



The promotional effect of Cr on catalytic activity of Pt/ZSM-35 for H₂-SCR in excess oxygen

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ABSTRACT

Selective catalytic reduction of NO by hydrogen was studied over Cr modified Pt/ZSM-35 catalysts. The preparation process greatly influenced catalytic activity and sample prepared by co-impregnation method exhibits the best activity. In situ DRIFT studies revealed that on Pt–Cr/ZSM-35, (1) new Pt–NO^{δ+} and NO species adsorbed on Pt were detected upon NO + O₂ adsorption; (2) much more ammonia species were formed under reaction condition. Cr addition not only enhanced the adsorption of NO_x but also promoted the formation of surface NH₄⁺ species, which should be the origin of promotional effect of Cr on Pt/ZSM-35 for H₂-SCR reaction.

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1. Introduction

Selective catalytic reduction (SCR) is one of the most effective and practical method of NO_x abatement in excess oxygen. In the past decades, hydrocarbon [1–4], ammonia [5,6] and hydrogen [7–11] were reported to be active reductants in SCR reaction. Among the reductants mentioned, less processed and less expensive nontoxic hydrogen is particularly attractive because of the high activity of H₂-SCR at low temperatures of <200 °C.

Platinum catalysts [12,13] and palladium catalysts [14,15] have been shown to be active for H₂-SCR reaction. For these catalysts, high activity and selectivity at relatively low temperature is of great challenge. Different modifiers have been employed to improve the activity and selectivity for certain H₂-SCR catalyst. Yokota et al. reported that addition of Mo and Na [16], which reduced the oxidation efficiency of Pt, enhanced the NO conversion and N₂ selectivity of Pt/SiO₂. Burch and Machida also studied the effect of Na addition on the performance of Pt/Al₂O₃ [17] and Pt–ZSM-5 [18], respectively. However, the effect of Na addition is very much dependent on the types of catalyst supports. Kureti et al. [19] claimed that the introduction of tungsten to Pt/ZrO₂ increased the electron density on Pt and thus activated the catalyst for H₂-SCR. The addition of Ti species also enhanced the activity and selectivity of Pt/Si-MCM-41 in H₂-SCR by changing existence state and dispersion of platinum [20].

ZSM-35 with two-dimensional channel system (10 MR of 4.2*5.4 Å and 8 MR of 3.5*4.8 Å) belongs to FER family. In our previous work [21], the performance of several Pt based zeolites for H₂-SCR reaction was investigated. Among all catalysts, Pt/ZSM-35 exhibited the most attractive activity (120 °C NO conversion of 80.8%, S_{N2} of 68.5%), which is better than Pt/ZSM-5 (120 °C NO conversion of 65.3%, S_{N2} of 42.7%). In the present work, ZSM-35 zeolite is still of our most concern. Chromium is selected and used as promoter to improve the performance of Pt/ZSM-35 in H₂-SCR. In situ DRIFT study together with H₂-TPR is employed to get insight into the origin of the promotional effect of Cr.

2. Experimental

2.1. Catalysts preparation

Parent NaZSM-35 zeolite (SiO₂/Al₂O₃ = 30) were kindly provided by Prof. Yuan's group of Nankai University. The hydrogen form zeolite was obtained by ion exchange of calcined NaZSM-35 with aqueous solution of ammonium nitrate three times at 80 °C for 10 h, followed by drying at 70 °C overnight and calcined at 550 °C for 6 h.

0.5%Pt/ZSM-35 catalyst was prepared by wet incipient impregnation using K₂PtCl₆ as precursor. For modification, the HZSM-35 powders were suspended in an aqueous solution of Cr(NO₃)₃ and K₂PtCl₆. For comparison, the impregnation order of Cr and Pt was also changed: xPt/yCr/ZSM-35 catalysts were obtained by depositing K₂PtCl₆ onto y%Cr/ZSM-35 sample while yCr/xPt/ZSM-35 catalysts were obtained by depositing Cr(NO₃)₃ onto x%Pt/ZSM-35. After impregnation, all samples were dried at 70 °C overnight and calcined at 550 °C in air for 3 h.

