

# THE EFFECT OF SO<sub>2</sub> ON THE CATALYTIC PERFORMANCE OF Co-ZEOLITES FOR THE SELECTIVE REDUCTION OF NO<sub>x</sub> BY METHANE

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Keywords: NO<sub>x</sub> reduction, SO<sub>2</sub> effect, Co-zeolites

## INTRODUCTION

Selective catalytic removal of NO<sub>x</sub> from stationary emission sources is an important and challenging task. Beyond the SCR (selective catalytic reduction of NO<sub>x</sub>) technology with ammonia, a variety of alternative approaches have been explored in the past few years, such as direct NO decomposition [1, and references therein] and NO reduction by hydrocarbons [2-14]. Most of the current studies involve C<sub>1</sub> to C<sub>3</sub> hydrocarbons as selective reducing agents for NO<sub>x</sub> over metal zeolite catalysts. Among many performance factors, e.g., activity, selectivity and catalyst stability, the inhibition or poison of catalyst by exhaust by-products, such as H<sub>2</sub>O, SO<sub>2</sub> and other compounds are also important issues. The effect of H<sub>2</sub>O on catalyst performance was tested for many of these systems. However, the effect of SO<sub>2</sub> on NO conversion for these systems has not been sufficiently addressed. Low levels of sulphur compounds exist in most of the fuel sources we use today and is known to poison many catalysts. Building upon our earlier work [2, 15-20], we extended our study to the effect of SO<sub>2</sub> on the catalyst performance. We describe here our studies on the effect of SO<sub>2</sub> and/or H<sub>2</sub>O on catalytic performance over Co-ZSM-5 and Co-ferrierite.

## EXPERIMENTAL

The preparations of Co-ZSM-5 and ferrierite were described previously [16], and they have the following compositions: Si/Al=11 and Co/Al=0.49 for Co-ZSM-5, and Si/Al=8.5 and Co/Al=0.39 for Co-ferrierite. The catalytic activities were measured using a micro-catalytic reactor in a steady-state plug flow mode. Normally a 0.10 g of sample was used for activity measurement. The feed mixture typically consisted of 850 ppm NO, 1000 ppm CH<sub>4</sub> and 2.5% O<sub>2</sub>, and the total flow rate was 100 cc/min. (The space velocity was 30,000 h<sup>-1</sup> based on the apparent bulk density of the zeolite catalyst, ~ 0.5 g/cc).

Water vapor was added to the feed using a H<sub>2</sub>O saturator comprised of a sealed glass bubbler with a medium-pore frit immersed in de-ionized H<sub>2</sub>O. Helium (25 cc/min) flowed through the bubbler, carrying the H<sub>2</sub>O vapor to the feed. For reactions involving SO<sub>2</sub>, a special, two-inlet reactor was used to minimize the contamination of the system by SO<sub>2</sub> exposure. A SO<sub>2</sub>/He mixture (212 ppm) was added to the reactor via a separate inlet, and this SO<sub>2</sub> stream was mixed with other gases (NO/He, O<sub>2</sub>/He and CH<sub>4</sub>/He) in the quartz reactor within the furnace. The final concentration of SO<sub>2</sub> in the mixture was 53 ppm.

TPD measurements were conducted in the same reactor system. For a typical TPD measurement, a 0.1 g sample was used. A sample was pretreated *in situ* at 500°C in flowing He for 1h. Alternatively, a catalyst was allowed to undergo a steady-state NO/CH<sub>4</sub>/O<sub>2</sub> reaction in the presence of SO<sub>2</sub> at 550°C for 2 h then flushed with He at the same temperature for 1h. In both cases, temperature was decreased to 25°C in flowing He. The NO adsorption was carried out at 25°C by flowing a NO/Ar/He mixture (1700 ppm NO, 5500 ppm Ar) through the sample at 100 cc/min, and the effluent of the reactor was continuously monitored by a mass spectrometer (UTI 100C). Typically, a period of 30 minutes is sufficient to achieve a saturation for NO adsorption with 0.1 g catalyst. After the NO adsorption, the sample was then flushed with a stream of He (100 cc/min.) at 25°C to eliminate gaseous NO and weakly adsorbed NO. As the gaseous NO level returned to near the background level of the mass spectrometer, the sample was heated to 500°C at a ramp rate of 8°C/min in flowing He (100 cc/min.), and the desorbed species were monitored continuously by the mass spectrometer as a function of time/temperature.

