Cluster quantum-chemical study of the interaction of carbon monoxide with surface acid centers of highly dispersed magnesium chloride

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Within the MINDO/3 method, cluster models giving a description of highly dispersed magnesium chloride containing all sets of acid sites, i.e. three-, four- and five-coordinate magnesium ions, and surface hydroxyl groups have been proposed. Three types of CO adsorption complexes on the magnesium chloride surface have been considered. The C–O stretching frequencies of these adsorption complexes and the O–H stretching frequencies of hydroxyl groups on magnesium chloride calculated by a harmonic oscillator approach are in good agreement with available experimental and theoretical data.

Keywords: magnesium chloride; carbon monoxide adsorption; quantum-chemical MINDO/3 calculations

1. Introduction

Highly dispersed magnesium chloride is one of the most effective supports used to prepare highly active catalysts for olefin polymerization [1]. By analogy with a Ziegler–Natta catalyst it contains titanium tetrachloride as an active component of the catalyst which is strongly adsorbed on magnesium chloride via interaction with surface low-coordinate magnesium ions. The experimental data is known to be a relation between the defectness of the crystal of magnesium chloride and the quantity of $TiCl_4$ strongly adsorbed on the support [2,3].

Quite recently, new experimental data on the surface low-coordinate magnesium ions (surface acid sites) for highly dispersed magnesium chloride have been obtained [4]. In ref. [4], diffuse reflectance IR spectroscopy has been used to study carbon monoxide adsorption on magnesium chloride due to increasing sensitivity compared to usual IR spectroscopy. These authors observed IR bands at 2210, 2190, 2170 and a broad band at 2100–2130 cm^{-1} upon adsorption of carbon mon-

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oxide on the various samples of magnesium chloride. The former three bands were attributed to carbon monoxide chemisorbed on cations of the magnesium chloride lattice and the latter band was referred to physically adsorbed carbon monoxide. It is interesting to note that a noticeable decrease of the 2210 and 2190 cm^{-1} band intensities is observed in these experiments when CO adsorbs on magnesium chloride heated to 200°C. At that time, the intensity of the band at 2170 cm^{-1} is practically unchanged. It has also been found that the samples of magnesium chloride studied contain adsorbed or hydrated water, which is not deleted either upon heating in vacuum to 200°C or by processing with a diethylaluminium chloride and/or with adsorption of titanium tetrachloride.

In this connection, it is interesting to find out how these experimental bands can be described within quantum-chemical calculations. In our opinion, such direct calculations of the stretching vibrational frequencies of the surface carbonyl structures will be useful for the determination of the molecular structure of the surface centers. In this paper an attempt is made to apply the semiempirical quantum-chemical MINDO/3 method to describe the active surface centers of magnesium chloride and to consider chemisorption of various molecules on its surface, in particular, the adsorption of carbon monoxide. Since the present study is going to form a basis for future studies of active titanium chloride stabilization on magnesium chloride systems, it is also interesting to investigate a priori the active sites of the support only. This method proves itself best on the calculation of the potential energy surfaces of organic compound reactions [5], and it is repeatedly used in calculations of chemisorption on alumina–silica, zeolites, magnesium oxide and zinc oxide [6–11].

2. Calculation method and surface model

Cluster quantum-chemical calculations have been carried out within the framework of the MINDO/3 method [12], with parameterization extended in order to consider magnesium containing compounds [13]. A magnesium chloride surface has been modeled by the cluster $Mg_9Cl_{16}(OH)_2$, representing a three-layer molecular structure and containing the most chemically active low-coordinate surface magnesium and chloride ions (Mg^{2+}_{LC} and Cl^{-}_{LC}) in various surface irregularities. These clusters differ from each other by the placement of hydroxyl anions compensating for the extra positive charges and connected by crystallo-chemically unequal cations of magnesium chloride, i.e. with three-, four- and five-coordinate magnesium ions. In the calculations, full optimization of the geometry of both the initial cluster and adsorbate molecule and various chemisorption complexes up to the total energy minimum was carried out. It should be noted that such a supermolecular approach correctly describes both the relaxation of the surface active sites and their influence on the energetics of the chemosorptive processes (see for example ref. [13]).

