

Thermal Decomposition of (η^6 -Benzene)tricarbonylchromium(0) Inside the α -Cages of the Na₅₆Y Zeolite

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Apresentamos aqui os primeiros resultados que mostram a diferença de estabilidade térmica do complexo (η^6 -benzeno)tricarbonilcromo(0), [Cr(η^6 -C₆H₆)(CO)₃], quando ancorado em sítios diferentes dentro das cavidades α do zeólito Na₅₆Y, sítios 1 e 2. Quando o sistema é aquecido sob vácuo dinâmico, o complexo ancorado no sítio 1, onde as interações C₆H₆-Na⁺ e Na⁺-OC são mais fortes, decompõe mais rapidamente que o complexo ancorado no sítio 2, onde tais interações são mais fracas. Sob vácuo estático, a velocidade de decomposição do complexo nos dois sítios é quase a mesma. O complexo no interior de Na₅₆Y é menos estável que o mesmo complexo no estado sólido.

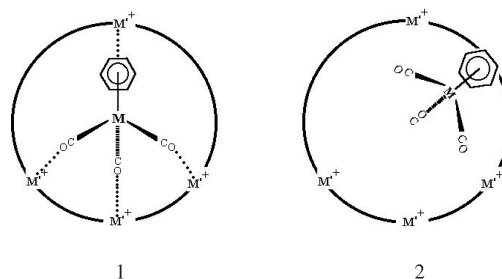
We present here the first results that show the different thermal stabilities of the complex (η^6 -benzene)tricarbonylchromium(0), [Cr(η^6 -C₆H₆)(CO)₃], when anchored at different sites inside the α -cages of zeolite Na₅₆Y, sites 1 and 2. When the system is heated under dynamic vacuum, the complex anchored at site 1, in which the interactions C₆H₆-Na⁺ and Na⁺-OC are stronger, decomposes slower than the complex anchored at site 2, in which such interactions are weaker. When the system is heated under static vacuum, the rates of decomposition of the complex anchored in both sites are comparable. The complex inside Na₅₆Y is less stable than the same complex in the solid state.

Keywords: (η^6 -benzene)tricarbonylchromium(0), Na₅₆Y zeolite, intrazeolite, thermal decomposition, FTIR spectra

Introduction

One of the most studied host-guest systems involves a wide range of zeolite hosts and organometallic guests, because of their unique capacity to provide the shape selectivity of zeolites simultaneously with the reactivity of metal centers.^{1,2} In particular, the incorporation of a variety of transition metal carbonyl complexes is relevant, considering the modifications of the structure and reactivity of these molecules after occlusion in the zeolite cavities. A comprehensive study of intrazeolite group VI metal hexacarbonyls and sub-carbonyls topotaxy was published by Özkar *et al.*,³ followed by the reports of the first kinetic study of an intrazeolite reaction.⁴ In the case of the complex [Mo(η^6 -C₆H₆)(CO)₃], in faujasitic zeolites, Brémard *et al.*⁵ proposed two different sorption sites based on molecular simulations carried out at 300 K and at fixed loading. The first evidenced sorption site, 1, corresponds to the π -electron density of the C₆H₆ moiety interacting

with one extraframework Na⁺ cation. Considering that the four Na⁺ cations are located in the vertices of a tetrahedron inside the α -cage, in the site 1, each of the other three Na⁺ cations are interacting with the oxygen end of each CO ligand. This leads to a decrease in the symmetry of the complex from C_{3v} to C_s or C₁.^{3,6,7} In the second site, 2, the C₆H₆ moiety is centered in the 12-ring window of the α -cavity, and the ligands CO are far from the Na⁺ cations, and the Cr(CO)₃ fragment maintain its C_{3v} symmetry.



Here we report on the results of the thermal decomposition of [Cr(η^6 -C₆H₆)(CO)₃] inside the α -cages of the zeolite Na₅₆Y.

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Results and Discussion

The organometallic complex was sublimed into a zeolite wafer inside the vacuum chamber of an IR cell similar to the one described by Pastore *et al.*⁸ The spectrum at 393 K, shown in Figure 1a, is consistent with the theoretical proposal⁵ of anchoring in two different sites 1 and 2, with loading of *ca.* one molecule *per* α -cage.