## RESULTS AND DISCUSSION

The effect of SO<sub>2</sub> addition on the NO conversion over a Co-ZSM-5 catalyst was tested first with a dry feed. In the absence of SO<sub>2</sub>, 39% NO was converted to N<sub>2</sub> at 500°C. Upon addition of 53 ppm of SO<sub>2</sub>, the NO conversion quickly increased to >50%, then gradually decreased with time and reached to a stable level (~ 32%) in ~ 2.5 h. The dramatic change of NO conversion in the initial period upon SO<sub>2</sub> addition reflects the accumulation process of SO<sub>2</sub> on the catalyst. Obviously, the first portion of SO<sub>2</sub> deposited on the catalyst has most impact on the NO conversion, and the steady-state NO conversion obtained after 2h in the SO<sub>2</sub> containing stream indicates an achievement of an equilibrium condition for adsorption and desorption of SO<sub>2</sub>. Interestingly, increasing the reaction temperature to 550°C in the presence

of SO<sub>2</sub> raised the NO conversion to a new steady-state level at 55%, which is even higher than that with a SO<sub>2</sub>-free feed at the same temperature (27%). Further increasing the temperature to 600°C decreased the NO conversion to 42%, which is still twice of that in the absence of SO<sub>2</sub> (Table 1). Note, in the absence of SO<sub>2</sub>, the NO conversion has a maximum level at ~ 450°C on Co-ZSM-5. The addition of SO<sub>2</sub> shifts the optimum temperature to ~ 550°C. Therefore, much higher NO conversions can be obtained at T ≥ 550°C in a SO<sub>2</sub> containing stream.

Table 1 summarizes the impact of SO<sub>2</sub> and/or H<sub>2</sub>O on the catalytic performance of Co-ZSM-5. At 600°C, the addition of H<sub>2</sub>O (2%) + SO<sub>2</sub> (53 ppm) does not have a significant impact on the NO conversion. However, at T ≥ 550°C, the presence of both SO<sub>2</sub> and H<sub>2</sub>O significantly reduces the stabilized NO conversion. The positive effect of SO<sub>2</sub> with a dry feed at 550°C diminishes when H<sub>2</sub>O is added. Note, at 550°C 2% H<sub>2</sub>O alone has no impact on the conversion.

Addition of SO<sub>2</sub> also decreases the CH<sub>4</sub> conversion (see Table 1) in a way consistent with the change in NO conversion. When SO<sub>2</sub> was added to the feed at 500°C, a continuous decrease in CH<sub>4</sub> conversion was observed. For steady-state runs, substantially lower CH<sub>4</sub> conversions resulted from SO<sub>2</sub> addition. This decrease is more pronounced at lower temperatures and with the co-presence of H<sub>2</sub>O vapor. The selectivity of CH<sub>4</sub> is greatly enhanced as the result of SO<sub>2</sub> addition. At 500°C, CH<sub>4</sub> is consumed exclusively for the reduction of NO.

To determine the fraction of Co covered by SO<sub>2</sub> during a steady-state NO/CH<sub>4</sub>/O<sub>2</sub> reaction, NO adsorption at room temperature and TPD of NO were carried out on a fresh and SO<sub>2</sub> exposed Co-ZSM-5 catalysts. A fresh Co-ZSM-5 was pretreated *in situ* at 500°C for 1 h in flowing He (100 cc/min). A separate sample of Co-ZSM-5 was exposed to a feed containing 53 ppm SO<sub>2</sub>, 850 ppm NO, 1000 ppm CH<sub>4</sub>, 2.5% O<sub>2</sub> at 550°C for 2 h. The sample then was flushed with He at the same temperature for 1h to flush out the gaseous SO<sub>2</sub> and subsequently cooled down to room temperature in flowing He. The TPD measurements with the SO<sub>2</sub> exposed Co-ZSM-5 indicate a complete disappearance of the NO desorption peak at 360°C and decreased intensities for the desorption peaks at 290 and 220°C. The low temperature desorption peaks are unaffected. The quantification of the TPD measurements gives 0.88 mmol/g (1.35 NO/Co) and 0.65 mmol/g (1.0 NO/Co) for fresh and SO<sub>2</sub> exposed Co-ZSM-5, respectively. The SO<sub>2</sub> coverage is 26% of the total Co sites.