Calculations of the O–H and C–O stretching frequencies ν_{OH} and ν_{CO} of various surface hydroxyl groups and chemisorption complexes of carbon monoxide on magnesium chloride were carried out on the basis of a harmonic oscillator approach in the vicinity of the total energy minimum represented by a parabola at the optimized distance R_{OH} and at $R_{OH} \pm 0.0005$ nm, and at R_{CO} and $R_{CO} \pm 0.0005$ nm, respectively.

3. Results and discussion

To model the magnesium chloride surface containing all types of low-coordinate magnesium ions we tested the clusters with various sizes corresponding to the stoichiometric composition of Mg_nCl_{2n}. Unfortunately, such clusters contain "hanging" one-coordinate chloride ions which could lead to incorrectness in the calculated results. Some of these examples we would like to show in the appendix. On the other hand, one needs to use a relatively large cluster for reproduction of all sets of low-coordinate surface magnesium ions. The minimal clusters in the composition of $Mg_9Cl_{16}(OH)_2$, where $n = 9, 12, 15$, are satisfied to these demands. Since the transition from a $Mg_9Cl_{16}(OH)_2$ cluster to more extended $Mg_{15}Cl_{28}(OH)_2$ ones practically does not influence the structural and energetical characteristics of chemisorption complexes realized on the similar surface parts, we present below the results obtained using a "relatively" small $Mg_9Cl_{16}(OH)_2$ cluster, where the "hanging" one-coordinate chloride ions were substituted by two hydroxyl groups, i.e. the extra positive charge of the cluster is compensated by hydroxyl anions. The observation of the presence of water in the initial magnesium chloride samples [4] is in favor of the importance of using such a model.

Fig. 1 shows the $Mg_9Cl_{16}(OH)_2$ clusters, where hydroxyl groups are bonded to two three-, or four-, or five-coordinate magnesium cations for symmetry reasons. As an example, the geometry of one such a cluster is shown in table 1. As it was expected some dispersion in the Mg–Cl distance is observed due to inhomogeneity of the surface magnesium and chlorine atoms. The distance between magnesium cations equal to 0.3592 nm or between chloride anions in the same layer equal to 0.3551 nm is in good agreement with available crystallo-graphical data for magnesium chloride.

Table 1
Geometry characteristics (bond lengths, nm) of the cluster $Mg_9Cl_{16}(OH)_2$, where OH-groups are bonded to two three-coordinate magnesium cations as calculated with the MINDO/3 method

Bond type	Bond length	Bond type	Bond length
Mg_{6C}–Cl_{3C}	0.2492	Mg_{4C}–Cl_{2C}	0.2443
Mg_{5C}–Cl_{3C}	0.2473	Mg_{3C}–Cl_{2C}	0.2485
Mg_{5C}–Cl_{2C}	0.2464	Mg_{3C}–O	0.1837
Mg_{4C}–Cl_{3C}	0.2470	O–H	0.0929

