly lost its activity for NO conversion after the hydrothermal pretreatment. The Pd-modification of the Cu/H-MFI resulted in improved stability against the hydrothermal treatment when loading Pd approximately 0.2–0.3 wt.%. The dealumination of tetrahedral Al in MFI framework was completely prevented when loading Pd from 0.3 wt.% or higher. Further loading of Pd higher than 0.3% caused the larger crystallite size upon pretreatment as seen from the scanning electron micrographs (SEM). It has been suggested that there may be some changes in Pd and Cu on H-MFI, such as alloying and/or palladium oxides formation, leading to some loss of Cu<sup>2+</sup> active species for NO removal. This results in the limitation of NO conversion improvement for the pretreated Pd/Cu/H-MFI with the loading amount of Pd higher than approximately 0.3%. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Copper ion-exchanged MFI; Pd-modification; Stability improvement; NO removal; Hydrothermal pretreatment

## 1. Introduction

The environmental problems caused by emissions from stationary sources and transportation vehicles are still rising despite of the recent advances in catalytic technologies based on NH<sub>3</sub>-reduction and the use of three-way catalysts. NO emitted from combustion facilities and diesel engines causes acid rain and photochemical smog [1]. A number of studies concerning various types of catalyst for NO removal have been investigated. Cu ion-exchanged MFI type zeolite

(Cu/MFI) proposed by Iwamoto et al. is effective for NO removal under the excess oxygen condition [2,3]. Other kinds of metal ion-exchanged MFI such as gallium [4,5], iron [6,7], cobalt [8–10], cerium [11,12], platinum [13], palladium [14] were also studied for the reaction. In addition, other groups of active catalysts such as transition metal and/or metal oxide (Cu, Co, Mn, Fe, Cr, V, Ag) were also concerned [15–19]. Nevertheless, those types of catalyst referred above suffer from the deactivation under the condition of high temperature and the presence of steam possibly occurred in practical use [20–22]. On the other hand, platinum group metal catalysts have also been studied for NO conversion [23,24], and it is known that platinum group metal catalysts are highly resistant to the

\* Corresponding author. Tel.: +662-218-6711;  
fax: +662-218-6769.  
E-mail address: piyasan.p@chula.ac.th (P. Prasertthdram).

presence of steam [25]. Based on these reasons, therefore, this work aims to investigate the influence of severe conditions on the activity of Cu ion-exchanged MFI. The effect of Pd on the stability improvement of the catalyst for NO removal under such severe conditions was also studied.

## 2. Experimental

### 2.1. Catalyst preparation

MFI zeolite with Si/Al ratio of 50 in Na form supplied by ALSI-PENTA ZEOLITE SM-55 was used. The catalyst in  $\text{NH}_4$  form was made by ion exchange with ammonium nitrate solution to obtain  $\text{NH}_4$ -MFI. It was then washed, dried and calcined at  $540^\circ\text{C}$  for 3.5 h in air to convert into the protonated form (H-MFI). Cu ion-exchanged H-MFI and Pd ion-exchanged H-MFI, designated as Cu/H-MFI and Pd/H-MFI were prepared using an ion-exchange procedure at 80 and  $90^\circ\text{C}$ , respectively. They were washed, dried and calcined at  $540^\circ\text{C}$  for 3.5 h in air. For Pd/Cu/H-MFI, successive ion-exchange of H-MFI with palladium and then copper was carried out using the method described above. The amount of palladium was varied in the range of 0.1–1 wt.% Pd. In order to investigate the stability of the catalyst under severe conditions, the catalysts were heated in a He stream and the temperature was raised from room temperature to  $600^\circ\text{C}$  and 600 to  $800^\circ\text{C}$  with constant heating rates of 10 and  $1.67^\circ\text{C}/\text{min}$ , respectively. The catalyst samples were then kept at  $800^\circ\text{C}$  for 12 h under He atmosphere to which 10 mol% of water vapor were added. The catalysts were then cooled down to room temperature in the He stream. The catalysts, thus, obtained in powder form were tableted, crushed and sieved to 12–22 mesh for the reaction test.

### 2.2. Catalyst characterization

The bulk composition and BET surface area of the samples were measured by inductively coupled plasma analysis (ICP JOBIN YVON model JY 2000 S) and surface area analyzer (ASAP 2000, Micromeritics) using liquid nitrogen as a probe molecule, respectively. The crystallinity of MFI was estimated by using a SIEMENS D 5000 diffractometer with

Cu  $\text{K}\alpha$  radiation. Quantitative analysis of tetrahedral alumina in zeolites was conducted by Al magnetic angle spinning nuclear magnetic resonance ( $^{27}\text{Al}$  MAS NMR). The  $^{27}\text{Al}$  MAS NMR spectra were obtained using a BRUKER DPX-300 spectroscopy operating at 78.2 MHz. The morphology of the catalysts was observed using a scanning electron microscope (JEOL, JSM-35). For ESR measurement, to determine the state of  $\text{Cu}^{2+}$  in the catalysts, the sample pretreatment was made by calcining an exact weight of catalyst at  $500^\circ\text{C}$  for 2 h to remove adsorbed species.

### 2.3. Reaction method and analysis

The catalytic reaction test was performed using a tubular flow reactor at atmospheric pressure. A 0.25 g portion of the catalyst was packed into a quartz tube reactor of 6 mm i.d. It was heated from the ambient temperature to  $600^\circ\text{C}$  in a He flow at a constant heating rate of  $10^\circ\text{C}/\text{min}$ , and maintained at that temperature for 30 min. A feed gas composed of 1000 ppm NO, 1000 ppm  $n\text{-C}_8\text{H}_{18}$ , 2 mol%  $\text{O}_2$ , and 10 mol%  $\text{H}_2\text{O}$  balanced with He was then introduced into the reactor with a GHSV of  $30,000\text{ h}^{-1}$ . Every 30 min, after the catalytic activity was at steady state, the effluent gas composition was analyzed using gas chromatographs (SHIMADZU GC-8ATP with MS-5A column and SHIMADZU GC-8AIT with porapak Q column) equipped with integrators. The reactor temperature was then cooled down from 600 to  $200^\circ\text{C}$  with a constant cooling rate of  $10^\circ\text{C}/\text{min}$ . After every  $50^\circ\text{C}$  drop in temperature effluent gas was analyzed using the same method. The catalytic activities of NO reduction and  $n$ -octane combustion were investigated as the amount of nitrogen and carbon oxides ( $\text{CO}_X = \text{CO} + \text{CO}_2$ ) produced, respectively.