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2.2. Catalysts characterization

Temperature programmed reduction by hydrogen (H_2 -TPR) was carried out in a quartz U-shaped reactor and H_2 consumption was monitored by a calibrated thermal conductivity detector (GOW-MAC Instruments). 0.2 g of the sample was pretreated at 400 °C for 30 min in air flow at 50 ml/min, followed by cooling down to 25 °C in N_2 flow. Then H_2 -TPR of the samples was started by exposure to 5% H_2 /Ar and elevating the temperature to 550 °C at a heating rate of 10 °C/min.

2.3. Activity test

The selective catalytic reduction of NO by hydrogen at atmospheric pressure was carried out in a fixed-bed flow microreactor. The typical reactant gas composition was NO (1000 ppm), H_2 (5000 ppm), O_2 (6.7%), and the balance He. The total flow of the inlet gas was set at 100 ml/min. A sample weight of 50 mg was employed, corresponding to the gas hourly space velocity (GHSV) of 80000/h. Prior to testing, the samples were activated in He (100 ml/min) at 500 °C for 30 min. The products were analyzed on-line using a gas chromatograph (HP 6890 series) equipped with a TCD detector. A molecular sieve 5A column served for the separation of H_2 , N_2 , O_2 , and a porapak Q column for the separation of N_2O and NO. Simultaneous analysis of NO, NO_2 and NH_3 was accomplished by a three-channel multigas sensor (Limas 11HW, ABB, Germany). The results are described in

terms of NO conversion, N_2 selectivity (S_{N_2}) and H_2 conversion, which are calculated on the basis of Eqs. (1)–(3):

$$NO \text{ conv.} = \frac{[NO]_0 - [NO]}{[NO]_0} \times 100\% \quad (1)$$

$$N_2 \text{ conv.} = \frac{[H_2]_0 - [H_2]}{[H_2]_0} \times 100\% \quad (2)$$

$$S_{N_2} = \frac{2[N_2]}{1000 \times (NO \text{ conv.})} \times 100\% \quad (3)$$

$[NO]_0$ represents the inlet concentration of NO, $[NO]$ represents the outlet concentration of NO, $[H_2]_0$ represents the inlet concentration of H_2 , $[H_2]$ represents the outlet concentration of H_2 and $[N_2]$ represents the outlet concentration of N_2 .

2.4. In situ DRIFT studies

The in situ DRIFT studies were carried out using a Bruker Tensor 27 spectrometer equipped with a heatable and evacuable IR cell with ZnSe windows, connected to a gas dosing system. For each experiment, the catalyst was activated at 400 °C under helium for 1 h, and then its absorption was measured at each desired temperature (coded as S_c). The IR spectra of surface species shown

