Co^{2+}/Co^0 redox couple revealed by EPR spectroscopy triggers preferential coordination of reactants during SCR of NO_x with propene over cobalt-exchanged zeolites†

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Catalytic reduction of NO_x with propene over Co^{2+}-exchanged β and ZSM-5 zeolites occurs with formation of zero-valent cobalt; NO_x preferentially adsorbed on Co^{2+} plays the role of a metal reducing agent while ligation of propene is favored for Co^0 centers.

Catalytic removal of nitrogen oxides (NO_x) under lean-burn conditions is one of the most important targets in catalysis. A number of NO_x abatement methods such as direct decomposition (*de*NO_x), NO_x storage-reduction (NSR), and selective catalytic reduction (SCR) using various types of reducing agents and catalysts have been described so far.[1] However, many mechanistic issues of those reactions are still a matter of scientific debate.

At laboratory scale model studies of NO_x removal are carried out by SCR with methane or propene using transition-metal ion (TMI) exchanged zeolites.[1,2] Various TMI such as Cu, Co, Fe, Ni exhibit promising catalytic activities. There is also a consensus that they change their oxidation state during the SCR reaction, and that the catalyst has to sustain a mixed-valent state to be active.[3] Since by its very nature the NO_x reduction with hydrocarbons is simultaneous with catalyzed oxidation of the latter, some redox couples like Cu^{2+}/Cu^+, Ni^{2+}/Ni^+, and Fe^{3+}/Fe^{2+} have been postulated to be involved in this process.[3] Pronounced spin redistribution on passing from nitric oxide to dinitrogen and dioxygen is another noteworthy, though most frequently omitted issue in mechanistic studies of NO_x abatement.[4] The spin state of TMI may also change the coordination chemistry of the active site with respect to the reactants. Thus, NO_x species are known to exhibit enhanced affinity to high-spin oxidized sites, whereas CO and C_3H_6 are prone to low-spin reduced sites. For a more in-depth understanding of the SCR/*de*NO_x chemistry it is, therefore, important to elucidate the actual valence and spin state of the active sites during the reaction.

It is clear, however, that the valence state of a metal site may alter upon reaction with both NO_x and reductor. Experimental data indicate that reduction with hydrocarbons leads to results similar to those in the case of CO.[5] The well known formation of the intrazeolite univalent nickel[6] and cobalt[7] cations upon contact with CO or hydrocarbons may illustrate this point well. On the other hand, owing to its particular electronic configuration with an odd electron on the 2π* antibonding orbital, the chemical reactivity of the coordinated NO is chiefly featured in simple redox processes that involve removal of the unpaired electron to form a nitrosonium NO^+ cation or addition of an electron to this orbital, producing a nitroside anion NO^-. As a result the metal center can be either reduced or oxidized upon NO ligation.

A particular feature of cobalt zeolites is their ability to promote the removal of NO_x with a saturated hydrocarbon (*e.g.* CH_4) as a reductant.[8,9] This effect has been associated tentatively by Sachtler with the zero-valent state of cobalt, produced in the course of the SCR reaction.[9] However, until now no clear evidence of Co^0 formation upon contact with the SCR reagents has been provided, and the existence of an intrazeolite nCo^{2+}/Co^0_n couple has been based on H_2/TPR and H/D exchange results only.[9] More recent IR studies of cobalt reduction upon contact with CO at elevated temperatures suggest formation of a Co^{2+}/Co^+ redox couple.[7] Since the effect of NO co-presence has not been directly examined, their relevance for the working SCR catalysts remains indistinct.

In this work we describe an EPR examination (corroborated with IR and QMS) of the NO_x and C_3H_6 interaction with cobalt-exchanged zeolites in the presence and absence of oxygen, using CO as a probe molecule. Particular attention was focused on elucidation of the changes in the metal valence and spin states upon contact with the reactants, and the influence of these states on the ligation affinity toward NO_x and C_3H_6.

Co-zeolite samples were obtained by a standard ion exchange procedure.‡ The EPR spectra were recorded with a Bruker ELEXYS-500 X-band spectrometer equipped with a variable temperature unit. Computer simulations of the EPR spectra were carried out with the EPRsim32 software.[10] The valence state of cobalt was examined upon sequential *in situ* adsorption of NO_x, CO and propene at various temperatures.§ Owing to the characteristic EPR spectra of carbonyl adducts, CO was used as a probe molecule for resolving the valence of cobalt sites.