We reported earlier that Co-ferrierite is more active and selective than Co-ZSM-5 [16, 19]. However, Co-ferrierite is more sensitive to SO<sub>2</sub>. At 500°C (in the absence of H<sub>2</sub>O), upon addition of 53 ppm SO<sub>2</sub>, the NO conversion, initially 61%, decreased with time and stabilized at 16% after ~ 2 h. Increasing temperature to 550°C in the presence of SO<sub>2</sub> raised the NO conversion to 23% initially, and the conversion increased only slightly in 1.5 h. After eliminating the SO<sub>2</sub> from the feed the conversion increased with time (from 25 to 32% in 1.5 h). [As shown in Table 2, in the absence of SO<sub>2</sub> the NO conversion is 50% at 550°C] Note, a small further decrease resulted due to the addition of 2% H<sub>2</sub>O vapor in a SO<sub>2</sub> containing feed. In the presence of SO<sub>2</sub> and H<sub>2</sub>O, the optimum operating temperature is shifted to 600°C. With 2500 ppm CH<sub>4</sub> [Our normal [CH<sub>4</sub>] is 1000 ppm.], NO conversions of 65 and 45% were obtained in the presence of 53 ppm SO<sub>2</sub> under dry and wet conditions, respectively, which are comparable to those in a SO<sub>2</sub> free feed (56% in dry feed and 51% in wet feed). Similar to Co-ZSM-5, a dramatic decrease of CH<sub>4</sub> consumption was found due to SO<sub>2</sub> addition.

The TPD profiles performed on Co-ferrierite show a substantial reduction in intensity for the NO desorption peaks at ~ 160 and 220°C on the SO<sub>2</sub> exposed Co-ferrierite, while other desorption peaks remain same. The amounts of NO desorption integrated from the TPD measurements are 0.91 mmol/g (1.35 NO/Co) and 0.68 mmol/g (1.0 NO/Co) for fresh and SO<sub>2</sub> exposed Co-ferrierite, respectively (26% reduction of NO desorption on the SO<sub>2</sub> exposed Co-ferrierite).

Obviously, the change in topology of zeolite has a strong impact on the effect of SO<sub>2</sub>. With a dry, SO<sub>2</sub> free feed, Co-ferrierite is more active than Co-ZSM-5 for the NO/CH<sub>4</sub>/O<sub>2</sub> reaction, but in the presence of SO<sub>2</sub>, Co-ZSM-5 is more active. Under certain conditions, SO<sub>2</sub> even doubles the NO conversion on Co-ZSM-5. It is possible that SO<sub>2</sub> preferentially adsorbs on the sites on the outer surface of the zeolite or at the entrance of the 10-member rings. Based on our earlier studies of Co-zeolites with various exchange levels of Co<sup>2+</sup>, we believe these sites are less selective for the NO reduction but more active for the combustion of CH<sub>4</sub>. Exposure of SO<sub>2</sub> at high temperatures may selectively poison these sites. The TPD profile of Co-ZSM-5 indicates a wide distribution of sites. While on Co-ferrierite, the NO desorption is

dominated by the peak at 160 °C, and this peak was significantly reduced by SO<sub>2</sub> exposure. On Co-ferrierite SO<sub>2</sub> reduces the NO conversion at all temperatures. In contrast to SO<sub>2</sub> poisoning, H<sub>2</sub>O molecules adsorb on Co<sup>2+</sup> sites uniformly, and consequently the CH<sub>4</sub> selectivity does not change significantly (see Tables 1 & 2).