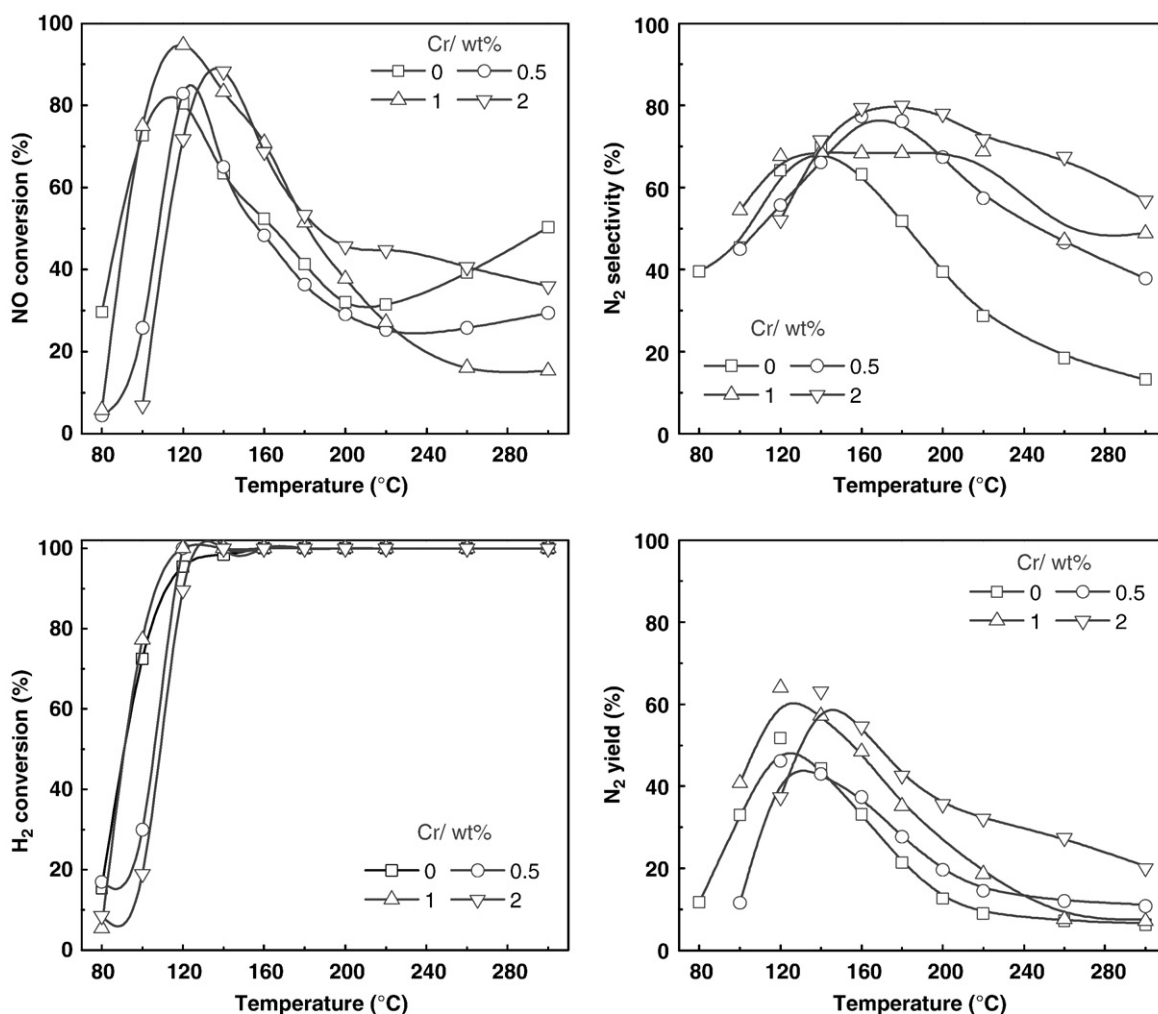


Fig. 1. Catalytic performance of 0.5Pt- x Cr/ZSM-35 in H_2 -SCR. Reaction conditions: 0.1% NO, 0.5% H_2 , 6.7% O_2 and He balance, GHSV = 80000 h^{-1} .

in the figures were obtained by subtracting S_c from each spectrum. The spectra were recorded with 4 cm^{-1} resolution and 50 scans. The reaction gas mixture used had the same composition as that applied for activity tests.

