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The transformation of formaldehyde on CoZSM-5 zeolites

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Abstract

The interaction of formaldehyde molecules with Co^{2+} ions in CoZSM-5 zeolites of various compositions containing various proportions between Co^{2+} in exchange positions and in oxide-like clusters, as well as the transformation of formaldehyde sorbed in zeolites was followed by IR spectroscopy. The interaction of formaldehyde with Co^{2+} resulted in a weakening of C=O bond, what can be partially due to π-back donation of d electrons of Co^{2+} to π^* antibonding orbitals of formaldehyde. Only Co^{2+} in exchange positions (contrary to Co^{2+} in oxide-like clusters) were able to interact with formaldehyde. IR studies illustrated also that formaldehyde molecules are oxidized to formate ions, by either Co^{3+} or Co^{2+} as oxidants. According to IR results Co^{3+} and Co^{2+} are reduced mostly to Co^+ and metallic Co.

Keywords: CoZSM-5 zeolite; Formaldehyde; IR spectroscopy

1. Introduction

Co-zeolites are interesting catalysts in numerous reactions such as the reduction of NO by hydrocarbons [1–4], alkanes amoxidation [5], Fisher-Tropsch synthesis [6], and others. IR spectroscopy is one of the most important characterization method providing information on the status and properties of Co^{3+} and Co^{2+} ions, on the interaction of Co ions with zeolite framework (by following the spectra of zeolites in ‘‘transmission window’’ [7,8], and localization of cobalt ions (by following the spectra of bulky molecules such as benzonitrile and *o*-toluonitrile) [9,10]. However, the most important information concerns the interaction of Co^{3+} or Co^{2+} with adsorbed probe molecules.

Earlier IR studies revealed three kinds of Co^{3+} (Co^{3+}–NO bands at 1940, 1950, and 1970 cm^{-1}) and three kinds of Co^{2+} ions in zeolites CoZSM-5 and CoBEA [11–19]. Montanari et al. [14], who realized ‘‘in situ’’ IR experiments of NO reduction with propene, concluded that Co^{3+} plays an important role in the denox process. According to literature, the origin of 2204 cm^{-1} CO band is not yet clarified. Usually, band at this frequency is assigned to Co^{2+}–CO monocarbonyls [11–19], however, it is also attributed to Co^{3+}–CO adducts [20–22]. According to our earlier results [11] Co^{2+} in zeolites CoZSM-5 was in the form exchange cations (characterized by Co^{2+}–CO band at 2204 cm^{-1}), in the form of oxide-like clusters (band at 2194 cm^{-1}), and in bulk CoO (band at 2179 cm^{-1}). There is discrimination between the nature of Co^{2+} in oxide-like clusters and in regular CoO. The various degree of the balance of the positive charge of cobalt by oxygens ions is reflected in the nature and electron-acceptor properties of cobalt, therefore, Co^{2+} ions present in the form of stoichiometric bulk CoO exhibit less electron-acceptor properties than oxide-like clusters of higher formal charge of cobalt cation.

CoO and oxide-like clusters were formed by hydrolysis of Co^{2+} with intrazeolitic water [11]. The contribution of Co^{2+} in exchange positions, as well as in oxide-like clusters and in CoO depends on the zeolite composition (Si/Al and Co content), as well as on the pretreatment conditions [11]. At low Si/Al (the distances between AlO_4^- are relatively short) Co^{2+} in exchange positions dominate, on the other hand, at high Si/Al (at long distances between AlO_4^-) Co^{2+} is mostly in the form of CoO and oxide-like clusters.

This study concerns the interaction of Co ions in CoZSM-5 with formaldehyde. Earlier IR studies [15] illustrated that formaldehyde sorbed in CuZSM-5 was oxidized to formate ions and Cu^{2+} ions were oxidant in this process. It was therefore interesting to find out if Co^{3+} ions (which are present in CoZSM-5) are able to oxidize formaldehyde (similarly as Cu^{2+} ions do). Moreover, the mechanism of the reaction of NO

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reduction by small hydrocarbon molecules (such as CH_4) proposed by Djega-Mariadassou and Boudart [16] assumes that hydrocarbons are first oxidized to alcohols or aldehydes and such oxygen-containing molecules are reducers for NO. As formaldehyde may be formed by methane oxidation we follow the interaction of Co ions with formaldehyde and the formaldehyde oxidation.