## 3. Results and discussion

### 3.1. Changes in physical properties upon pretreatment

Table 1 shows the physical properties of the catalysts before and after pretreatment. Crystallinity, as determined by XRD profiles, was calculated using the intensity of diffraction line at  $23.5^\circ 2\theta$ , which was compared with that of H-MFI as a reference. As shown in Table 1, H-MFI and Cu/H-MFI considerably lost

Table 1  
Data for bulk composition, BET surface area and crystallinity of catalysts

Catalyst	BET surface area (m <sup>2</sup> /g catalyst)		Me/Al atomic ratio				Crystallinity <sup>a</sup> (%)	
	Fresh	Pretreated	Cu/Al		Pd/Al		Fresh	Pretreated
			Fresh	Pretreated	Fresh	Pretreated		
H-ZSM-5	350	295	–	–	–	–	100	48
Cu/HZSM-5	326	286	0.911	0.913	–	–	100	85
0.1% Pd/Cu/HZSM-5	310	275	0.890	0.892	0.012	0.012	99	87
0.2% Pd/Cu/HZSM-5	310	289	0.901	0.892	0.023	0.022	99	97
0.3% Pd/Cu/HZSM-5	302	290	0.865	0.863	0.035	0.034	99	98
0.4% Pd/Cu/HZSM-5	300	289	0.864	0.860	0.042	0.048	98	98
0.6% Pd/Cu/HZSM-5	298	280	0.849	0.850	0.072	0.074	97	98
0.8% Pd/Cu/HZSM-5	298	288	0.827	0.824	0.088	0.089	97	97
1.0% Pd/Cu/HZSM-5	298	286	0.821	0.821	0.112	0.11	98	97

<sup>a</sup> Intensity are reference to diffraction line at 23.5° 2θ.

their crystallinity after pretreatment due to the structural collapse. Such tendency of loss in crystallinity and BET surface area was reduced with the presence of Pd, and no significant loss of crystallinity was observed on Pd/Cu/H-MFI catalysts with the amount of Pd up to 0.2 wt.% or more. This suggests the stabilization effect of Pd on MFI framework structure. It should be noted that though some loss of structure occurred after pretreatment, especially for the catalysts without Pd, the content of Cu or Pd loaded was not significantly changed by the pretreatment as seen from the ICP data. This indicated that there was no significant loss of metal species such as evaporation of metal due to the hydrothermal treatment. The result of <sup>27</sup>Al MAS NMR of the catalysts before and after pretreatment is shown in Fig. 1. The fresh catalysts exhibited only one sharp signal at ca. 50 ppm, which is assigned to the tetrahedral aluminum in the zeolite lattice [26–28]. Hydrothermal treatment of H-MFI, Cu/H-MFI and 0.1% Pd/Cu/H-MFI at 800°C caused the appearance of a new <sup>27</sup>Al MAS NMR signal at 0 ppm assigned to extra-framework Al atoms in octahedral co-ordination [26–28]. This is consistent with the previous report of loss in activity and stability after steam pretreatment due to framework dealumination of the zeolite [27]. However, only one signal of <sup>27</sup>Al MAS NMR at around 50 ppm was observed on Pd/Cu/H-MFI with 0.3 wt.% Pd loading or higher even after pretreatment and no peak relating to octahedral aluminum was noticed. This suggests that the

presence of a certain amount of Pd, approximately 0.3 wt.% loading as observed here, could stabilize the MFI framework structure by preventing the occurrence of dealumination.

Figs. 2–5 show the ESR spectra of Cu/H-MFI and 0.3% Pd/Cu/H-MFI. The spectra of both fresh catalysts were similar in shape which indicated the presence of two Cu<sup>2+</sup> species located in two different co-ordinations (i.e. a square pyramidal environment with  $g_{\parallel} = 2.31\text{--}2.33$ ,  $A_{\parallel} = 149\text{ G}$  (Cu<sup>A</sup>) and a square planar one with  $g_{\parallel} = 2.27\text{--}2.29$ ,  $A_{\parallel} \sim 157\text{ G}$  (Cu<sup>B</sup>), as is typically found in the literature [29–32]. Shelef [33] proposed that Cu<sup>2+</sup> in a square planar configuration is very active for NO removal. Since the features of the Cu<sup>2+</sup> species were the same for fresh Cu/H-MFI and fresh 0.3% Pd/Cu/H-MFI, it can be suggested that Pd does not change the configuration of Cu. In addition, the 0.3% Pd/Cu/H-MFI after pretreatment exhibited the same ESR features as the fresh one. Nevertheless, the ESR spectra of pretreated Cu/H-MFI and 0.1% Pd/Cu/H-MFI were different from those of the fresh one. Not only had the intensity of the ESR spectra reduced but the shape of signal also changed in case of the pretreated Cu/H-MFI and 0.1% Pd/Cu/H-MFI. This means that the amount of Cu<sup>2+</sup> species in both the square pyramidal and square planar co-ordination was diminished due to pretreatment. Additionally, a new spectrum with  $g_{\parallel} = 2.30$ ,  $A_{\parallel} = 160\text{ G}$  (Cu<sup>C</sup>) appeared indicating a change in the co-ordination of Cu<sup>2+</sup>, although, part of the two Cu<sup>2+</sup> species observed

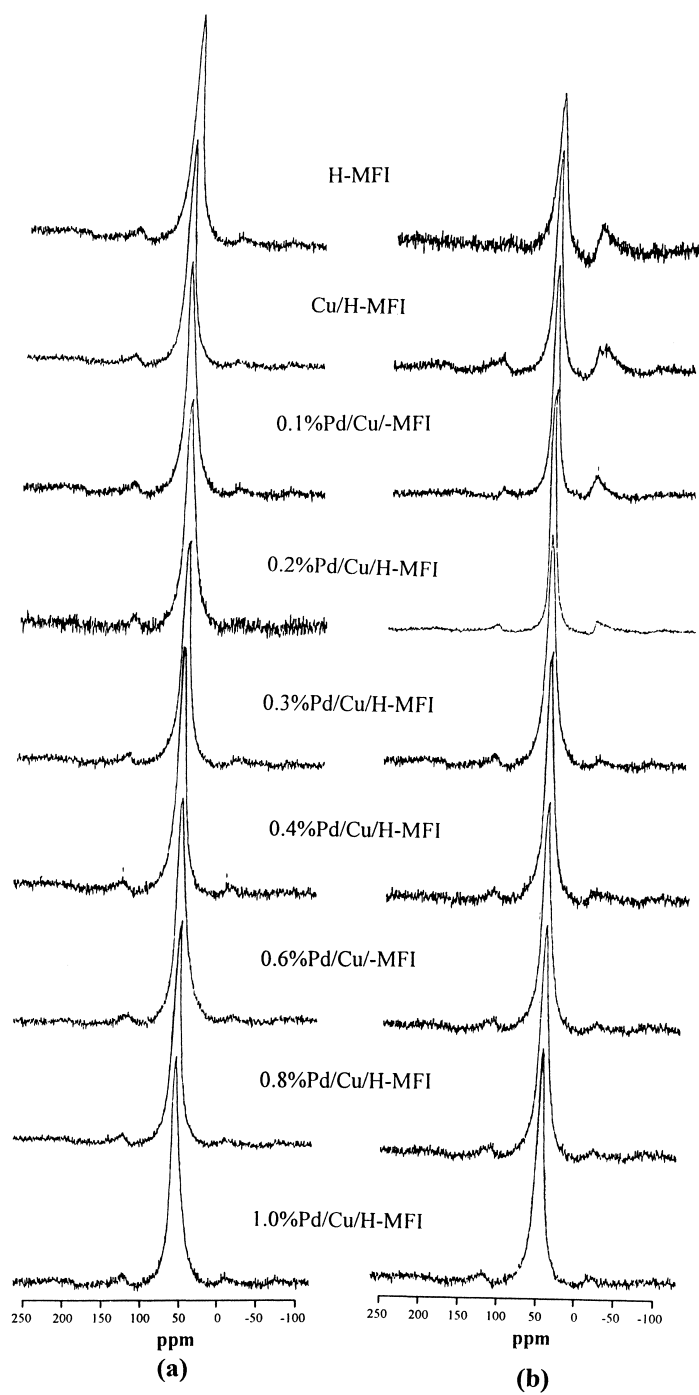


Fig. 1.  $^{27}\text{Al}$  MAS-NMR spectra of (a) fresh and (b) pretreated catalysts.