3. Results and discussion

3.1. Effect of Cr on H_2 -SCR activity

Fig. 1 depicts the catalytic performance of Pt–Cr/ZSM-35 catalysts with different chromium loading prepared by co-impregnation. The introduction of Cr species at different Cr loadings shows different effects on the performance of Pt–Cr/ZSM-35 catalysts. For 0.5%Pt–1%Cr/ZSM-35, a remarkable promotional effect is observed within the temperature range of 100–200 °C, and the NO conversion increases from 80.5% to 94.7% at 120 °C. The promotional effect of Cr can be observed more clearly in the profiles of N_2 yield vs. temperatures in Fig. 1. The maximal N_2 yield of ca. 64% is obtained on 0.5%Pt–1%Cr/ZSM-35, that is much higher than ca. 52% on 0.5%Pt/ZSM-35 at 120 °C. The maximal N_2 yield of ca. 63% is obtained on 0.5%Pt–2%Cr/ZSM-35 at 140 °C, which is 20 °C higher than that on 0.5%Pt–1%Cr/ZSM-35. The results indicate that 1 wt.% is the optimal Cr loading for modification of Pt/ZSM-35 by co-impregnation.

The influence of impregnation order of Cr on the catalytic activity was further investigated and the results are shown in Fig. 2. Obviously, 0.5%Pt–1%Cr/ZSM-35 catalyst prepared by co-impregna-

tion exhibits much more attractive activity than the other two catalysts prepared by sequential impregnation. It suggests that co-impregnation is the best way to introduce Cr to Pt/ZSM-35.

3.2. H_2 -TPR results

H_2 -TPR experiments are carried out to investigate the reducibility of metal species in the catalysts and the results are shown in Fig. 3. No peak corresponding to the reduction of platinum oxides can be observed on 0.5%Pt/ZSM-35. It indicates that Pt species are reduced from Pt^{4+} to Pt^0 and maintained in metallic state after preparation and calcination. For 1%Cr/ZSM-35, a broad peak centered at 430 °C is observed, assigned to the reduction of Cr^{VI} to Cr^{III} and perhaps to Cr^{II} [22]. It implies that Cr species are oxidized from Cr^{3+} to Cr^{6+} during preparation and calcination in air. When Pt and Cr is co-impregnated to ZSM-35, the reduction peak of Cr species shifted to ca. 285 °C with a small shoulder at ca. 471 °C. It indicates that the reduction of Cr on 0.5%Pt–1%Cr/ZSM-35 is much easier than that on 1%Cr/ZSM-35. Considering that H_2 would adsorb and dissociate on Pt rather than Cr, the promoted reduction of Cr reveals that H_2 , dissociated on Pt, maybe spillover to the surrounded Cr and reduces Cr at relatively low temperatures. It also suggests that an interaction exists between Pt and Cr species. According to Raman results that no chromate or dichromate surface species were detected (not shown here), we speculate that during co-impregnation, Cr species interact with acid sites and are fixed as cations near to Pt species on ZSM-35 zeolite.

