Enhanced catalytic performance of Co/MFI by hydrothermal treatment

Bin Wen and Wolfgang M.H. Sachtler *

V.N. Ipatieff Laboratory, Center for Catalysis and Surface Science, Department of Chemistry,
Northwestern University, Evanston, IL 60208, USA

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Hydrothermal treatment of Co/MFI catalysts at high temperature increases their performance for NO_x reduction with methane. As this treatment also shifts the TPR peak of isolated Co ions upward by 20 °C, the results suggest that the hydrothermal treatment induces transport of Co^{2+} ions from α to β positions.

KEY WORDS: NO_x reduction with methane; Co/MFI catalysts; positions of Co ions in zeolite cavities; ion mobility in zeolite channels.

1. Introduction

State of the art catalysis by transition metal ions in zeolite cages indicates that the activity of such ions depends critically on their location in the network of cavities. A case in point is the group of Co/MFI catalysts (the MFI zeolite is often called ZSM-5) that have the remarkable propensity of catalyzing the selective reduction of NO_x with CH_4 in the presence of a large excess of oxygen [1,2]. For this class of catalysts the group of Wichterlová [3,4] has identified three preferred locations of the Co^{2+} ions, which they call α, β and γ respectively (see figure 1). They also showed that the intrinsic activity is highest for the Co^{2+} ions at β sites in this zeolite [1]. These findings motivated us to try to enhance the performance of Co/MFI catalysts by transporting Co^{2+} ions from α to β positions of the MFI zeolite.

Among the numerous methods to prepare Co/MFI [5–7], sublimation of $CoBr_2$ onto H/MFI was found to result in catalysts with superior performance for NO reduction with CH_4 [6]. As it is also known that cobalt aquo complexes $[Co(H_2O)_x]^{2+}$ are much more mobile than bare Co ions [8,9], a hydrothermal catalyst treatment procedure was applied to transport Co^{2+} ions from their original positions to the β sites, which implies lowering the Gibbs free energy of the system.

2. Experimental

Co/MFI was prepared by subliming $CoBr_2$ (Aldrich) in an Ar flow at 600 °C onto heated H/MFI, prepared by ion exchange of Na/MFI with NH_4NO_3 followed by calcination. The Na/MFI was kindly provided by UOP (Lot #994995060001). The procedure was described previously in detail [10]. The catalysts prepared in this way will be called Co-sub. Elemental analysis via inductively coupled plasma spectroscopy gives the following compositions expressed as atomic ratios: $Co/Al = 1.01$, $Si/Al = 23$, $Na/Al = 0$. For the hydrothermal treatment, 7% H_2O in He flow at a rate of 80 ml/min was passed for 12 h through a quartz reactor loaded with the Co-sub catalyst at 500 °C. The resulting Co/MFI is called Co-sub-H_2O.

Catalysts were tested in a flow reactor where NO reduction with methane was carried out under the same conditions as described previously [11], but using a different GHSV. A typical feed contains 1000 ppm NO, 2000 ppm CH_4, and 2% O_2 with ultrahigh-purity He as diluent (GHSV = 30 000/h). The conversion of NO was calculated from the formation of N_2 and that of CH_4 from the CO_2 in the effluent. CO or N_2O have never been observed. The competitiveness factor CF is defined as the ratio of the actual N_2 production and the calculated maximum production at the actual CH_4 conversion. This CF value is a useful yardstick for the selectivity of a catalyst.

H_2-TPR was carried out with an H_2/Ar (5%) flow of 40 ml/min with a ramp of 8 °C/min, the details of which have been given previously [11,12]. Prior to this, the samples (50 mg) were treated for 1 h at 550 °C in pure O_2. The H_2 consumption was determined by a TCD detector, with H_2O being trapped in a dry ice-cooled trap. CuO/SiO_2 (quartz) was used as a standard to calibrate the consumption of H_2.

XRD patterns were recorded using a Rigaku diffractometer using CuKα radiation at 40 kV and 20 mA. Step-scan data were recorded at $2\theta = 10$–70° with a 0.02° step and 10 s counting time.