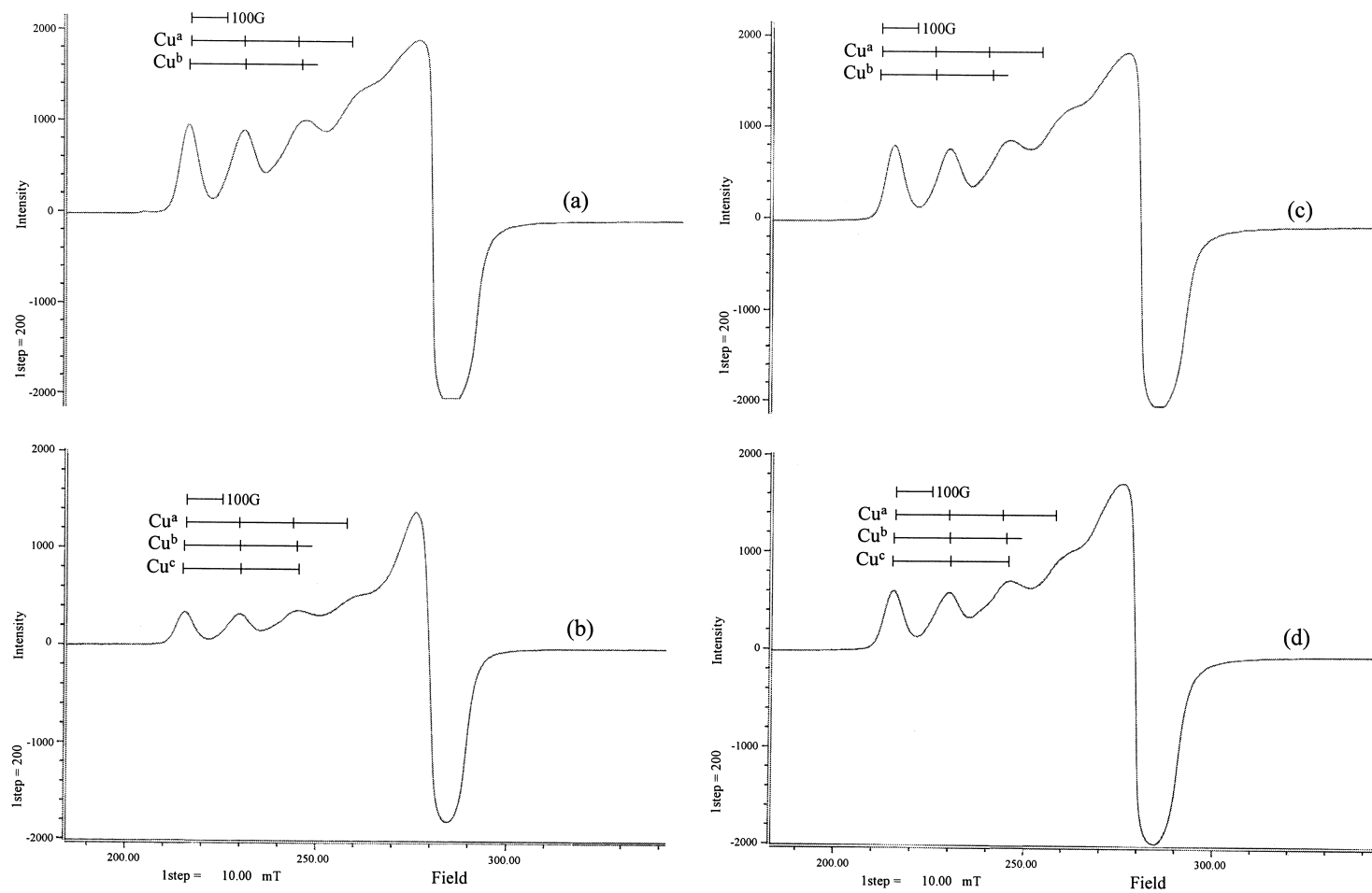


Fig. 2. ESR spectra of high spin  $\text{Cu}^{2+}$  of Cu/H-MFI and Pd/Cu/H-MFI with and without pretreatment at  $800^\circ\text{C}$ , 10%  $\text{H}_2\text{O}$ : (a) fresh Cu/H-MFI; (b) pretreated Cu/H-MFI; (c) fresh 0.1% Pd/Cu/H-MFI; (d) pretreated 0.1% Pd/Cu/H-MFI.