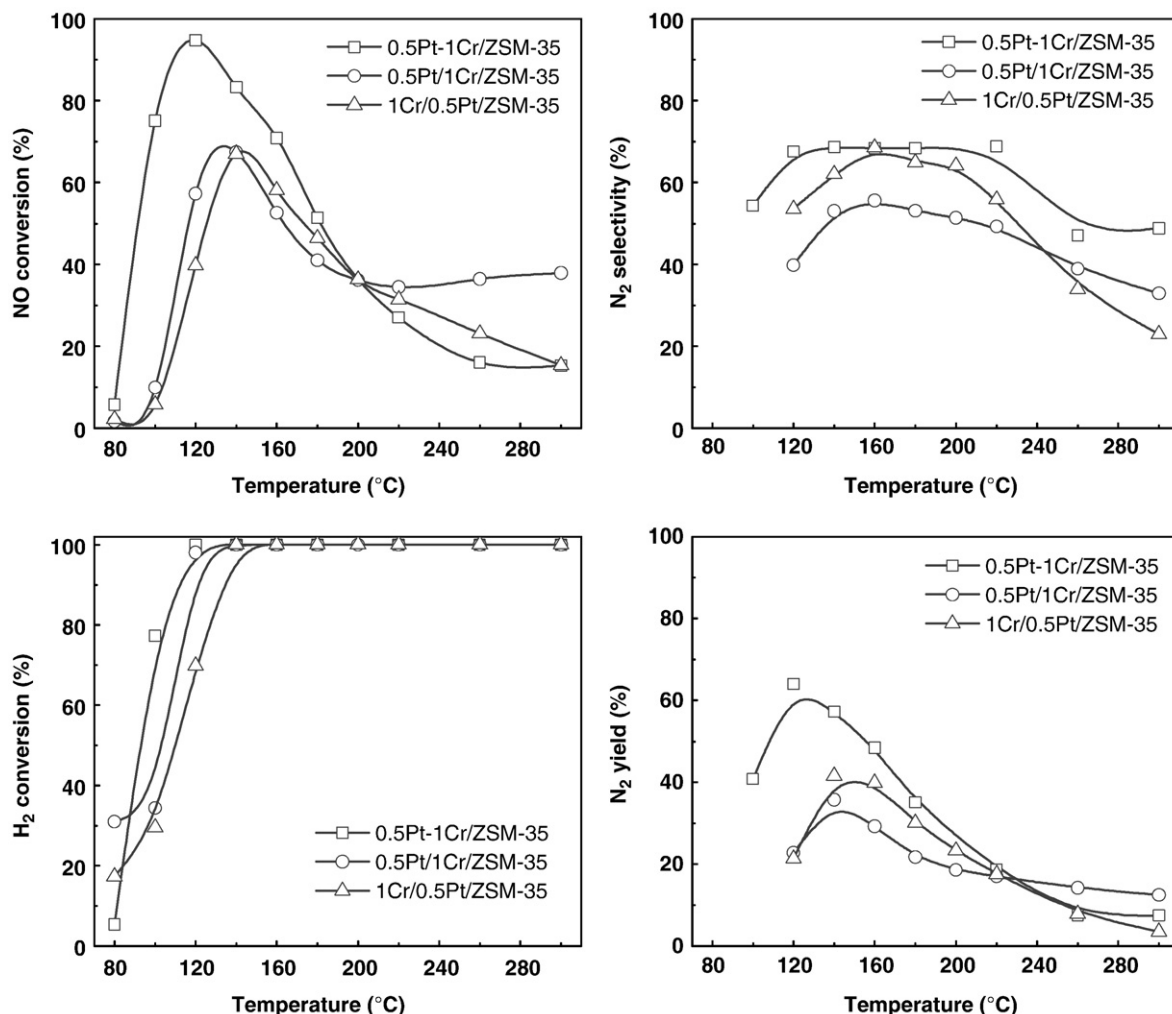


Fig. 2. Catalytic performance of 1%Cr and 0.5%Pt modified ZSM-35 in H_2 -SCR. Reaction conditions: 0.1% NO, 0.5% H_2 , 6.7% O_2 and He balance, GHSV = 80000 h^{-1} .

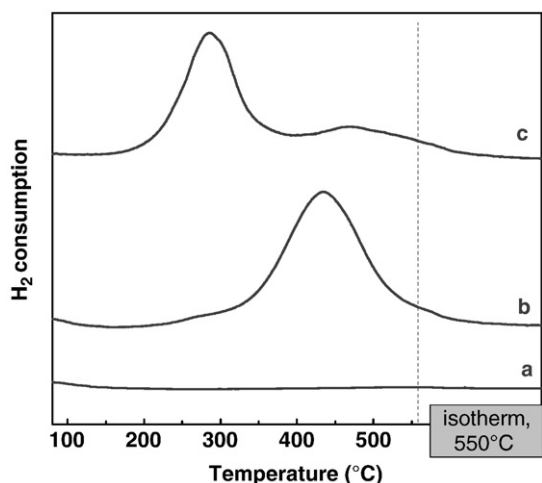


Fig. 3. H₂-TPR profiles of 0.5%Pt/ZSM-35 (a), 1%Cr/ZSM-35 (b) and 0.5%Pt-1%Cr/ZSM-35 (c).

