

Redox couples in the selective catalytic reduction of NO_x with hydrocarbons over Co-ZSM-5 and Ni-ZSM-5 catalysts: an FT-IR study

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On the basis of IR spectroscopy studies it is concluded that the redox couples Co²⁺/Co⁺ and Ni²⁺/Ni⁺ operate in the selective catalytic reduction of nitrogen oxides with hydrocarbons over Co-ZSM-5 and Ni-ZSM-5.

Selective catalytic reduction of NO_x with hydrocarbons (HC-SCR) has been one of the most studied catalytic reactions during the past decade. An important peculiarity of the process is that the catalyst has to ensure that the hydrocarbons are preferentially oxidized by NO_x. There is no doubt that in laboratory-scale experiments different metal-exchanged zeolites are the best catalysts. Thus, the classic HC-SCR catalyst is Cu-ZSM-5.^{1,2} Recently, many hopes were concentrated on Co-ZSM-5³⁻⁵ and Ni-ZSM-5^{3,6} because of their ability to lead the reaction with methane as a reducing agent. A lot of mechanistic studies, performed mainly by IR spectroscopy, have helped with understanding many peculiarities of the process. However, there is still disagreement concerning some basic questions. For instance, the problem of the redox couples is not fully elucidated.

Some catalysts such as alumina and H-ZSM-5 are active in HC-SCR² and it is evident that, in these cases, there is no redox couple participating in the process. However, the most active catalysts contain transition metal cations and there is consensus that these cations change their oxidation state during the process. Let us consider the classic HC-SCR catalyst, Cu-ZSM-5. It is now well established that, although the majority of the copper cations are in the Cu²⁺ state under the reaction conditions, the Cu²⁺/Cu⁺ redox couple is essential for the process.⁷ Concerning the cobalt catalysts, it is believed that Co³⁺/Co²⁺ redox couples operate in the reaction mechanism.⁸ However, some years ago, Sachtler *et al.*⁴ pointed out that two reaction mechanisms, with two different redox couples, are active for these catalysts. On the basis of TPR data, showing reduction of Co²⁺ to Co⁰, the authors proposed that one of the redox couples operating in the process was namely the nCo²⁺/Co_n⁰ couple.⁴

There are many data showing that reduction with hydrogen and reduction with carbon monoxide result in different products. Thus, supported Cu²⁺ ions are reduced by hydrogen to Cu⁰, whereas the final product of its reduction with CO is, over a large temperature interval, Cu⁺.⁹ Chromium is reduced to Cr³⁺ by H₂, but it is reported that CO reduction leads quantitatively to Cr²⁺ cations.¹⁰ There are also data showing that reduction with hydrocarbons is rather similar to CO reduction.¹¹ That is why one can suppose that the products of reduction with hydrocarbons (expected under SCR conditions) could differ from those obtained *via* hydrogen reduction. Recently, we reported that univalent cations are produced when both Co-ZSM-5^{12,13} and Ni-ZSM-5^{14,15} are reduced by CO. It is normal to expect that the same product will be obtained after reduction with hydrocarbons. The aim of this work is to study, by means of IR spectroscopy, the interaction of hydrocarbons with Co-ZSM-5 and Ni-ZSM-5 and to draw some conclusions about the redox couples of these catalysts, especially under "reductive" conditions. Two hydrocarbons were studied: propene and methane. The former is a typical SCR reducer, while methane is important since it could replace ammonia as a reducing agent in stationary NO_x emitters.

The samples were prepared by conventional ion-exchange as described elsewhere.¹²⁻¹⁵ The metal concentration in Co-ZSM-5 was 2.0 wt%, and in Ni-ZSM-5, 0.4%. The IR investigations were carried out using a Nicolet Avatar 360 spectrometer with a spectral resolution of 2 cm⁻¹ and accumulating 64 scans. Self-supporting pellets (~10 mg cm⁻²) were prepared by pressing the samples at 10⁴ kPa and were directly treated in the IR cell. The latter was connected to a vacuum apparatus with a residual pressure of about 10⁻³ Pa. Prior to the adsorption measurements, the samples were activated by heating for 1 h at 723 K under oxygen and evacuation for 1 h at the same temperature. Carbon monoxide (99.5%) was supplied by Merck, and nitrogen monoxide (>99.0%), methane (>99.9%) and propene (99.95%), by Messer Griesheim GmbH. Before adsorption, carbon monoxide and methane were passed through a liquid nitrogen trap.