## CONCLUSIONS

Co-ZSM-5 and Co-ferrierite behave differently in response to SO<sub>2</sub> addition. Over Co-ZSM-5, SO<sub>2</sub> significantly enhances the NO conversion at T > 500°C in a dry feed; while over Co-ferrierite, SO<sub>2</sub> greatly reduces the NO conversion. However, Co-ZSM-5 suffers significant activity loss when both SO<sub>2</sub> and H<sub>2</sub>O are added to the feed. On Co-ferrierite, the presence of both SO<sub>2</sub> and H<sub>2</sub>O only caused a modest decrease in NO conversion compared to SO<sub>2</sub> alone. On the other hand, on both catalysts SO<sub>2</sub> inhibits the CH<sub>4</sub> combustion activity more than NO reduction. As a result, the CH<sub>4</sub> selectivity improved dramatically. SO<sub>2</sub> poisons the catalyst by strongly adsorbing on the Co<sup>2+</sup> sites. The degree of the reduction of the number of sites over both catalysts was measured by TPD and revealed that about 30% of the Co<sup>2+</sup> sites are blocked under steady-state reaction conditions at 550°C. Interestingly, the preference of SO<sub>2</sub> adsorption on Co<sup>2+</sup> sites is not the same on these two catalysts (due to their different structural characteristics), which may be the reason why they response to SO<sub>2</sub> addition differently.

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Table 1 Effect of SO<sub>2</sub> on conversions/selectivity over Co-ZSM-5<sup>a</sup>

	[SO <sub>2</sub> ] (ppm)	500 °C		550 °C		600 °C	
		dry	wet <sup>b</sup>	dry	wet <sup>b</sup>	dry	wet <sup>b</sup>
NO conv.	0	39	30	27	28	21	22
(%)	53	32 <sup>d</sup>	15	55	25, 18 <sup>c</sup>	42	24
CH <sub>4</sub> conv.	0	91	38	100	86	100	100
(%)	53	13 <sup>d</sup>	6	47	25, 19 <sup>c</sup>	93	78
Selectivity	0	18	33	11	14	9	9
(%)	53	~100 <sup>d</sup>	-100	50	43, 40 <sup>c</sup>	19	13

<sup>a</sup> Feed: 850 ppm NO, 1000 ppm CH<sub>4</sub>, 2.5% O<sub>2</sub>; <sup>b</sup> 2% H<sub>2</sub>O added; <sup>c</sup> overnight run; <sup>d</sup> stabilized conversion or selectivity.

Table 2 Effect of SO<sub>2</sub> on conversions/selectivity over Co-ferrierite<sup>a</sup>

	[SO <sub>2</sub> ] (ppm)	500 °C		550 °C		600 °C	
		dry	wet <sup>b</sup>	dry	wet <sup>b</sup>	dry	wet <sup>b</sup>
NO conv.	0	61	28	50	40	40, 56 <sup>d</sup>	32, 51 <sup>d</sup>
(%)	53	16 <sup>c</sup>	13	25	18	30, 65 <sup>d</sup>	24, 45 <sup>d</sup>
CH <sub>4</sub> conv.	0	60	23	93	75	100, 100 <sup>d</sup>	100, 100 <sup>d</sup>
(%)	53	6 <sup>c</sup>	5	10	9	53, 56 <sup>d</sup>	31, 55 <sup>d</sup>
CH <sub>4</sub> selec.	0	43	52	22	23	17, 10 <sup>d</sup>	14, 9 <sup>d</sup>
(%)	53	~100 <sup>c</sup>	~100	100	85	24, 20 <sup>d</sup>	33, 14 <sup>d</sup>

<sup>a</sup> Feed: 850 ppm NO, 1000 ppm CH<sub>4</sub>, 2.5% O<sub>2</sub>; <sup>b</sup> 2% H<sub>2</sub>O added; <sup>c</sup> stabilized conversion <sup>d</sup> [CH<sub>4</sub>] = 2500ppm.