3.3. In situ DRIFT study

In situ DRIFT spectra of surface species formed during NO-O₂ adsorption at 120 °C are shown in Fig. 4. For Pt/ZSM-35 and Cr/ZSM-35, bands at 1594 cm⁻¹ (due to bidentate nitrates [4,5]) and 1635 cm⁻¹ (nitrates [23] and adsorbed water [24,25]) appear. During pretreatment, water desorbed from catalyst may be adsorbed on the surface of IR cell. When catalyst is cooling down, water may be readsorbed on catalyst, which also gives band at 1635 cm⁻¹. So, when assigning this band, the contribution of water cannot be excluded. Nitrates mentioned above also appeared upon NO-O₂ adsorption on Pt-Cr/ZSM-35. Concomitantly, new surface N-containing species, charged NO⁶⁺ on Pt species (2009, 1889 cm⁻¹ [26,27]) and neutral NO species on Pt (1836 cm⁻¹ [26]) were formed. It implies that Cr addition promotes NO-O₂ adsorption and formation of surface N_xO_y species. Taking account of results in activity test, it may be one origin of the promotional effect of Cr on Pt/ZSM-35 for H₂-SCR reaction.

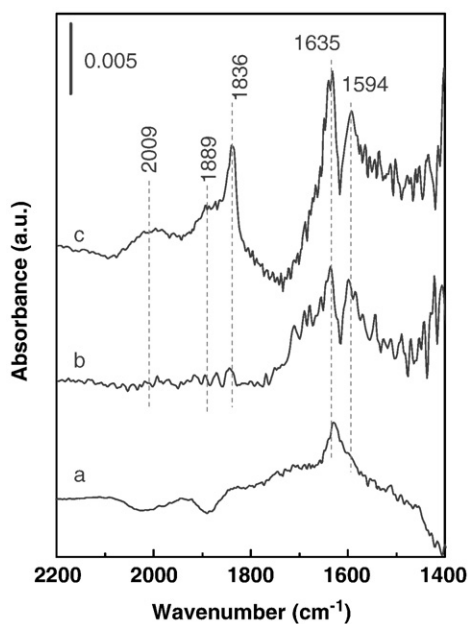


Fig. 4. DRIFT spectra of surface species formed on 1%Cr/ZSM-35 (a), 0.5%Pt/ZSM-35 (b) and 0.5%Pt-1%Cr/ZSM-35 (c) at 120 °C during NO + O₂ adsorption. Conditions: 0.1% NO, 6.7% O₂ and He balance.

Fig. 5 shows DRIFT spectra recorded during H₂-SCR reaction at 120 °C. For Pt/ZSM-35, bands of NH₄⁺ species at 3040, 2842, 1621 and 1450 cm⁻¹ [28,29] appear after steady reaction, together with band at 3282 cm⁻¹ due to NH stretching mode [30]. Bands due to adsorbed water at 3684, 3600–2800 and 1621 cm⁻¹ [25] are present as well, which overlap with bands corresponding to NH₄⁺ species. When Cr is introduced to Pt/ZSM-35 catalyst, more intense bands corresponding to NH₄⁺ species (e.g. at 1450 cm⁻¹) are clearly observed. In contrast, the band at 3684 cm⁻¹ due to adsorbed water on Pt-Cr/ZSM-35 is less intense than that on Pt/ZSM-35. Since the H₂ conversion on Pt/ZSM-35 and Pt-Cr/ZSM-35 at 120 °C is similar, the less intense band of adsorbed water suggests that Cr addition promotes the desorption of water. For Cr/ZSM-35, only adsorbed water is observed under the same condition. The above results indicate that Cr introduction not only promotes the formation of surface NH₄⁺ species but also promotes the desorption of formed water. NH₄⁺ ions on Brønsted acid sites, e.g. band at 1450 cm⁻¹, are observed as key intermediate for H₂-SCR on Pt catalysts supported on zeolites [12]. If NO is “hydrogenated” by H₂ to form NH₃, NH₃ can be stabilized on the Brønsted acid sites of zeolite as NH₄⁺ ions. It is well known that zeolite-fixed NH₄⁺ ions can reduce NO in excess oxygen to produce N₂ and H₂O [5,31]. For different Pt-zeolite catalysts, the highest intensity of IR bands corresponding to NH₄⁺ ions is observed on the catalyst with highest H₂-SCR activity [12]. For a given catalyst, higher H₂-SCR activity is obtained at the temperature when higher intensity of IR band corresponding to NH₄⁺ species is observed. So, the promotion of NH₄⁺ species formation should be another reason for the promotional effect of Cr on the catalytic activity in H₂-SCR reaction.