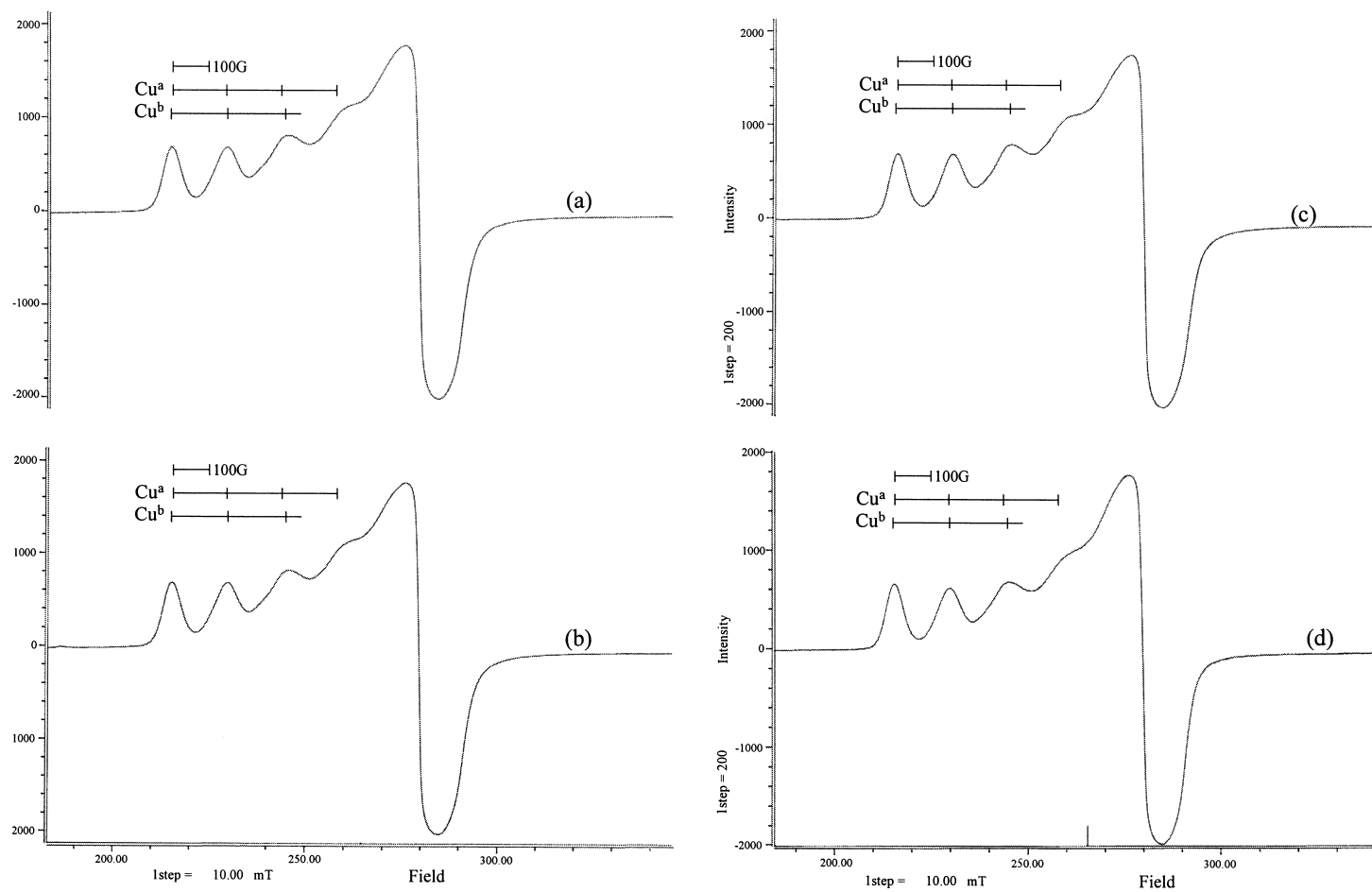


Fig. 3. ESR spectra of high spin  $\text{Cu}^{2+}$  of Cu/H-MFI and Pd/Cu/H-MFI with and without pretreatment at  $800^\circ\text{C}$ , 10%  $\text{H}_2\text{O}$ : (a) fresh 0.2% Pd/Cu/H-MFI; (b) pretreated 0.2% Pd/Cu/H-MFI; (c) fresh 0.3% Pd/Cu/H-MFI; (d) pretreated 0.3% Pd/Cu/H-MFI.

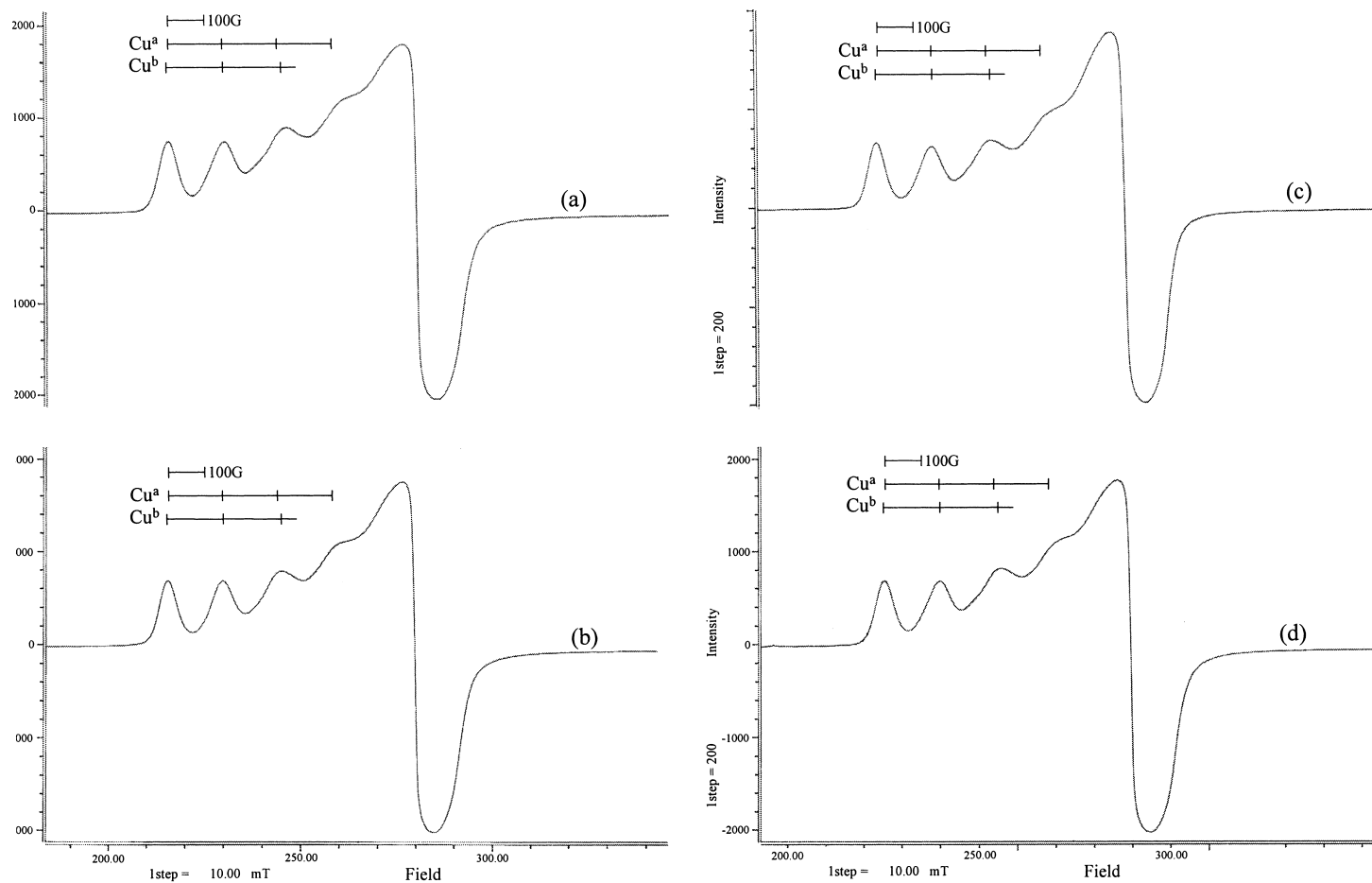


Fig. 4. ESR spectra of high spin  $\text{Cu}^{2+}$  of Cu/H-MFI and Pd/Cu/H-MFI with and without pretreatment at  $800^\circ\text{C}$  10%  $\text{H}_2\text{O}$ : (a) fresh 0.4% Pd/Cu/H-MFI; (b) pretreated 0.4% Pd/Cu/H-MFI; (c) fresh 0.6% Pd/Cu/H-MFI; (d) pretreated 0.6% Pd/Cu/H-MFI.