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* To whom correspondence should be addressed.
E-mail: wmhs@northwestern.edu

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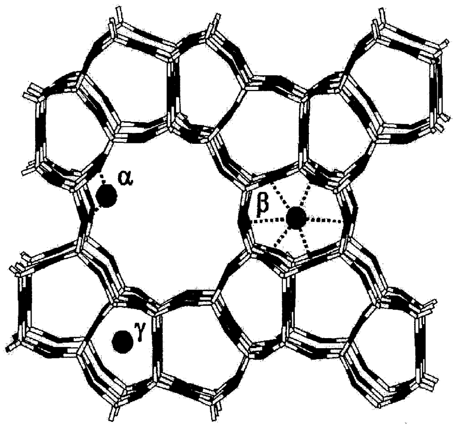

Figure 1. Sites occupied by Co ions in MFI, as given by Kaucký *et al.* [1].

Infrared spectra were obtained using a Nicolet 60 SX FTIR spectrometer equipped with a liquid N_2 cooled mercury cadmium telluride (MCT) detector. Details of the spectroscopic measurements are given elsewhere [11], but in the present study very thin self-supporting pellets ($\sim$3 mg/cm^2) have been used and 128 scans were accumulated with a spectral resolution of 1 cm^{-1}.

3. Results

NO and CH_4 conversions over Co-sub and Co-sub-H_2O at 500 °C are shown in figure 2 as a function of time on stream. The data show that water vapor pretreatment of Co/MFI for 12 h significantly enhances NO reduction to N_2 from 26 to 42%. Remarkably, the CH_4 conversion is reduced from 76 to 62%. It follows that the effect of the water treatment is an increase in catalyst selectivity, the competitiveness factor is doubled from 0.17 to 0.34. To our knowledge this is the first report of an increase in catalytic performance for NO reduction with CH_4 of any TM/zeolite catalyst that is achieved by a hydrothermal treatment. It is known that exposure of zeolite-based catalysts to water vapor often leads to a reduction of their catalytic performance. For the enhancement of NO_x reduction it is crucial that the hydrothermal treatment is carried out at high temperature. No significant change of the N_2 yield from NO reduction over Co-sub is observed after water treatment at 400 °C for 12 h. XRD patterns (not shown) of Co-sub and Co-sub-H_2O are essentially identical, indicating that the water vapor pretreatment at 500 °C does not change the zeolite lattice parameters, although it may create some voids locally [13]. Neither CO_3O_4 nor CoO was detected by XRD.

To identify the effects of the hydrothermal treatment on the structure of the catalyst, the H_2-TPR profiles are compared in figure 3 for the four stages for which the catalytic performance is given in figure 2, i.e. (a) Co-sub, (b) Co-sub-H_2O, (c) (a) after NO–CH_4–O_2 reaction for12 h, and (d) (b) after NO–CH_4–O_2 reaction for 12 h. In a previous paper it was shown that the three TPR peaks of Co-sub (figure 3(a)) centered at 262, 348, and 675 °C correspond to the reduction of Co oxo-ions, finely dispersed CO_3O_4, and isolated Co^{2+} ions in exchange positions respectively [6]. After the hydrothermal treatment (figure 3(b)) the first shallow peak disappears; this change appears to have little