4. Conclusions

The catalytic activity of the bimetal based ZSM-35 zeolites in selective catalytic reduction of NO by hydrogen was studied. The preparation procedure had strong influence on catalytic activity of Cr modified Pt/ZSM-35. An attractive increase of NO conversion from 80.5% to 94.7% was obtained at 120 °C on Pt-Cr/ZSM-35 sample. These results indicated that some interaction between Pt and Cr might exist and led to the distinct activity of co-impregnation sample. In situ DRIFT study shown that new surface N-containing species, Pt-NO⁶⁺ and NO species adsorbed on Pt, were formed on Pt-Cr/ZSM-35 during NO + O₂ adsorption. It may be one origin of the enhanced activity of Pt-Cr/ZSM-35 in H₂-SCR reaction. Moreover, much more NH₄⁺ species were formed on Pt-Cr/ZSM-35 than that on Pt/ZSM-35. It indicates that the presence of Cr promotes the formation of surface NH₄⁺

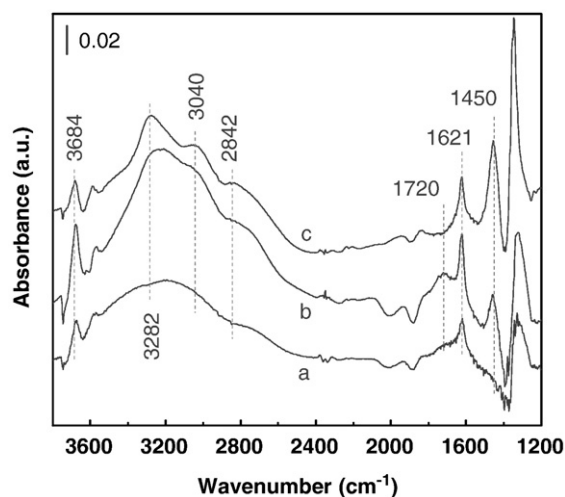


Fig. 5. DRIFT spectra of surface species formed on 1%Cr/ZSM-35 (a), 0.5%Pt/ZSM-35 (b) and 0.5%Pt-1%Cr/ZSM-35 (c) during H₂-SCR reaction at 120 °C. Reaction conditions: 0.1% NO, 0.5% H₂, 6.7% O₂ and He balance.

species. And it may be the other origin of promotional effect of Cr on the catalytic activity in H₂-SCR reaction.