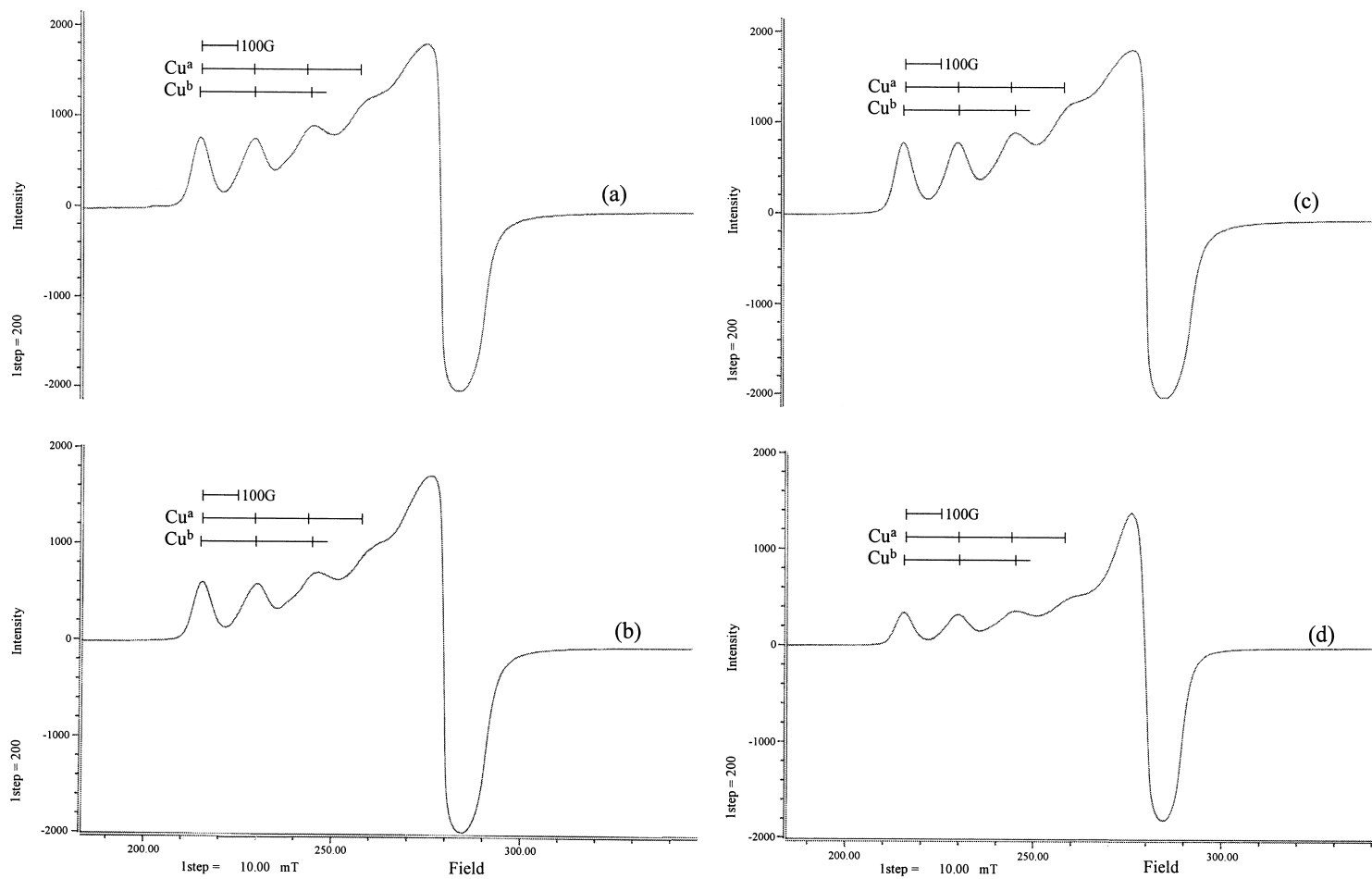
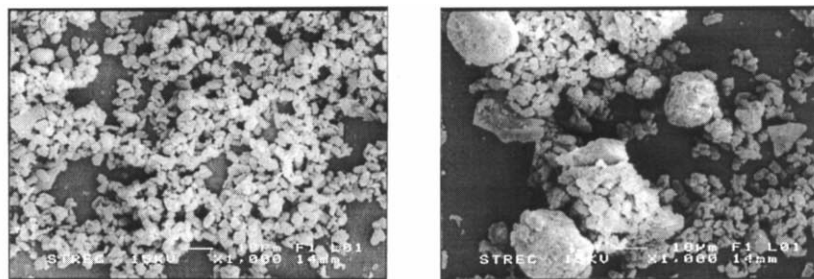
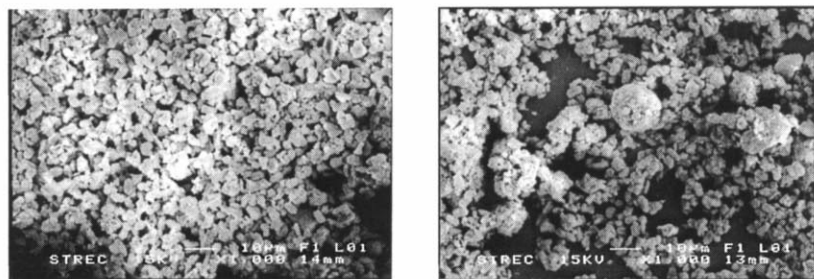


Fig. 5. ESR spectra of high spin  $\text{Cu}^{2+}$  of Cu/H-MFI and Pd/Cu/H-MFI with and without pretreatment at  $800^\circ\text{C}$  10%  $\text{H}_2\text{O}$ : (a) fresh 0.8% Pd/Cu/H-MFI; (b) pretreated 0.8% Pd/Cu/H-MFI; (c) fresh 1.0% Pd/Cu/H-MFI; (d) pretreated 1.0% Pd/Cu/H-MFI.

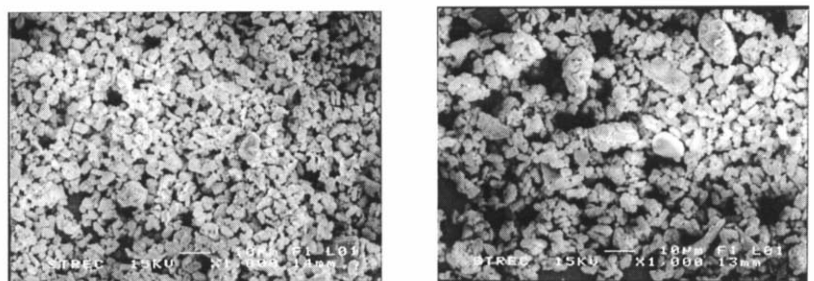




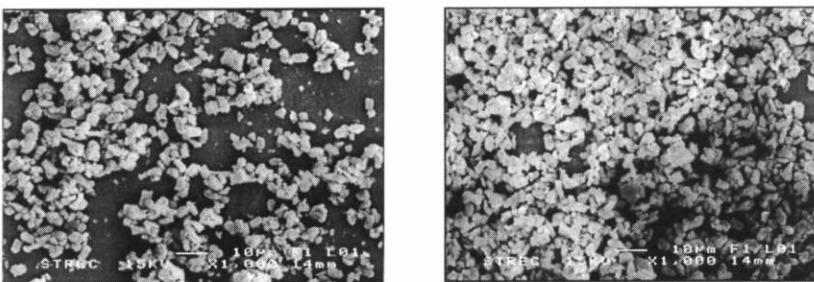
Cu/H-ZSM-5



0.1%Pd/Cu/HZSM-5



0.2%Pd/Cu/H-ZSM-5



0.3%Pd/Cu/H-ZSM-5

(a) Fresh

(b) Pretreated

Fig. 6. Scanning electron micrographs of catalysts: (a) fresh and (b) pretreated catalysts.