Two zeolites have been studied: CoZSM-5 of Si/Al = 15 (Co/Al = 0.18) containing Co^{2+} mostly in exchange positions and CoZSM-5 of Si/Al = 40 (Co/Al = 0.43) containing Co^{2+} mostly in the form of oxide-like clusters and CoO [11]. Preliminary experiments evidenced also that first one contained important Co^{3+} amounts, contrary to the latter one for which the contribution of Co^{3+} was smaller [11]. The nature of Co^{3+} cannot be well defined. It is highly improbable that such trivalent ions could exist in the exchangeable positions and could be neutralized by three AlO_4^- tetrahedra. It is therefore not excluded that Co^{3+} bears the form of an oxide.

2. Experimental

The parent NH_4ZSM-5 zeolites (Zeolyst) had Si/Al ratios of 15 and 40. They were here called HZSM-5/15 and HZSM-5/40. The CoNH$_4$ZSM-5 samples were prepared by ion exchange with 0.1 M $Co(NO_3)_2$ at room temperature. The Co content determined by ASA (PerkinElmer) was 1.09 wt% for zeolite of Si/Al = 15 and 1.00 wt% for zeolite of Si/Al = 40 corresponding to Co/Al = 0.18 and 0.43, respectively. The Co-samples were called CoZSM-5/15/0.18 and CoZSM-5/40/0.43. We used also NaZSM-5, HZSM-5 and MgZSM-5 obtained by ionic exchange with $Mg(NO_3)_2$ solution of NaZSM-5 (of Si/Al = 35 and Mg/Al = 0.20). NO and CO were used as probe molecules. Gaseous formaldehyde was produced by heating (at ca. 370 K) of paraldehyde (Aldrich).

For the IR studies the zeolite samples were pressed into thin wafers and activated in situ in IR cell in vacuum at 820 K for 1 h. In some experiments small doses of adsorbates (CO or NO) ca. 0.5 μmol were introduced into the cell at room temperature (NO) or at 170 K (CO). IR spectra were recorded with a Bruker Equinox 55 spectrometer equipped with an MCT detector with spectral resolution 2 cm^{-1}.

3. Results and discussion

3.1. The interaction of formaldehyde with cobalt ions

The spectra of gaseous formaldehyde and formaldehyde sorbed in zeolites: HZSM-5, NaZSM-5, MgZSM-5, CoZSM-5/15/0.18, and CuZSM-5 are presented in Fig. 1A. The spectrum of gaseous formaldehyde (spectrum a) shows an intensive band at 1745 cm^{-1} of stretching of C=O group as well as weaker 1501 cm^{-1} band of scissoring vibrations of CH_2 group. The interaction of carbonyl group with Si(OH)Al in HZSM-5 (spectrum b) results in red shift of C=O band to 1713 cm^{-1} ($\Delta\nu = 32$ cm^{-1}). A smaller shift to 1730 cm^{-1} ($\Delta\nu = 15$ cm^{-1}) was observed if formaldehyde interacted with Na^+ ions in NaZSM-5 (spectrum c). The interaction of carbonyl group with Mg^{2+} ions in MgZSM-5 (spectrum d) resulted in larger red shift to 1720 cm^{-1} ($\Delta\nu = 25$ cm^{-1}). This larger frequency shift in comparison with Na^+ may be due to the stronger interaction of carbonyl group with divalent Mg^{2+} than with monovalent Na^+. Spectrum e was recorded upon the sorption of formaldehyde in CoZSM-5/15.0.18. Apart from the C=O band at 1713 cm^{-1} being result of an interaction of formaldehyde with zeolitic Si–(OH)–Al groups a new band of C=O group at 1700 cm^{-1} is appeared, the red frequency shift of which (to 1700 cm^{-1}, $\Delta\nu = 45$ cm^{-1}) is larger than for Mg^{2+} even if positive charge of Co^{2+} is comparable as for Mg^{2+}. We suppose that more important C=O bond weakening for Co^{2+} than for Mg^{2+} may be the result of π-back donation of d electrons of Co^{2+} to π* antibonding orbital of formaldehyde. The effect of π-back donation for Co^{2+} ions is however smaller than for Cu^+ for which larger red frequency shift (to 1689 cm^{-1} ($\Delta\nu = 56$ cm^{-1}) was observed (spectrum f). In CuZSM-5 two additional bands at 1730 and 1713 cm^{-1} are attributed to formaldehyde interacting with Na^+ (remaining after not complete Na^+/Cu^+ ion exchange) and Si–(OH)–Al groups, respectively. Besides of mentioned above band of C=O and CH_2 groups, the spectrum of formaldehyde sorbed in CoZSM-5/15/0.18 (spectrum d) shows also two other bands: 1580 and 1650 cm^{-1}, the interpretation of which will be discussed later.