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References

- [1] M. Shelef, *Chem. Rev.* 95 (1995) 209–225.
- [2] L.D. Li, J.X. Chen, S.J. Zhang, N.J. Guan, M. Richter, R. Eckelt, R. Fricke, *J. Catal.* 28 (2004) 12–22.
- [3] L.D. Li, F.X. Zhang, N.J. Guan, M. Richter, R. Fricke, *Catal. Commun.* 8 (2007) 583–588.
- [4] Q. Yu, X. Wang, N. Xing, H. Yang, S. Zhang, *J. Catal.* 245 (2007) 124–132.
- [5] M. Richter, A. Trunschke, U. Bentrup, K.W. Brzezinka, E. Schreier, M. Schneider, M. M. Pohl, R. Fricke, *J. Catal.* 206 (2002) 98–113.
- [6] G.S. Qi, R.T. Yang, *J. Catal.* 217 (2004) 434–441.
- [7] R. Burch, M.D. Coleman, *Appl. Catal. B* 23 (1999) 115–121.
- [8] M. Machida, S. Ikeda, D. Kurogi, T. Kijima, *Appl. Catal. B* 35 (2001) 107–116.
- [9] C.N. Costa, P.G. Savva, J.G. Fierro, A.M. Efstathiou, *Appl. Catal. B* 75 (2007) 149–158.
- [10] C.N. Costa, V.N. Stathopoulos, V.C. Belessi, A.M. Efstathiou, *J. Catal.* 197 (2001) 350–364.
- [11] A. Tomita, T. Yoshii, S. Teranishi, M. Nagao, T. Hibino, *J. Catal.* 247 (2007) 137–144.
- [12] J. Shibata, M. Hashimoto, K. Shimizu, H. Yoshida, T. Hattori, A. Satsuma, *J. Phys. Chem. B* 108 (2004) 18327–18335.
- [13] C.N. Costa, P.G. Savva, C. Andronikou, P.S. Lambrou, K. Polychronopoulou, V.C. Belessi, V.N. Stathopoulos, P.J. Pomonis, A.M. Efstathiou, *J. Catal.* 209 (2002) 456–471.
- [14] J.B. Yang, O.Z. Fu, D.Y. Wu, S.D. Wang, *Appl. Catal. B* 49 (2004) 61–65.
- [15] L.D. Li, F.X. Zhang, N.J. Guan, E. Schreier, M. Richter, *Catal. Commun.* 9 (2008) 1827–1832.
- [16] K. Yokota, M. Fukui, T. Tanaka, *Appl. Surf. Catal.* 121/122 (1997) 273–277.
- [17] R. Burch, M.D. Coleman, *J. Catal.* 208 (2002) 435–447.
- [18] M. Machida, T. Watanabe, *Appl. Catal. B* 52 (2004) 281–286.
- [19] F.J.P. Schott, P. Balle, J. Adler, S. Kureti, *Appl. Catal. B* 87 (2009) 18–29.
- [20] L.D. Li, P. Wu, Q. Yu, G.J. Wu, N.J. Guan, *Appl. Catal. B* 94 (2010) 254–262.
- [21] Q. Yu, F.X. Kong, G.J. Wu, L.D. Li, N.J. Guan, 7th APCSEET, China, 2009, p. 50.
- [22] K. Hadjiivanov, A. Penkova, R. Kefirov, S. Dzwigaj, M. Che, *Micropor. Mesopor. Mater.* 124 (2009) 59–69.
- [23] E. Ivanova, K. Hadjiivanov, D. Klissurski, M. Bevilacqua, T. Armaroli, G. Busca, *Micropor. Mesopor. Mater.* 46 (2001) 299–309.
- [24] K. Hadjiivanov, J. Saussey, J.L. Freysz, J.C. Lavalley, *Catal. Lett.* 52 (1998) 103–108.
- [25] U. Bentrup, A. Brückner, M. Richter, R. Fricke, *Appl. Catal. B* 32 (2001) 229–241.
- [26] P.G. Savva, A.M. Efstathiou, *J. Catal.* 257 (2008) 324–333.
- [27] T. Hirano, Y. Ozawa, T. Sekido, T. Ogino, T. Miyao, S. Naito, *Appl. Catal. A* 320 (2007) 91–97.
- [28] N. Macleod, R.M. Lambert, *Catal. Lett.* 90 (2003) 111–115.
- [29] G.S. Qi, R.T. Yang, F.C. Rinaldi, *J. Catal.* 237 (2006) 381–392.
- [30] G.S. Qi, R.T. Yang, R. Chang, *Appl. Catal. B* 51 (2004) 93–106.
- [31] M. Richter, R. Eckelt, B. Parltitz, R. Fricke, *Appl. Catal. B* 15 (1998) 129–146.