Introduction of CO to the activated Ni-ZSM-5 sample results in the appearance of a band at 2212 cm⁻¹ with a shoulder at 2220 cm⁻¹.¹⁴ Both bands are assigned to Ni²⁺-CO species. When CO is adsorbed on the activated Co-ZSM-5 sample, one band at 2207 cm⁻¹ with a shoulder at 2217 cm⁻¹ is detected.¹² These bands arise from Co²⁺-CO species. The results evidence that the oxidation state of the metal cations in activated Co-ZSM-5 and Ni-ZSM-5 samples is 2+.

Let us first recall the carbonyl chemistry of Co⁺ and Ni⁺ in ZSM-5. Reduction of Co-ZSM-5 and Ni-ZSM-5 with CO at 673 K leads to production of Co⁺ or Ni⁺ ions, respectively. Carbon monoxide adsorption on reduced Co-ZSM-5 results in formation of Co⁺(CO)₂ dicarbonyls (ν_s at 2113 and ν_{as} at 2042 cm⁻¹).^{12,13} Under CO equilibrium pressure these species are converted into tricarbonyls (bands at 2137, 2089 and 2079 cm⁻¹). With CO the Ni⁺ ions in Ni-ZSM-5 form stable monocarbonyls (2109 cm⁻¹) which pass into dicarbonyls (ν_s at 2136 and ν_{as} at 2092 cm⁻¹) in the presence of CO in the gas phase.^{14,15}

Introduction of methane to the activated Co-ZSM-5 sample does not lead to formation of any adsorption species. The sample was heated in a methane atmosphere (6.67 kPa for 50 min at 803 K), then the gas phase evacuated at the same temperature and CO (2.67 kPa equilibrium pressure) introduced into the IR cell. As a result, six bands were registered in the carbonyl region, their maxima being at 2205, 2137, 2112, 2088, 2078 and 2039 cm⁻¹ (Fig. 1, spectrum a). The band at 2205 cm⁻¹ was assigned to Co²⁺-CO species. According to data from the literature,^{12,13} the bands at 2137, 2088 and 2078 cm⁻¹ characterize Co⁺(CO)₃ tricarbonyls, while the bands at 2112 and 2039 cm⁻¹ are typical of Co⁺(CO)₂ dicarbonyl species. After evacuation the Co²⁺-CO band decreases in intensity and the bands at 2137, 2088 and 2078 cm⁻¹ disappear. The dicarbonyl bands at 2112 and 2039 cm⁻¹ develop at their expense.

As in the case of Co-ZSM-5, no adsorption species were evidenced when methane was introduced to the activated Ni-ZSM-5. After interaction with methane at 803 K (6.67 kPa, 50 min, evacuation at 803 K) the sample was tested by CO. Adsorption of CO (2.67 kPa) provoked the appearance of three main bands in the carbonyl region: Ni²⁺-CO at 2212 cm⁻¹ and Ni⁺(CO)₂ at 2136 and 2091 cm⁻¹ (Fig. 2, spectrum a).^{14,15} Evacuation resulted in a decrease in intensity of the Ni²⁺-CO band and conversion of the

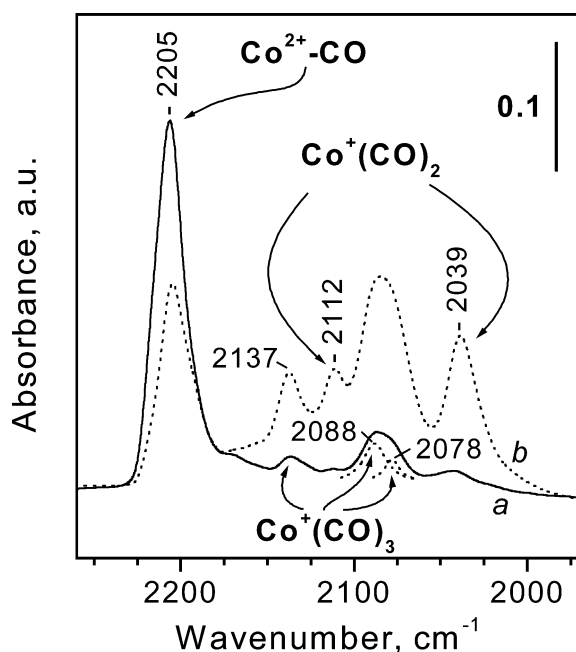


Fig. 1 FTIR spectra of CO (2.67 kPa) adsorbed on Co-ZSM-5. Sample pre-reduced with CH₄ at 803 K (a) and with C₃H₆ at 573 K (b) (for details see text). The spectra are background corrected and the gas phase CO spectrum subtracted.