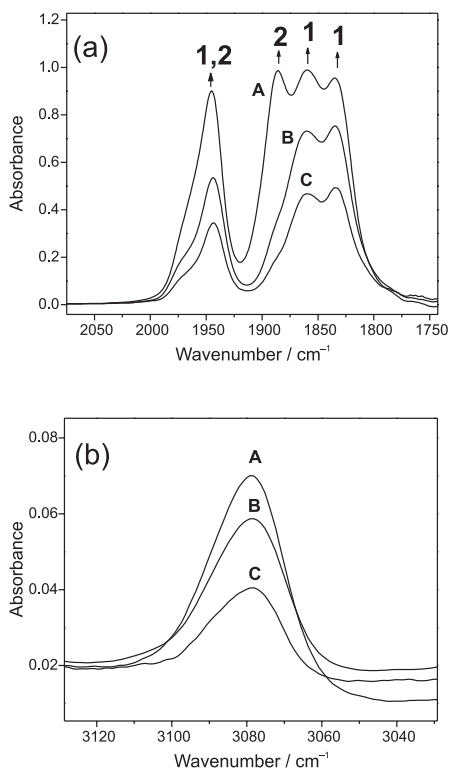


Figure 1. FTIR spectra of $[Cr(\eta^6-C_6H_6)(CO)_3]-Na_{56}Y$ heated under dynamic vacuum: a) in the ν_{CO} region: A) 393 K for 40 min, sites 1, 2: 1946 cm^{-1} , site 2: 1887 cm^{-1} , site 1: 1860 and 1834 cm^{-1} ; (B) 393 K for 40 min, 433 K for 2 h; (C) 393 K for 40 min, 433 K for 4 h. b) in the ν_{CH} region: A) 393 K for 40 min, 3078 cm^{-1} ; (B) 393 K for 40 min, 433 K for 2 h; (C) 393 K for 40 min, 433 K for 4 h.

The spectrum A in Figure 1a is typical of the newly loaded complex: no decomposition occurred during the first 40 min at 393 K. The assignment of the two differently anchored species was made considering the position of the ν_{CO} bands corresponding to the unsymmetrical stretching, E. The bands at lower wavenumbers (1860 and 1834 cm^{-1}) were attributed to the site where the interaction Na^+-OC is stronger (site 1). The band located at higher wave number (1887 cm^{-1}) was related to the site where the interaction Na^+-OC is weaker (site 2).

According to this interpretation, from room temperature up to 393 K both sites are equally favored judging by the intensities of the bands at 1946, 1860, and 1834 cm^{-1} , assuming that the molar absorptivities are similar. Thermal

treatment at temperatures higher than 393 K, in dynamic vacuum, showed that the complex at sites 1 and 2 has different stabilities. In Figure 1a, the intensity of the stretching ν_{CO} bands, corresponding to both sites, decrease as the thermal treatment progresses. However, it is observed that after heating for 2 hours at 433 K the band at 1887 cm^{-1} disappears almost completely while the other bands, at 1946, 1860 and 1834 cm^{-1} , attributed to stretching modes A_1 and E, remain *ca.* 55% of the original absorbances. Since the band at 1887 cm^{-1} was attributed to site 2, it means that the organometallic anchored to this site decarbonilates or detaches from the site faster than when anchored to site 1, which shows bands at 1860 and 1834 cm^{-1} . The profile of the band at 1946 cm^{-1} shows a little change when compared to the bands belonging to mode E. The shoulder close to 1980 cm^{-1} becomes more apparent. Probably it is associated with the complex in site 1. If it were associated to site 2 it would vanish after thermal treatment at 433 K. This attribution is in agreement with the reduction of the symmetry of the complex after anchoring to site 1. Since the band at 1946 cm^{-1} is related to both anchoring sites, it is difficult to carry out a detailed analysis, with unequivocal assignments. The band at *ca.* 3078 cm^{-1} , attributed to the stretching ν_{CH} of C_6H_6 in $[Cr(\eta^6-C_6H_6)(CO)_3]-Na_{56}Y$, is shown in Figure 1b. Like the ν_{CO} bands the intensity of the ν_{CH} band decreases throughout thermal treatment but, contrary to the observed for the ν_{CO} bands, the profile of the ν_{CH} band does not change very much. The spectra in Figure 1 suggest that the organometallic species initially anchored in sites 1 and 2 decomposes when submitted to temperatures higher than 393 K in dynamic vacuum. The decomposition is complete after eight hours, at 433 K. In these conditions both free CO and C_6H_6 are removed completely from the zeolite. The presence of chromium metal in the wafer was detected by X-ray fluorescence, showing that the thermal decomposition of the complex occurs inside the α -cages.