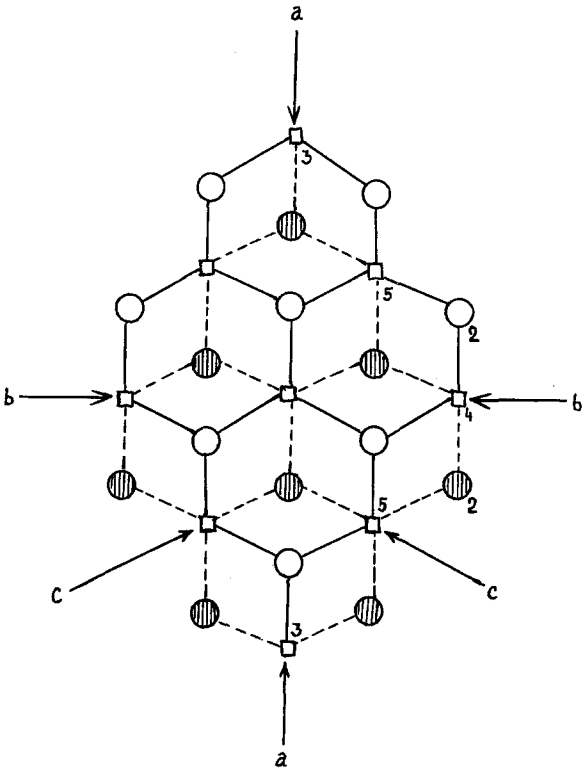

Fig. 1. $Mg_9Cl_{16}(OH)_2$ cluster modeled magnesium chloride surfaces. Coordination numbers of bulk magnesium cations and chloride anions are equal to 6 and 3, respectively. The magnesium atom layer is situated between two layers of chlorine atoms. This results in the formation of a three-layer structure. The sites of formation of OH-groups on three-, four- and five-coordinate magnesium cations are shown as a, b and c, respectively. Numerals correspond to the coordination number of the surface magnesium cations and chloride anions.

Perhaps, the magnesium chloride contains at least three types of surface hydroxyl groups which differ from one another by the coordination number of magnesium cations in the first coordination sphere, i.e. they are Mg_{5C}–OH, Mg_{4C}–OH and Mg_{3C}–OH. We have calculated O–H stretching frequencies ν_{OH} of these three types of hydroxyl groups on the magnesium chloride surface. It should be noted that we used the same scaling factor for hydroxyl groups, which was found for hydroxyl groups on magnesium oxide [14] and equals $f = 0.924$. According to our MINDO/3 calculations, these O–H stretching frequencies ν_{OH} equal 3674, 3763 and 3765 cm, respectively, for Mg_{5C}–OH, Mg_{4C}–OH and Mg_{3C}–OH. Clearly, the acidity of these hydroxyl groups corresponds to a similar one for magnesium oxide and displays the same dependence of ν_{OH} on the coordination number of magnesium atom as suggested in ref. [14].

Let us move on to consider the results of the calculations of carbon monoxide adsorption on magnesium chloride using this $Mg_9Cl_{16}(OH)_2$ cluster, where

hydroxyl groups are bonded to two five-coordinate magnesium cations (fig. 1c). In this case, three various types of adsorption sites are easily accessible for the CO molecule, i.e. they are three-, four- and five-coordinate magnesium cations. Table 2 shows the heats of adsorption of CO in the corresponding adsorption structures, the most essential geometry characteristics and the calculated C–O stretching frequencies ν_{CO}. The former are calculated as total energy differences between an adsorption complex and the sum of the noninteracting cluster and the CO molecule. As was expected, adsorption of the carbon monoxide molecule on a three-coordinate Lewis acid center of magnesium chloride is energetically most favorable. This form of adsorption results in the formation of a carbonyl complex and leads to the largest increase of the stretching frequency ν_{CO} compared to a free carbon monoxide molecule. The variations of the stretching frequency ν_{CO} in the adsorption complexes correlate directly with it s bond lengths, i.e. the lower the C–O bond length the higher the stretching frequency ν_{CO}. The electron density is partially transferred from adsorbate molecule to the surface upon adsorption and equals 0.240, 0.209 and 0.165 e^-, respectively, for the adsorption of CO on three-, four- and five-coordinate magnesium cations. These results are in good agreement with the experimental data mentioned above [4]. In our opinion, the bands at 2210, 2190 and 2170 cm^{-1} detected in the experiments [4] should be attributed to the adsorption complexes of carbon monoxide with three-, four- and five-coordinate Lewis acid sites of magnesium chloride, respectively.