Ni⁺(CO)₂ species into monocarbonyls (band at 2109 cm⁻¹). Thus, the results on both Co-ZSM-5 and Ni-ZSM-5 demonstrate that univalent cations are produced after interaction of the samples with methane. Note that neither metallic cobalt, nor metallic nickel were detected after the reduction pretreatment.

It is known that propene is more effective as a reducing agent than is methane. On both samples (Co-ZSM-5 and Ni-ZSM-5) propene is adsorbed even at room temperature. Here the results will not be described in details since this is beyond the aim of the present communication. After reaction of the samples with propene (2.67 kPa, 10 min, 573 K), the gas phase was evacuated at 723 K and CO adsorbed on the samples (see Figs. 1 and 2, spectra b). The results show that a large fraction of Co⁺ or Ni⁺ cations respectively have been created on the samples (the carbonyl bands corresponding to the univalent ions were definitely more intense than those registered on the methane-reduced samples). Thus, it is evident that propene easily reduces Co²⁺ and Ni²⁺ cations to their univalent counterparts. Here again, no reduction to Ni⁰ or Co⁰ occurred.

Similar results were obtained when testing samples with previously formed nitrates (the latter were produced by co-adsorption of NO + O₂¹⁶) which were then subjected to interaction with hydrocarbons.

Let us now consider the results from the point of view of the HC-SCR mechanism. SCR proceeds in excess oxygen and the reaction medium has to be considered as oxidative.² However, on a molecular scale, the active ensemble reacts with the hydrocarbon molecule which, according to our results, is likely to produce univalent cations. The formation of univalent cations is more favorable when using propene instead of methane. On the other hand, it has been reported that both Co⁺ and Ni⁺ are easily reoxidized in the

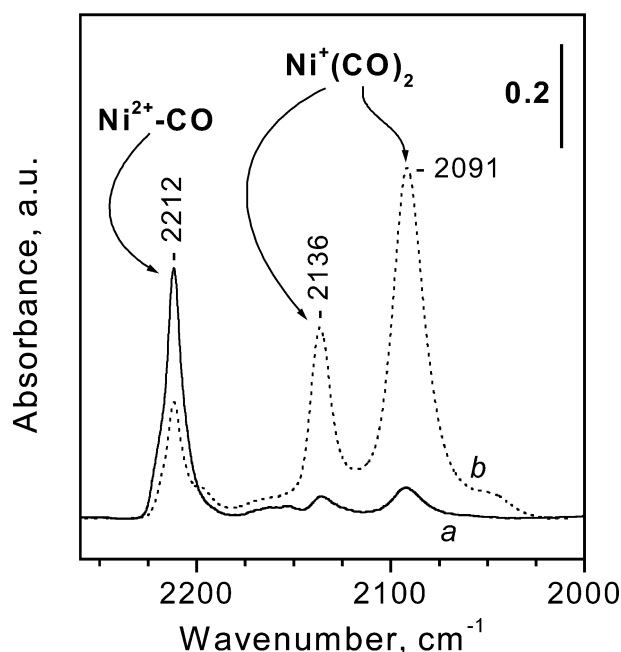


Fig. 2 FTIR spectra of CO (2.67 kPa) adsorbed on Ni-ZSM-5. Sample pre-reduced with CH₄ at 803 K (a) and with C₃H₆ at 573 K (b) (for details see text). The spectra are background corrected and the gas phase CO spectrum subtracted.

presence of NO_x. Thus, we can speculate that the Co²⁺/Co⁺ and Ni²⁺/Ni⁺ redox couples operate in the HC-SCR. They are most important (i) under reductive conditions; (ii) at high temperatures and (iii) in the presence of C₂₊ hydrocarbons.

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