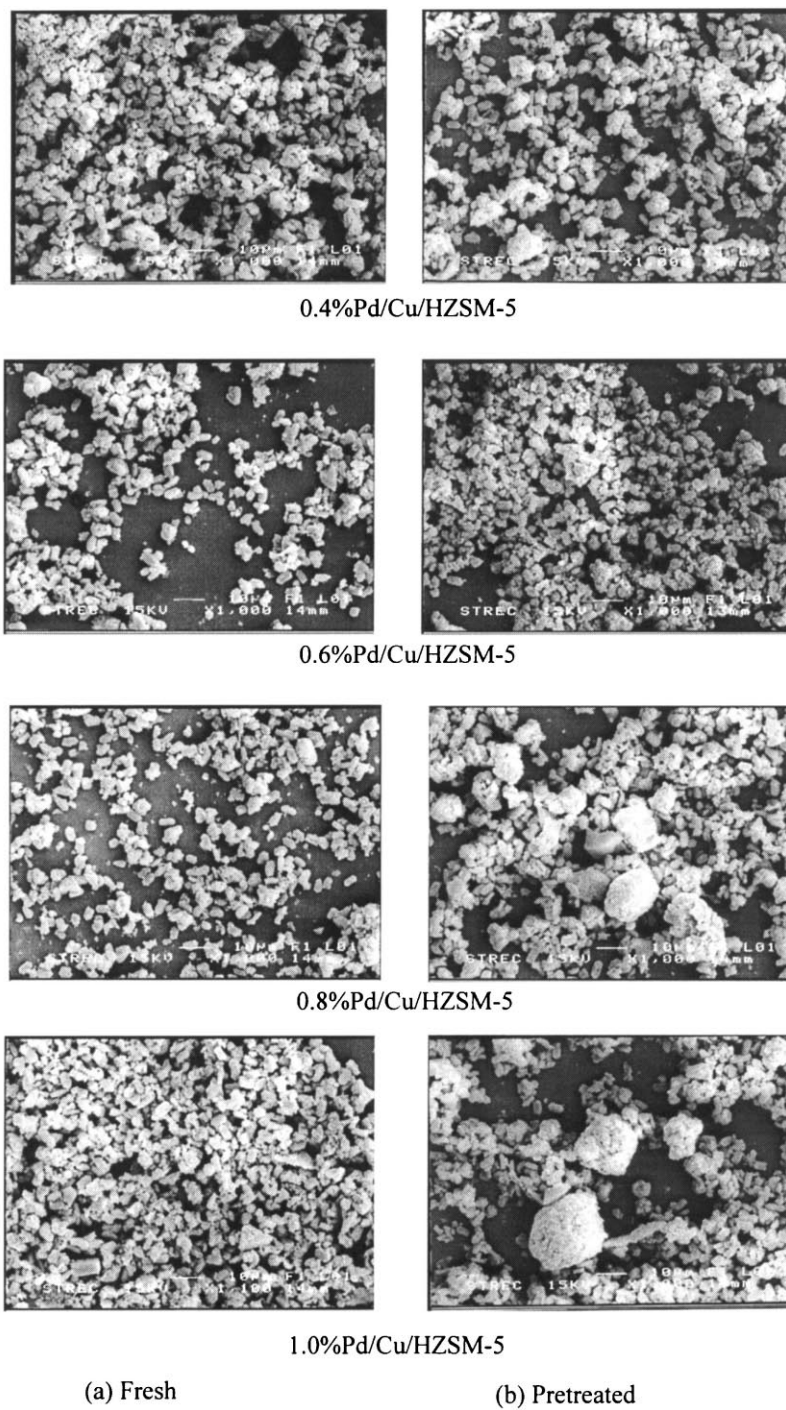


Fig. 7. Scanning electron micrographs of catalysts: (a) fresh and (b) pretreated catalysts.

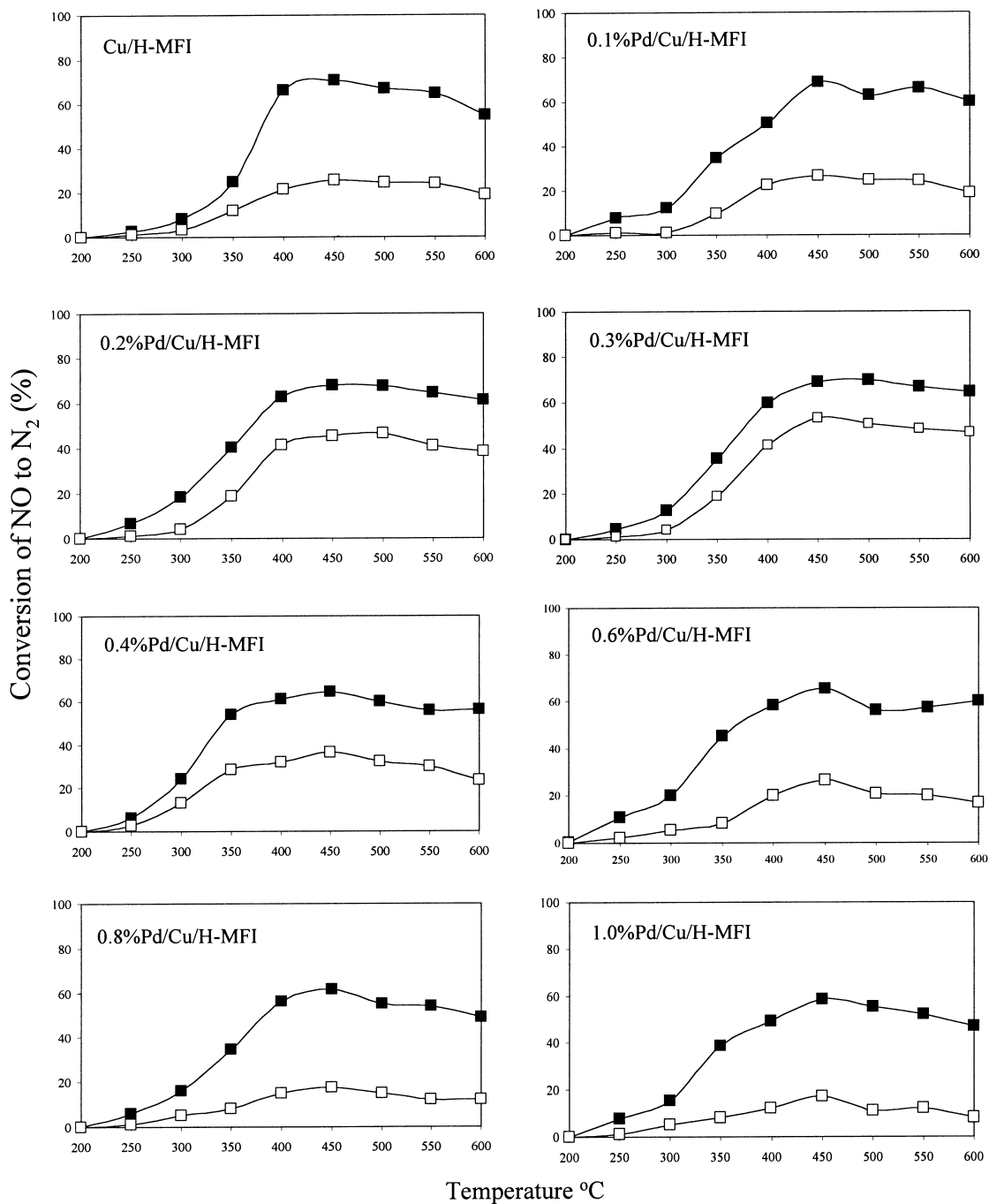


Fig. 8. The effect of hydrothermal-treatment on the activity of NO conversion of Cu/H-MFI, Pd/Cu/H-MFI: (close symbol) fresh catalysts; (open symbol) pretreated catalysts.