4. Conclusion

Cluster models giving a description of highly dispersed magnesium chloride containing all sets of low-coordinate magnesium ions and surface hydroxyl groups have been proposed. Adsorption of carbon monoxide on the magnesium chloride surface leads to the formation of three types of carbonyl complexes. The C–O stretching frequencies of various adsorption complexes calculated allow one to attribute the bands of 2210, 2190 and 2170 cm^{-1} detected in the experiments [4] to

Table 2
Heats of adsorption (ΔE, kcal/mol), geometry characteristics (bond lengths, nm) and C–O stretching frequencies ν_{CO} (cm^{-1}) of various adsorption structures on magnesium chloride modeled by $Mg_9Cl_{16}(OH)_2$ cluster as calculated by MINDO/3 method

Type of complex	ΔE	Geometry characteristics	ν_{CO} [a]
Mg_{5C}–CO	9.5	MgC, 0.2356; CO, 0.1131	2168
Mg_{4C}–CO	20.1	MgC, 0.2259; CO, 0.1129	2177
Mg_{3C}–CO	25.5	MgC, 0.2202; CO, 0.1126	2197

[a] C–O stretching frequencies ν_{CO} are calculated using the scaling factor $f = 0.943$. The latter was found from the optimal conformity of calculated ν_{CO} with the experimental C–O stretching frequency for free carbon monoxide molecule (2143 cm^{-1} in the gas phase).

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Appendix

As was mentioned above, we tested clusters with various sizes corresponding to the stoichiometric composition of Mg_nCl_{2n}. As an example, below is shown the cluster of Mg_9Cl_{18}, where the "hanging" one-coordinate chloride ions are bonded to two three-, or four-, or five-coordinate magnesium cations for symmetry reasons (cf. fig. 1). As was expected, some differences both in the optimized geometry of these clusters and the dispersion in the Mg–Cl distance are observed compared to similar clusters with a composition of $Mg_9Cl_{16}(OH)_2$. For example, the distance between magnesium cations equals 0.3511 nm and the distance between chloride anions in the same layer equals 0.3486 nm. These distances slightly differ from those in a similar cluster of $Mg_9Cl_{16}(OH)_2$ with hydroxyl groups on three-coordinate magnesium cations (see text). The relative stability of these clusters is the same as for OH-containing clusters, i.e. one-coordinate chloride anions are preferably bonded to two three-coordinate magnesium cations.

The main differences are found when we consider the adsorption of carbon monoxide on these clusters. Below, the results obtained using Mg_9Cl_{18} cluster, where one-coordinate chloride anions are bonded to two five-coordinate magnesium cations, are shown. Table 3 shows the heats of CO adsorption in the corresponding adsorption structures. The most essential geometry characteristics and calculated C–O stretching frequencies ν_{CO} are also shown.

Here, as was also expected, the adsorption of a carbon monoxide molecule on a three-coordinate Lewis acid center of magnesium chloride is energetically most

Table 3
Heats of adsorption (ΔE, kcal/mol), geometry characteristics (bond lengths, nm) and C–O stretching frequencies ν_{CO} (cm^{-1}) of various adsorption structures on magnesium chloride modeled by Mg_9Cl_{18} cluster as calculated by MINDO/3 method

Type of complex	ΔE	Geometry characteristics	ν_{CO} [a]
Mg_{5C}–CO	18.1	MgC, 0.2360; CO, 0.1131	2169
Mg_{4C}–CO	27.1	MgC, 0.2280; CO, 0.1131	2164
Mg_{3C}–CO	33.0	MgC, 0.2246; CO, 0.1127	2195

[a] See footnote to table 2.

favorable compared to the other two molecules, although these values are slightly overestimated for this type of interaction (cf. table 2). This form of adsorption results in the formation of a carbonyl complex and leads to the largest increase of the stretching frequency ν_{CO}, compared to the free carbon monoxide molecule. In contrast to the similar OH-containing cluster calculations, we could not find any correlation between the stability of adsorption complexes of CO and the corresponding stretching frequency ν_{CO}. Moreover, the latter is not in good agreement with the experimental bands mentioned above. The electron density is partially transferred from adsorbate molecule to the surface upon adsorption, but there is no dependence between their quantity and the corresponding stability of adsorption complexes. These values are equal to 0.228, 0.289 and 0.264 e^-, respectively, for the adsorption of CO on three-, four- and five-coordinate magnesium cations. Perhaps, this "failure" is due to using a "relatively" small Mg_9Cl_{18} cluster, in which "hanging" one-coordinate chloride ions have a relatively large orbital extent compared to hydroxyl groups thereby strongly influencing the CO adsorptive interaction on the "nearest" four-coordinate magnesium site.

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