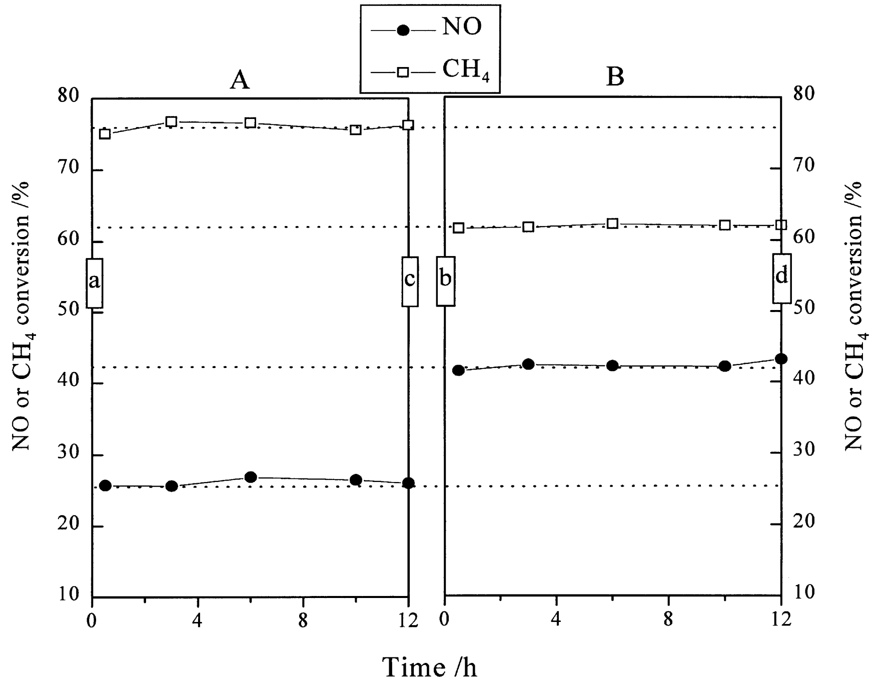

Figure 2. Conversions of NO and CH_4 over Co-sub (A) and Co-sub-H_2O (B) at 500 °C as a function of time on stream. NO, 1000 ppm; CH_4, 2000 ppm; O_2, 2%; GHSV = 30 000/h.