The EPR spectrum of CoBEA (zeolite β) registered at temperatures above 77 K (Fig. 1A) exhibits only a rather narrow line ($g_{iso} = 2.003$) usually assigned to the residual carbon radicals or defect centers. The absence of a signal attributable to Co^{2+} (d^7, $S = 3/2$) is in line with its high-spin state $^4A_2$ with $g_\perp^{eff} = 5.8–5.4$ and $g_\parallel^{eff} = 2.0$ typical of zeolites, which due to the fast relaxation time requires liquid helium temperatures to become detectable.[11]

Adsorption of CO at 77 K led to the formation of a low-spin ($S = ½$) $Co^{2+}CO$ adduct, as can readily be deduced from the EPR spectrum (Fig. 2A), with clear hyperfine structure due to the ^{59}Co

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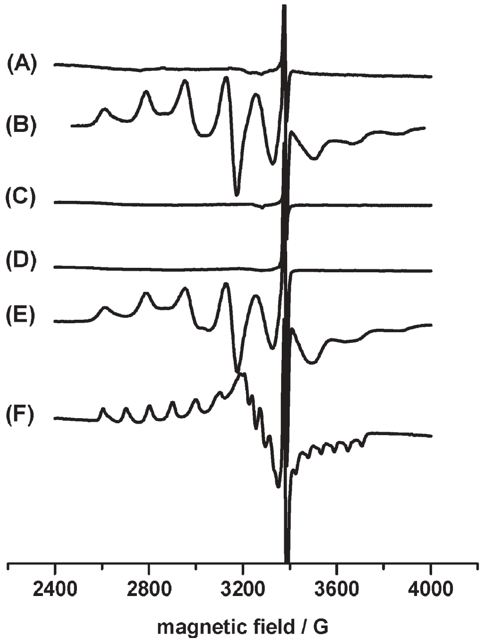

Fig. 1 Sequence of X-band EPR spectra at 77 K of thermally activated CoBEA sample (A) before adsorption, (B) after adsorption of 8 Torr of NO, (C) 12 Torr of propene and (D) after evacuation, (E) after adsorption of 8 Torr of NO, (F) 12 Torr of propene after thermal decomposition (573 K in vacuum) of dinitrosyl species (spectrum E).

nucleus (I = 7/2, 100%) proving the divalent state of cobalt definitely. In particular, computer simulation made it possible to distinguish three different component signals with $g_x^1 = 2.234$, $g_y^1 = 2.179$, $g_z^1 = 2.016$, $|A_x^1| = 4.4$, $|A_y^1| = 3.4$, $|A_z^1| = 7.6$ mT, $g_x^2 = 2.259$, $g_y^2 = 2.149$, $g_z^2 = 1.986$, $|A_x^2| = 3.5$, $|A_y^2| = 1.8$, $|A_z^2| = 5.8$ mT, and $g_x^3 = 2.239$, $g_y^3 = 2.155$, $g_z^3 = 2.066$, $|A_x^3| = 4.5$, $|A_y^3| = 3.7$, $|A_z^3| = 7.6$ mT, reflecting speciation of cobalt into three closely related species, usually associated with α, β and γ sitting sites.[3] Analogous results were obtained for CoZSM-5. From our previous studies[12] and from the literature[7] it is known that for both zeolites a number of IR bands in the range 2217–2190 cm^{-1} can be distinguished, which are characteristic of monocarbonyl $Co^{2+}CO$ adducts. Heating the samples in the presence of CO led to a gradual decrease of the EPR signal intensity (up to 70% of the initial level), accounted for by the reduction of Co^{2+} (d^7) to EPR silent Co^+(d^8) in line with recent IR studies.[7]

Saturation of the sample with NO gave rise to a doublet band in the IR spectra located at $\nu_s = 1900$ and $\nu_{as} = 1815$ cm^{-1} and assigned to the collective, symmetric and antisymmetric, vibrations of a cobalt(II) dinitrosyl adduct. Being paramagnetic, the dinitrosyl $Co^{2+}(NO)_2$ complex gives rise to an EPR spectrum with clear hyperfine structure due to ^{59}Co (Fig. 1B). The spin-Hamiltonian parameters, $g_x = 2.081$, $g_y = 2.195$, $g_z = 2.086$, $|A_x| = 18.2$, $|A_y| = 10.2$, $|A_z| = 3.1$ mT, were determined by the computer simulation (Fig. 2B). Closer inspection of this spectrum and calculation of its 3rd derivative made it possible to distinguish the superhyperfine structure due to two nitrogen nuclei (^{14}N, I = 1), confirming formation of the dinitrosyl species. The simulated parameters are indicative of $S = ½$ species, yet are quite distinct from those observed for the $Co^{2+}CO$ adduct. Formation of this new cage complex can be rationalized in terms of a spin pairing between the cobalt sites in a spin quartet state $^4Co^{2+}(d^7)$ and two NO ($^2\Pi_{1/2}$) radical ligands: $^4Co^{2+} + 2\ NO \rightarrow [^2Co(NO)_2]^{2+}$. The resultant spin density is largely located on the metal center ($\rho^{3d} \approx 80\%$). Thus the electronic configuration of cobalt in the dinitrosyl complex corresponds to d^9, which formally is tantamount to the zero-valent state of cobalt.