The spectra recorded at the sorption of increasing amounts of formaldehyde in CoZSM-5/15/0.18 are presented in Fig. 1B. The presented spectra suggest that formaldehyde molecule react with two kinds of adsorption sites: Si–OH–Al groups (the band at 1714 cm^{-1}), and Co^{2+} groups (the band at 1700 cm^{-1}) choosing Co^{2+} cations as the most energetically favorable. This proves that Co^{2+} ions bond with formaldehyde stronger than with zeolitic hydroxyls.

The spectra of formaldehyde sorbed in CoZSM-5/15/0.18 and CoZSM-5/40/0.43 are presented in Fig. 1C. The doses of formaldehyde were sorbed until the maximum intensity of C=O band interacting with Co^{2+}. According to chemical analysis both zeolites contain almost the same amount of Co (1.09 and 1.00 wt%, respectively) but ealier IR experiments of CO sorption evidenced [11] that CoZSM-5/15/0.18 contained Co^{2+} mostly in exchange positions whereas CoZSM-5/40/0.43 most of Co^{2+} is in the form of oxide-like clusters and CoO. In CoZSM-5/15/0.18 the intensity of Co^{2+} ...C=O band was significantly higher suggesting that only Co^{2+} in exchange positions are capable to bond formaldehyde.

3.2. Oxidation of formaldehyde in CoZSM-5 zeolites

3.2.1. Reaction of formaldehyde at elevated temperature

Apart from the bands of formaldehyde interacting with Co^{2+}, the spectrum of formaldehyde sorbed in CoZSM-5/15.0.18 at room temperature shows also weaker bands at 1580 and 1650 cm^{-1} (Fig. 1B). These bands grow in intensity if zeolite with formaldehyde is heated up to 420 K (Fig. 2, spectra a–d). Above 350 K two weaker bands 1380 and 1390 cm^{-1} appear and the 1590 cm^{-1} band becomes larger and more complex. According to Knőzinger and co-workers [16,17], and Miller et al. [18] the intensive bands at 1580 and 1600 cm^{-1} together

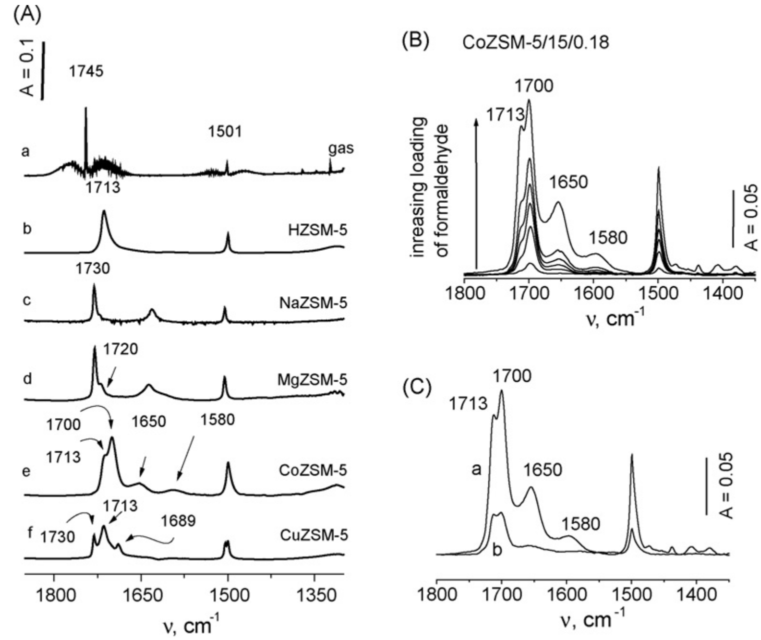

Fig. 1. (A) IR spectra of formaldehyde gaseous (a), sorbed in zeolite HZSM-5 (b), NaZSM-5 (c), MgZSM-5 (d), CoZSM-5/15/0.18 (e), and CuZSM-5(f). (B) IR spectra recorded at the sorption of increasing amounts of formaldehyde at room temperature. (C) The highest intensities of the $Co^{2+}–O═CH_2$ bands corresponding to the maximum amounts of Co^{2+} ions capable to interact with formaldehyde in (a) CoZSM-5/15/0.18 and (b) CoZSM-5/40/0.43.