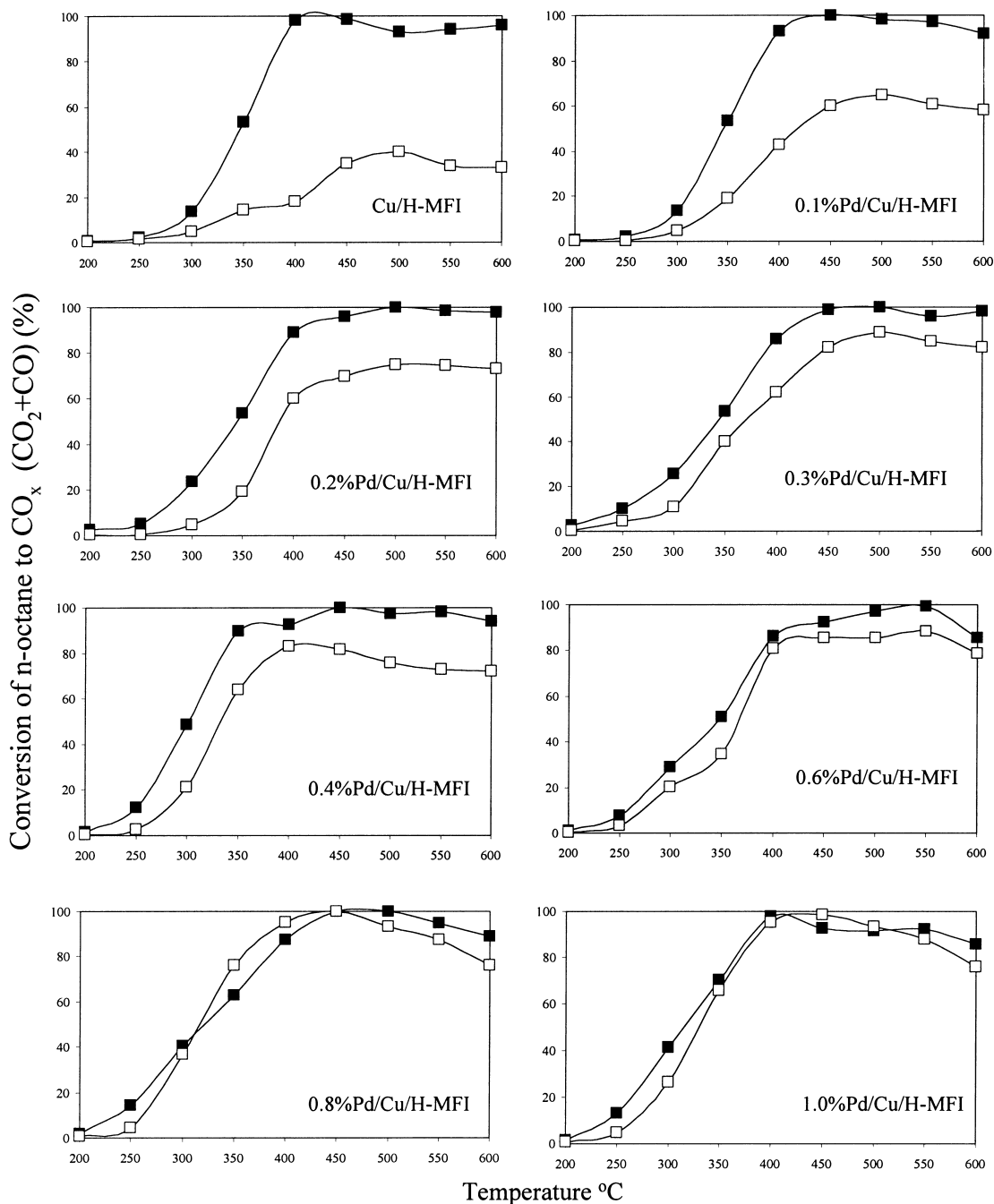


Fig. 9. The effect of hydrothermal-treatment on the activity of *n*-octane conversion of Cu/H-MFI, Pd/Cu/H-MFI: (close symbol) fresh catalysts; (open symbol) pretreated catalysts.

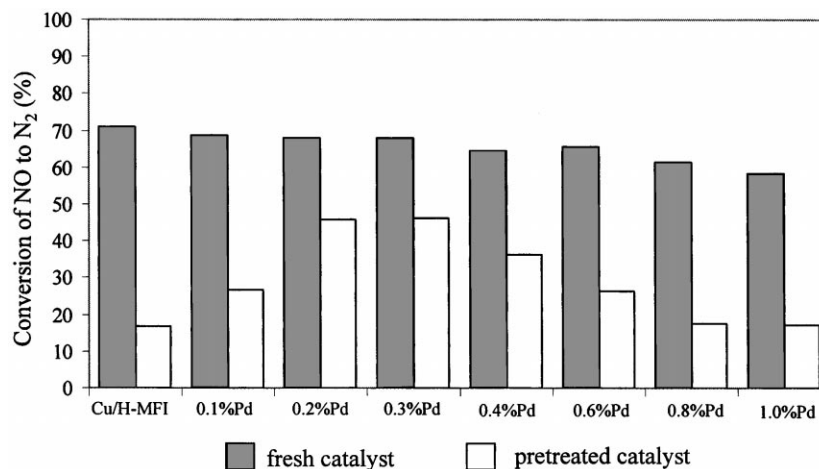


Fig. 10. Maximum NO conversion of catalysts.

in the fresh samples still remain. This new signal may be attributed to the migration of Cu ions to the locations near five-membered oxygen rings as suggested by Iwamoto et al. [34]. On the other hand, the pretreated catalysts with 0.8–1.0 wt.% Pd loading did not show any change of co-ordinated  $\text{Cu}^{2+}$  species, however, some decrease of the intensity of ESR spectra has been observed. This means that the amounts of two  $\text{Cu}^{2+}$  species in both square pyramidal and square planar co-ordination are diminished due to some changes in Pd and Cu on H-MFI such as alloying and/or oxides formation.

The scanning electron micrographs (SEM) of the catalysts before and after hydrothermal treatment are shown in Figs. 6 and 7. Cu/H-MFI showed an obvious agglomeration after pretreatment. As for Pd/Cu/H-MFI with 0.3–0.6 wt.% Pd loading, such agglomeration seems to be prevented considerably. However, the larger crystallite size was clearly observed on the samples with 0.8 and 1.0 wt.% Pd loading. This suggests that there should be some change in the Pd and Cu on the H-MFI, such as alloying, due to the hydrothermal treatment provided that the Pd loading is higher than a certain level. It is interesting to note that an optimum amount of Pd is necessary to stabilize the crystal morphology of Cu/H-MFI subjected to hydrothermal treatment at the temperature as high as 800°C.