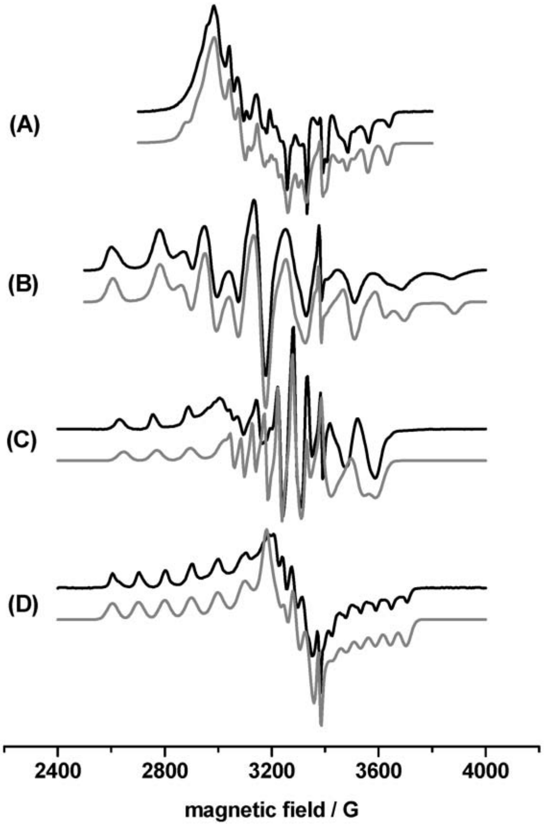

Fig. 2 X-band experimental (black line) and simulated (grey line) EPR spectra of CoBEA sample after adsorption at 77 K of (A) 10 Torr CO, (B) 6 Torr NO, (C) 10 Torr CO after thermal decomposition (573 K in vacuum) of dinitrosyl species (spectrum B), and (D) 10 Torr propene heated at 443 K after thermal decomposition (573 K in vacuum) of dinitrosyl species (spectrum B).

To confirm the change in the valence of cobalt in the SCR conditions we performed *in situ* temperature-programmed adsorption of NO_x and propene. At first, a blank adsorption of propene on the activated Co^{2+}BEA sample was carried out. No new EPR signal was observed, either at 77 K or at room temperature (Fig. 1C). In the next experiment the sample with the preadsorbed nitric oxide was evacuated in vacuum at temperatures increasing from 373 to 573 K. After such treatment the valence of cobalt was probed with CO, leading to an EPR signal (Fig. 2C) completely different from that previously observed for the cobalt(II) carbonyl complex (Fig. 2A). Its spin-Hamiltonian parameters ($g_x = 2.105$, $g_y = 2.199$, $g_z = 1.973$, $|A_x| = 4.8$, $|A_y| = 12.5$, $|A_z| = 3.5$ mT) are consistent with the cobalt(0) carbonyl species. Similar signals have already been observed in the case of the well established organometallic cobalt(0) molecular complexes.[13] The observed changes can be rationalized in terms of the thermally induced ligand-to-metal electron transfer (LMET), previously detected and

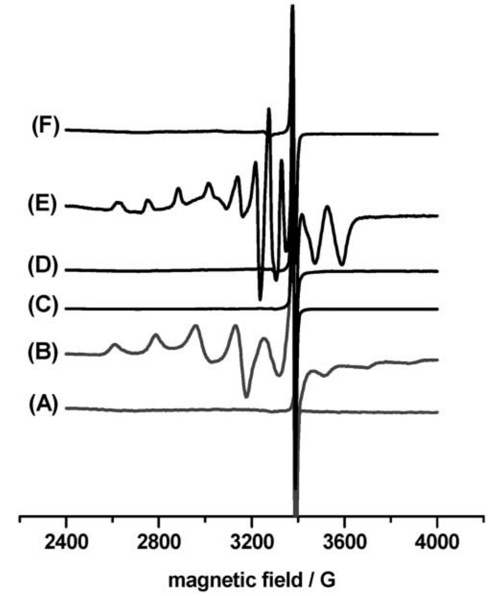

Fig. 3 EPR monitoring of NO_2 SCR with propene over CoBEA. Particular spectra obtained after quenching at 77 K correspond to (A) adsorption of 12 Torr propene, (B) coadsorption of 3 Torr NO_2, (C) heating the mixture at 373 K, (D) 473 K, (E) 573 K, and (F) 773 K.