with weaker one at 1380 and 1390 cm^{-1} can be attributed to formate ions: bands at 1580 and 1380 cm^{-1} are due to antisymmetric and symmetric stretching vibrations, respectively, of COO^- group, whereas weak band at 1390 cm^{-1} to C–H bending in $H–COO^-$.

The spectrum of cobalt formate (in KBr pellet) is also presented in Fig. 2 (spectrum f). The spectrum shows the large and intensive band ($\nu_{as\,coo^-}$) very similar as in the spectra of product of formaldehyde transformation on CoZSM-5/15/0.18 as well as three weaker bands at 1360, 1380 and 1400 cm^{-1}. Two of this set of bands can be attributed to $\nu_{sym\,coo^-}$ and $\delta_{C–H}$. The assignment of the third one is not known. The fact that formate ions are produced upon adsorption of formaldehyde in CoZSM-5/15/0.18 points to oxidation of formaldehyde.

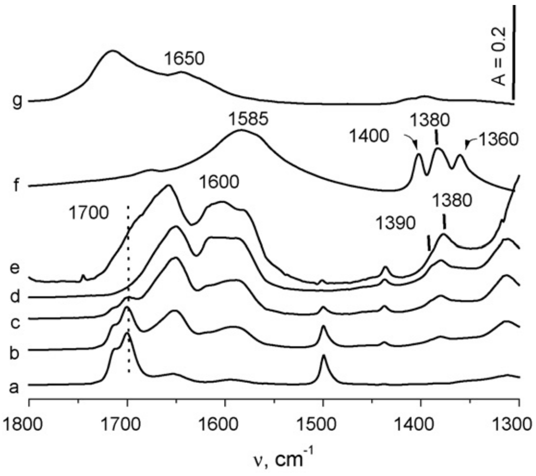

Fig. 2. (a–d) The spectra of formaldehyde sorbed at room temperature in CoZSM-5/15/0.18 (a), heated to 350 K (b), 390 K (c) and 420 K (d). (e) The spectra of formaldehyde sorbed at room temperature in CoZSM-5/40/0.43 and heated to 420 K. (f) The spectrum of solid cobalt formate in KBr disc. (g) The spectrum recorded upon the sorption of formic acid in zeolite HZSM-5 and heated to 420 K.

The spectra recorded upon the sorption of formaldehyde show (besides of mentioned above bands of formate ions: 1380, 1390, and 1590 cm^{-1}) another intensive band at 1650 cm^{-1}. Even though the frequency of this band is the same as the deformation frequency of molecular water, this band cannot be attributed to water because another typical of water band around 3400 cm^{-1} is absent (spectra not shown). The assignment of 1650 cm^{-1} band is not clear. It is not excluded that this band may be originate form formate ions produced by the reaction of formic acid with extraframework Al species which are present in our ZSM-5 of Si/Al = 15. Moreover, the similar band appears if formic acid is sorbed in HZSM-5 zeolite (Fig. 3, spectrum g). It should be also noted that acetate ions were produced if acetic acid was sorbed in HY zeolite [23]. The origin of formic acid will be discussed later.

All the presented above results were obtained with CoZSM-5/15/0.18 containing relatively high contribution of Co^{3+} (most probably bears an oxide form) and Co^{2+} in exchange positions [11]. The transformations of formaldehyde in CoZSM-5/40/0.43 containing less amount of Co^{3+} but more Co^{2+} in oxide-like clusters was also examined (Fig. 2, spectrum e). The results were similar as obtained with CoZSM-5/15/0.18. Formate ions are also produced but their concentration was somewhat higher than in CoZSM-5/15/0.18 (Fig. 2, spectrum d).