One of the most interesting features of the thermal treatment of the $[Cr(\eta^6-C_6H_6)(CO)_3]-Na_{56}Y$ system is that, contrary to the observed in the zeolite NaX,⁶ the anchored $Cr(CO)_3$ moiety is not formed. When the $[Cr(\eta^6-C_6H_6)(CO)_3]-NaX$ system is submitted to temperatures around 423 K, the complex loses the C_6H_6 , and the resulting $Cr(CO)_3$ moiety remains anchored in the oxygen atoms of the zeolite network.⁶ This sub-carbonyl is also formed from the thermal treatment of complex $[Cr(CO)_6]$ in the temperature interval of 373–423 K³ while in zeolite NaX, the anchored sub-carbonyl forms at *ca.* 303 K.⁶ An explanation for the different temperatures of decarbonylation of $[Cr(CO)_6]$ in

zeolites NaX and NaY is that the sub-carbonyls are stabilized by the Lewis basicity of the framework oxygen atoms to which they are bonded. Since zeolite NaX is more basic⁶ the sub-carbonyls are formed at lower temperatures when compared to the zeolite NaY. Further decarbonylation of $\text{Cr}(\text{CO})_3$ starts at 423 K in the zeolite Y while in the zeolite NaX it starts at 500 K. Therefore the anchored $\text{Cr}(\text{CO})_3$ sub-carbonyl is thermally more stable in NaX than in NaY.

We speculate that in the system $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]\text{-Na}_{56}\text{Y}$ the formation of $\text{Cr}(\text{CO})_3$ might occur at temperatures above 413 K. However, according to Özkar *et al.*³ decarbonylation of $\text{Cr}(\text{CO})_3$ obtained from $[\text{Cr}(\text{CO})_6]$ occurs at around 420 K. Presumably, the first step of the decomposition of $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]$ occluded in NaY is dissociation of C_6H_6 , followed by immediate decarbonylation of the resulting sub-carbonyl.

Experiments in static vacuum show that the species $(\eta^6\text{-C}_6\text{H}_6)\text{Cr-Na}_{56}\text{Y}$ is not formed during the decomposition. The spectrum B in Figure 2b obtained after the thermal treatment, compared to the spectra A and C, indicates the presence of free benzene in the zeolite wafer.

Under static vacuum, contrary to the observed under dynamic vacuum, the complexes in both sites (schematic 1

and 2) decompose at comparable rates as shown by the FTIR spectra in Figure 2a. In static vacuum the system is closed and free benzene is observed inside the cavities as shown by the FTIR spectra in Figure 2b. Huang and Poissant⁷ mixed mechanically the zeolite NaY with crystalline $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]$ in a closed vessel, and obtained a different metal carbonyl species, $[\text{Cr}(\text{CO})_6]$. In our system, the presence of free benzene, and some CO, inside the cavities, retard the rate of decomposition in site 2.

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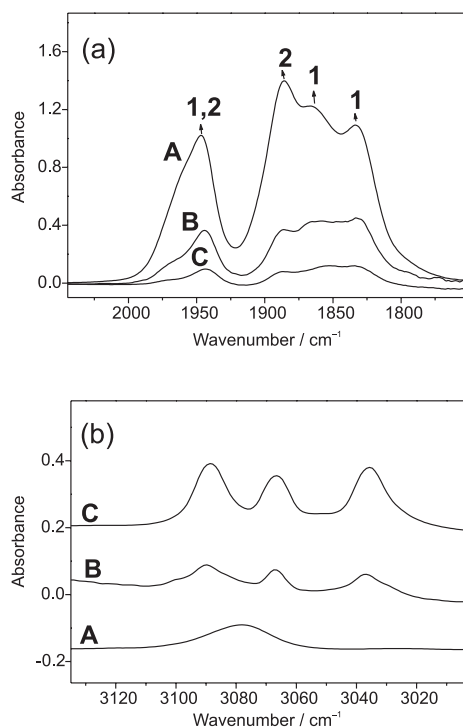


Figure 2. FTIR spectra of $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]\text{-Na}_{56}\text{Y}$ heated under static vacuum. (a) in the ν_{CO} region: (A) 393 K for 40 min.; sites 1,2: 1945 cm^{-1} ; site 2: 1887 cm^{-1} ; site 1: 1860 and 1834 cm^{-1} , (B) 393 K for 40 min, 433 K for 2 hours. (C) 393 K for 40 min, 433 K for 4 h. (b) in the ν_{CH} region: (A) before thermal treatment; (B) after thermal treatment; (C) free C_6H_6 occluded in Na_{56}Y .

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