quantified for nickel(II) grafted on a silica surface,[14] following the simplified reaction sequence:

$$Co^{2+} \rightarrow Co^{2+}(NO)_2 \rightarrow Co^0(NO^+)_2 \rightarrow Co^0(CO)_n \qquad (1)$$

As a consequence, the reduction of cobalt sites changes the chemistry of the system since Co^0 is known to form complexes with hydrocarbons quite readily, in contrast to the Co^{2+} sites. Indeed, after adsorption of propene (11 Torr heated up to 443 K) on an NO-reduced sample a new EPR signal with well-resolved cobalt hyperfine structure was obtained (Fig. 1F, 2D). The EPR parameters, $g_x = 2.096$, $g_y = 1.924$, $g_z = 2.297$, $|A_x| = 1.2$, $|A_y| = 5.2$, $|A_z| = 9.9$ mT, similar to those of molecular complexes of cobalt(0), provide another indication of the cobalt(0) state.

To verify the relevance of the observed changes in cobalt valence for the SCR process, *in situ* reactions with three gas-phase compositions: propene (12 Torr) with NO_2 (3 Torr), NO (6 Torr) or with a mixture of NO (5 Torr) and O_2 (2 Torr) were monitored with EPR in the temperature range 295–773 K. Typical spectra for the mixture with NO_2 are shown in Fig. 3. These experiments were performed for the values of $R \leqslant 0.1$, corresponding to the reducing conditions. The coefficient $R = ([NO] + 2[O_2])/9[C_3H_6]$ was calculated following Tanaka *et al.*[15] At 77 K and at room temperature only the EPR signal due to the dinitrosyl species was observed, for both $NO–C_3H_6$ and $NO_2–C_3H_6$ mixtures. At 473 K this signal disappeared, but at 573 K, *i.e.* when the SCR process starts,[16] the signal of the cobalt(0) carbonyl was observed (Fig. 3E). Further temperature increase led to the disappearance of all EPR signals that could indicate total oxidation of CO to CO_2, and regeneration of the active centers back to Co^{2+}, invisible at 77 K as explained above. Readsorption of NO on such a sample gave rise to the formation of the cobalt dinitrosyl species, formally closing the cycle. Indeed, subsequent QMS analysis of the gas products evolved in the course of the reaction revealed the presence of N_2, CO_x, and absence of NO_x, indicating that the SCR process was accomplished successfully. Thus, the obtained results showed clearly that in the SCR conditions cobalt(II) was reduced to cobalt(0) by NO_x, whereas propene, coordinated to zero-valent cobalt sites, was oxidized to CO_x.

In conclusion, it was shown for the first time that at SCR temperatures the interaction of NO_x with Co-zeolites, alone or in the co-presence of propene, leads to the reduction of Co(II) to Co(0) *via* dinitrosyl intermediates. The cobalt(0) sites generated during decomposition of the dinitrosyl species exhibit enhanced affinity toward coordination of CO and propene, giving rise to the corresponding adducts with characteristic EPR spectra. The same adducts are found during SCR of NO_x with propene, indicating that the two electron Co^{2+}/Co^0 redox couple operates in the reaction mechanism, in accordance with the earlier suppositions.[9] The key intermediates, $Co^{2+}(NO)_2$, $Co^0(C_3H_6)_n$, and $Co^0(CO)_n$, appearing during the whole reaction were identified.

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Notes and references

‡ Co-zeolites were prepared from the parent ammonium forms of ZSM-5 (Zeolyst, Inc.) and BEA (Tricat Zeolites) zeolites of SiO_2/Al_2O_3 ranging from 20 to 40 by a standard ion exchange procedure. A mixture of 0.1 M $Co(NO_3)_2$ aqueous solution in the proportion 1 g zeolite/100 cm^3 was stirred for 20 h at 323 K. The final pH of the solution was 5. After drying at 353 K the samples were characterized by ICP, revealing a Co/Al exchange degree of 0.5 and 0.8 level (for ZSM-5 and BEA, respectively).

§ Prior to adsorption the samples were evacuated in vacuum ($\sim 10^{-5}$ Pa) at 773 K (6 K min^{-1}) for 3 h. Before adsorption, the gas reactants, NO and NO_2 (Aldrich, 98.5 and 99.5%, respectively) were purified by the freeze–pump–thaw technique, whereas O_2, CO and propene (Aldrich, 99.95%) were adsorbed directly. Adsorption was carried out at 77 K or at room temperature and the samples were exposed to various temperatures.

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