The process of formaldehyde oxidation to formate ions and the origin of formic acid will be now discussed. It may be supposed that formaldehyde can be oxidized by CoO or by oxide-like clusters as well as by Co^{3+} existing mainly in the

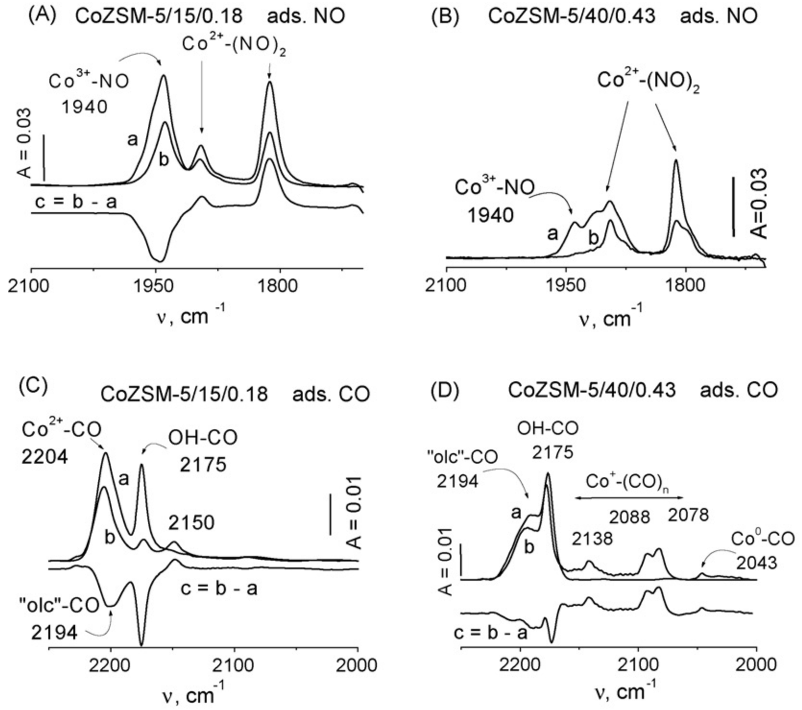

Fig. 3. The spectra of NO sorbed at room temperature (A and B) and CO sorbed at 170 K (C and D) in zeolites CoZSM-5/15/0.18 (A and C) and CoZSM-5/40/0.43 (B and D). (a) The spectra of NO and CO sorbed in zeolites non-treated with formaldehyde, (b) the spectra of NO and CO sorbed in zeolites in which formaldehyde was sorbed at room temperature, next zeolite with formaldehyde was heated to 420 K, and subsequently formate ions were decomposed by evacuation at 650 K and (c) difference spectra (c = b − a).

form of an oxide (presented here as Co_2O_3).

$$2CoO + HCOH = Co_2O + HCOOH \qquad (1.1)$$

$$Co_2O + 2HCOOH = 2Co^+ + 2HCOO^- + H_2O \qquad (1.2)$$

or

$$Co_2O_3 + HCOH = 2CoO + HCOOH \qquad (2.1)$$

$$CoO + 2HCOOH = Co^{2+} + 2HCOO^- + H_2O \qquad (2.2)$$

In both schemes formic acid produced may react with cobalt oxides giving formate ions (1590 cm^{-1} band) or with extraframework Al species giving other kind of formate species (1650 cm^{-1}).

It should be noted that very weak bands at 1440 cm^{-1} (Fig. 2) and 2965 cm^{-1} (spectra not shown) are present in our spectra. It is not excluded that these bands may be attributed to metoxy groups [27] suggesting that a Cannizzaro-type disproportionation may occur. However, the intensity 1440 and 2963 cm^{-1} bands for both zeolites is very small suggesting that not a Cannizzaro-type disproportionation but oxidation of formaldehyde is the main path of reaction.