### 3.2. Catalytic performance

NO conversion reactions were carried out on the catalysts both with and without pretreatment. The effect of reaction temperatures on NO conversion to  $\text{N}_2$  for Cu/H-MFI and Pd/Cu/H-MFI with different amount of Pd is shown in Fig. 8. The conversion of *n*-octane to carbon oxides (CO and  $\text{CO}_2$ ) is also demonstrated. It has been found that the conversion of NO markedly decreased at any reaction temperatures after hydrothermal treatment. However, the margin difference in catalyst activity before and after pretreatment was alleviated with the presence of a certain amount of Pd (ca. 0.2–0.3 wt.% loading). When the amount of Pd was raised higher than 0.3 wt.%, such beneficial effect on the stabilization of Cu/H-MFI was surprisingly lost. As for the conversion of *n*-octane to carbon oxides shown in Fig. 9, Cu/H-MFI also exhibited a substantial decrease in *n*-octane conversion upon pretreatment. The presence of Pd improved the *n*-octane conversion of the pretreated catalysts similar to NO conversion. Nevertheless, while the improvement of NO conversion for the pretreated catalysts was limited with the presence of a certain amount of Pd, the *n*-octane conversion was almost continuously improved with the increasing amount of Pd. Pd/Cu/H-MFI catalysts with 0.8 and 1.0 wt.% Pd loading, in particular, exerted more or less conversion of *n*-octane at the reaction

temperatures higher than 400°C after hydrothermal treatment. This indicates that *n*-octane would not be effective for use in NO conversion on Pd/Cu/H-MFI with high Pd loading. Therefore, this should be one of the reasons for the limitation of NO conversion improvement on Pd/Cu/H-MFI after hydrothermal treatment by an optimum amount of Pd. In addition, the possibility of any changes in Pd and Cu on H-MFI such as alloying and/or the formation of palladium oxides in case of high Pd loading should not be ruled out.

#### 4. Conclusions

The MFI framework stability of Cu/H-MFI was maintained after pretreatment at 800°C in a He stream with 10 mol% H<sub>2</sub>O by the presence of Pd. The dealumination of tetrahedral Al in MFI framework was completely prevented when the amount of Pd loading was 0.3 wt.% or higher. The stabilization effects of Pd are due to the prevention of dealumination and the ability to maintain the active Cu<sup>2+</sup> species. The presence of an optimum amount of Pd in Pd/Cu/H-MFI, approximately 0.2–0.3 wt.% loading, improved the catalysts stability for NO removal under hydrothermal treatment conditions as concluded in Fig. 10. Further loading of Pd higher than 0.3 wt.% may cause some changes in Pd and Cu on H-MFI, such as alloying and/or palladium oxides formation, leading to some loss of Cu<sup>2+</sup> active species for NO removal. This results in the limitation of NO conversion improvement for the pretreated Pd/Cu/H-MFI with Pd loading higher than approximately 0.3 wt.%.

#### Acknowledgements

The authors wish to express their deep appreciation to the Thailand Research Fund (TRF) for the financial support to this work.

#### References

- [1] R. Impens, *Stud. Surf. Sci. Catal.* 30 (1987) 11.
- [2] M. Iwamoto, H. Yahiro, K. Tanda, N. Mizuno, Y. Mine, S. Kagawa, *J. Phys. Chem.* 95 (1991) 3727.
- [3] M. Iwamoto, H. Yahiro, N. Mizuno, W. Zhang, Y. Mine, H. Furukawa, S. Kagawa, *J. Phys. Chem.* 96 (1992) 9360.
- [4] R. Burch, S. Scire, *Appl. Catal. B* 3 (1994) 295.
- [5] K. Yogo, S. Tanaka, M. Ihara, T. Hishiki, E. Kikuchi, *Chem. Lett.* (1992) 1025.
- [6] T. Tabata, M. Kokitsu, O. Okada, *Appl. Catal. B* 2 (1993) L1.
- [7] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu, N. Mizuno, *Appl. Catal.* 69 (1991) L15.
- [8] S. Sato, H. Hirabayashi, H. Yahiro, N. Mizuno, M. Iwamoto, *Catal. Lett.* 12 (1992) 193.
- [9] Y. Li, J.N. Armor, *Appl. Catal. B* 2 (1993) 239.
- [10] Y. Li, J.N. Armor, *Appl. Catal. B* 3 (1993) 55.
- [11] A.W. Aylor, L.J. Lobree, J.A. Reimer, A.T. Bell, *Stud. Surf. Sci. Catal.* 101 (1996) 661.
- [12] C. Yokoyama, M. Misono, *Catal. Lett.* 29 (1994) 1.
- [13] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki, T. Ito, *Catal. Lett.* 6 (1990) 239.
- [14] H. Hirabayashi, H. Yahiro, N. Mizuno, M. Iwamoto, *Chem. Lett.* (1992) 2235.
- [15] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, *Appl. Catal.* 64 (1990) L1.
- [16] M. Tabata, H. Tsuchida, K. Miyamoto, T. Yoshinari, H. Yamazaki, H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, *Appl. Catal. B* 6 (1995) 169.
- [17] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, M. Tabata, *Appl. Catal.* 75 (1991) L1.
- [18] T. Miyadera, *Appl. Catal. B* 2 (1993) 199.
- [19] Y. Ukisu, S. Sato, A. Abe, K. Yoshida, *Appl. Catal. B* 2 (1993) 147.
- [20] R. Burch, A. Ramli, *Appl. Catal. B* 15 (1998) 49.
- [21] K.C.C. Kharas, H.J. Robota, D.J. Liu, *Appl. Catal. B* 2 (1993) 225.
- [22] A. Martinez, S.A. Gomez, G.A. Fuentes, *Catal. Deactiv.* (1997) 225.
- [23] R. Burch, S. Scire, *Appl. Catal. B* 3 (1994) 295.
- [24] R. Burch, A. Ramli, *Appl. Catal. B* 15 (1998) 49.
- [25] H. Hirabayashi, H. Yahiro, N. Mizuno, M. Iwamoto, *Chem. Lett.* (1992) 2235.
- [26] T. Tanabe, T. Iijima, A. Kaiwai, J. Mizuno, K. Yokota, A. Isogai, *Appl. Catal. B* 6 (1995) 145.
- [27] P. Budi, E.C. Hyde, R.F. Howe, *Catal. Lett.* 41 (1996) 47.
- [28] T. Tanabe, M. Kokitsu, O. Okada, T. Nakayama, T. Yasumatsu, H. Sakane, *Stud. Surf. Sci. Catal.* 88 (1994) 409.
- [29] S. Matsumoto, K. Yokota, H. Doi, M. Kimura, K. Sekizawa, S. Kasahara, *Catal. Today* 22 (1994) 127.
- [30] W. Grunert, N.W. Hayes, R.W. Joyner, E.S. Shpiro, M.R.H. Siddiqui, N. Baeva, *J. Phys. Chem.* 98 (1994) 10832.
- [31] A.V. Kucherov, A.N. Shigapov, A.A. Ivanov, M. Shelef, *J. Catal.* 186 (1999) 334.
- [32] D. Tapanee, P. Piyasan, J.B. Kim, T. Inui, *Adv. Environ. Res.* 3 (2000) 450.
- [33] M. Shelef, *Catal. Lett.* 15 (1992) 305.
- [34] M. Iwamoto, J. Wang, K.M. Sperati, T. Sajaki, M. Misono, *Chem. Lett.* (1997) 1281.