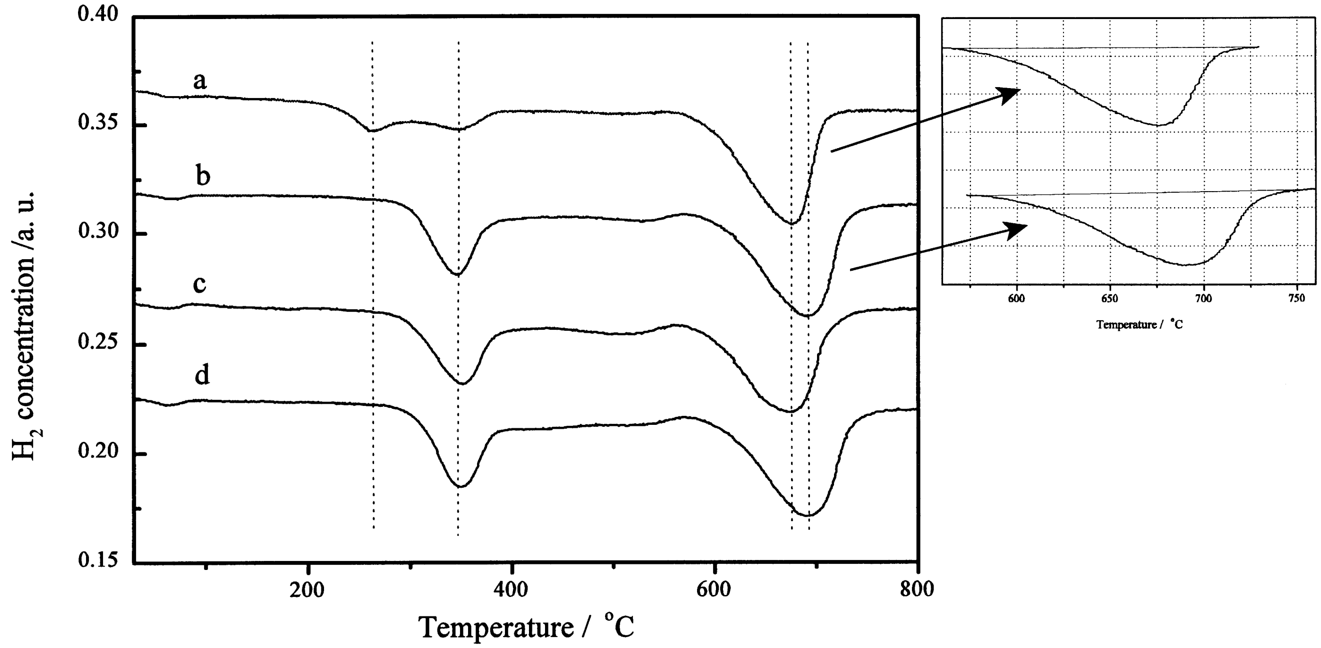

Figure 3. H_2-TPR profiles of (a) Co-sub, (b) Co-sub-H_2O, (c) (a) after NO–CH_4–O_2 reaction at 500 °C for 12 h, and (d) (b) after NO–CH_4–O_2 reaction at 500 °C for 12 h.

consequence for the catalyst performance. The largest peak, ascribed to Co^{2+} ions, is shifted upward by about 20 °C. As shown in figure 2, the catalytic performance of the sample at stage (d) is much higher for NO reduction than that at stage (c). However, the only difference in the H_2-TPR profiles of these two samples is the shift of the reduction peak of the isolated Co ions. This leaves no doubt that the effect of the water treatment on isolated Co ions, leading to this peak shift, is also responsible for the enhanced catalytic performance of Co/MFI. Since this peak is a combination of the three individual peaks for Co-α, β and γ, we conclude that the relative contributions of these peaks have been changed by the hydrothermal treatment. We discuss that in detail below. As profiles (b) and (d) are identical, it also follows that the distribution of Co ions after the hydrothermal treatment is fairly stable under NO reduction conditions.

4. Discussion

The present results show that hydrothermal treatment of Co/MFI at high temperature enhances the catalytic performance significantly by improving the selectivity for NO reduction by methane. The change of performance is accompanied by a change of the H_2-TPR peak for isolated Co^{2+} ions which indicates a redistribution of the Co ions over the three zeolite sites called α, β and γ. To unravel the precise nature of this redistribution it is essential to remember that the γ sites are inside small cages of the framework, as shown in figure 1. They are the most stable positions for Co^{2+} ions and will be filled after the calcination treatment of the catalysts in catalyst preparation. In these positions, Co^{2+} ions are inaccessible for most molecules and therefore catalytically insignificant [1]. It follows that the hydrothermal treatment as done in this study will affect the distribution of the Co^{2+} ions over the α and β sites. As shown by Wichterlová *et al.* [3,4], the Co ions in the α positions are coordinated to framework oxygens of six-membered rings composed of two five-membered rings. The β Co sites are coordinated to oxygens in the deformed six-membered rings of the MFI structure. For catalysis this position at the intersection of the straight and sinusoidal channels is very advantageous. Wichterlová *et al.* [1] therefore conclude that Co^{2+} ions in the β positions of the MFI lattice have the highest intrinsic activity for NO_x reduction. As the TPR peak of these Co^{2+} ions is located at a higher temperature than that of the Co^{2+} ions in α sites, the present results indicate that the main cause of the enhanced catalytic performance is a transport of Co^{2+} ions from the α to the β positions of this zeolite.

The driving force for this transport is the better coordination of Co in the β positions. Their transport from α to β is thermodynamically favored. The action of the water vapor is presumably to increase the mobility of these ions by providing them with water ligands, which implies less strong interaction with cage and channel walls [8,9,14].

In previous work [6] we emphasized the catalytic function of dinuclear oxygen-bridged Co ions which are easily reduced to Co^0 and likely to play a role in the activation of methane. In the present work conditions were chosen such that the representation of these ions in the H_2-TPR profile is weak, while isolated ions prevail. Under the conditions of NO_x reduction these ions might be either bare or carry an OH^- ion, i.e. be present as mono-positive $[Co–OH]^+$ entities. The Co/Al ratio near unity is in accordance with the assumption that $[Co–OH]^+$ ions predominate among the Co ions.

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