3.2.2. The status of Co^{3+}–NO adsorption

According to the scheme presented above Co^{2+} (in the form of oxide) in reduced to Co^+ and Co^{3+} is reduced to Co^{2+} (also in the form of oxide) which can be subsequently reduced to Co^+. The reaction of formaldehyde in CoZSM-5 is therefore expected to reduce the concentration of Co^{3+} and Co^{2+} and produce Co^+ ions. To support this hypothesis the IR study of the sorption of probe molecules as NO (probe for Co^{3+}) and CO (probe for Co^{2+}) were undertaken. The results are presented in Fig. 3. The spectrum of NO sorbed in CoZSM-5/15/0.18 non-treated with formaldehyde exhibits the 1940 cm^{-1} band of Co^{3+}–NO as well as the bands of dinitrosyls $Co^{2+}(NO)_2$ (1815 and 1895 cm^{-1}) [25,26] (Fig. 3A, spectrum a). NO was also adsorbed in zeolite in which the formate ions were produced by the reaction of formaldehyde at 420 K and subsequently decomposed by the evacuation at 650 (the disappearance of formate ions bands were observed (Fig. 3A, spectrum b)). In both cases the doses of NO were sorbed until maximum intensity of the Co^{3+}–NO band at c.a. 1940 cm^{-1}. This band shows three submaxima at 1940, 1955, and 1970 cm^{-1}. The comparison of the spectra a and b in Fig. 3A reveals that the Co^{3+}–NO band decreased in zeolite treated with formaldehyde pointing to the reduction of some Co^{3+}. It is interesting note that (as difference spectrum shows) Co^{3+} ions characterized by high frequency Co^{3+}–NO bands at 1950 and 1970 cm^{-1} are most prone for the reduction. The spectra of NO sorbed in CoZSM-5/40/0.43 non-treated and treated with formaldehyde (spectra a and b in Fig. 3B) shows that all these Co^{3+} are reduced by formaldehyde.

3.2.3. The status of Co^{2+}–CO adsorption

The information on the status of Co^{2+} was obtained by CO adsorption. The spectrum of CO sorbed in CoZSM-5/15/0.18 (Fig. 3C, spectrum a) shows a band at 2204 cm^{-1} of CO interacting with Co^{2+} as well as a (hardly seen) low frequency shoulder of CO bonded to Co^{2+} in oxide-like clusters, and 2175 cm^{-1} band of CO bonded to Si–OH–Al. The treatment with formaldehyde decreases the contribution of Co^{2+} but the analysis of difference spectrum (spectrum c in Fig. 3C) points to the reduction of Co^{2+} in oxide-like clusters, whereas the contribution of Co^{2+} in exchange positions consumed by formaldehyde is relatively smaller. Similar situation was observed in CoZSM-5/40/0.43, Co^{2+} in exchange positions and those in oxide-like clusters are reduced (Fig. 3D, spectrum c). According to the data presented in Fig. 3C and D, reduction of Co^{3+} and Co^{2+} results in appearance of CO bands in the region 2040–2150 cm^{-1}. These bands are attributed to CO bonded to Co^{+} [13], whereas weak band at 2043 cm^{-1} is assigned CO bonded to metallic Co. All results point to the Co^{3+} and Co^{2+} are reduced to Co^{+} and metal by formaldehyde. It should be underlined that the formation of Co^{+} was postulated (in schema (1.1)) as the products of formaldehyde oxidation to formic acid and formate ions.

The reduction of Co^{3+} and Co^{2+} by H_2, CO, and NO was followed in our laboratory [24]. Both H_2 and CO reduced Co^{3+} to Co^{2+}. Similarly NO reduced Co^{3+} to Co^{2+} at room temperature, whereas at 670 K molecules of NO were able to reduce Co^{2+} to lower oxidation state (probably Co^{+}). Contrary to formaldehyde, which reduced mostly Co^{2+} in oxide-like clusters, NO was capable to reduce only Co^{2+} in exchange positions. According to the Eqs. (1.1) and (2.1), both Co^{3+} and Co^{2+} in the form of oxides are reduced by formaldehyde. This hypothesis is supported by the experimental data (the reduction of Co^{2+} in oxide-like clusters as evidenced by CO sorption, Fig. 3C and D).

4. Conclusions

(1) The interaction of formaldehyde molecules with Co^{2+} ions in CoZSM-5 zeolites results in the weakening of C=O bond which is caused by the effect of π-back donation of d electrons of $Co^{2+}$to π^* antibonding orbitals of molecule.

(2) In CoZSM-5 zeolites, only Co^{2+} ions in exchange positions (contrary to Co^{2+} in oxide-like clusters and in CoO) are able to bond formaldehyde.

(3) Formaldehyde molecules sorbed in CoZSM-5 zeolites are oxidized to formate ions. IR experiments of NO and CO sorption illustrated that Co^{3+} and Co^{2+} ions (mostly in oxide form) are oxidants, being reduced to Co^{+} and metallic Co.

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