Cluster model study on the surface interactions of γ-alumina-supported metal oxides

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Abstract

Cluster models embodying the periodicity and symmetry of atomic arrangement on the surface of γ-Al_2O_3, as a support, have been applied to discuss the dispersion state of metal oxide (i.e., MoO_3, NiO, or CuO) on the basis of the incorporation model from the theoretical chemistry's point of view. The preference occupation of the tetrahedral or octahedral vacant sites available on the surface of γ-Al_2O_3 by the dispersed metal cations is related to the intrinsic properties and the amount of the dispersed metal oxide as well as the calcination temperature used for sample preparation. The results are in good agreement with the experimental facts. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many studies have suggested that upon dispersing a transition metal oxide (e.g., CuO, NiO, MoO_3, WO_3, or V_2O_5, etc.) on an oxide support (e.g., Al_2O_3, TiO_2, SiO_2, or CeO_2, etc.) [1–11], a two-dimensional overlayer of the oxide species can be formed. The molecular structure and reactivity of the dispersed transition metal oxide species have been intensively studied because of their importance in understanding the nature of the interaction between oxide and support and because of their important application in numerous catalytic reactions [1–12]. Metal oxide supported on γ-Al_2O_3 has

widely been the subject of interest, and it has been well accepted that the role of γ-Al_2O_3, as a support, is not merely that of dispersing the metal oxide, however, the exact nature of the interaction between many metal oxides and γ-Al_2O_3 is still not clearly understood.

Several surface models relating to the interactions between metal oxide and γ-Al_2O_3 have been proposed in the literature. For example, Bruggraf et al. [13] have proposed that on γ-alumina supported nickel oxide Ni^{2+} ions can diffuse into the surface lattice vacancies of γ-Al_2O_3 until which is saturated with nickel cations, then the growth of nickel oxide microcrystals follows. Jacono et al. [14] have suggested that nickel ions might occupy the tetrahedral and octahedral sites of γ-alumina with the

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formation of what they called a surface spinel with an average thickness of about 0.1 to 0.4 nm. In contrast, the penetration of Mo^{6+} ions into alumina subsurface has been argued to be almost impossible [15]. An oligomer model has been proposed by Weigold [16] based on the consideration that molybdate species react with hydroxyl groups on the support and undergo oligomerization. On the other hand, many authors have suggested that under appropriate conditions a monolayer of MoO_3 might cover the surface of γ-alumina. According to Schuit and Gates [17] a two-dimensional monolayer of MoO_3 is formed by epitaxial growth on the (110) plane of alumina, and at full coverage, the MoO_3 monolayer can still maintain the symmetry of the (110) plane of γ-alumina. Xie and Tang [18] have found that many oxides and salts can disperse spontaneously as a monolayer on the surface of supports upon the calcination of their mechanical mixtures, and a so-called close-packed monolayer model has been used to estimate the dispersion capacity of MoO_3 supported on γ-alumina, however, for metal oxides with lower valence types, e.g., NiO, MgO and Li_2O, etc., the experimental results are always lower than the values expected by the close-packed monolayer model. Hall [19] has proposed that at Mo loading close to monolayer capacity, the dispersed molybdena species are present in small clusters or islands containing presumably seven Mo atoms and being two layers thick, and part of the alumina surface remains uncovered. It has also been suggested that it may be more appropriate to consider that the Mo^{6+} cations are located in the first two or three surface layers of alumina instead of just staying on the top of its surface [20]. Taking into consideration the surface structure of the support and the valence type of the dispersed ionic compounds, an incorporation model has been proposed by one of the authors [21,22]. With the assumption that the cations of the dispersed ionic compound are incorporated into the vacant sites available on the surface layer of the support and the accompanied anions are

positioning on the top of the incorporated cations for charge compensation, the model has been applied successfully in several systems to quantitatively estimate the dispersion capacity of ionic compounds of various types. As a matter of fact, various explanations and models from different point of views can often be found in the literature, and as concluded by Massoth [15] in his review paper although some of the proposed models have their advocates, none can be considered definitely proven at present. The discrepancies that appeared in different studies are usually attributed to the differences in preparation conditions which might produce critical influences on the dispersion state of the supported oxides, and also to the different characterization methods used, as most of the physical techniques are comparative in nature, which might lead to some misunderstanding concerning the details of the dispersed species which are usually nonstoichiometric. Hence, it is not surprising to see with the emergence of better surface techniques and the improvements of experimental and theoretical studies, some of the old explanations as well as some models on supported oxide system are revised.

The term monolayer has been used very often in describing the dispersion of supported metal oxides, especially when their loading amounts are low. Indeed, this might be the case for samples prepared by ion exchange or incipient wetness impregnation, for these samples the anchored cations are linked to the surface mostly by the interaction between the hydroxyl groups on support and on the hydrated cations from solution, under these kinds of circumstances it is reasonable to argue that a compact monolayer might be formed on the surface of the support. However, for samples prepared after calcining under high temperature which might be higher than the Tamman temperature of the dispersed metal oxide, it seems more reasonable to consider that the solid state diffusion process and the interaction between the dispersed species and the support can no longer be neglected. Consequently, the dispersed species are mostly

interacted with the support instead of just physically deposited or dispersed on it, to get a deeper insight on the nature of the dispersed species and their interaction with the support, the intrinsic properties of the dispersed ionic compounds (e.g., their electronic structure and valence type, etc.) and of the support (e.g., their surface structure, chemical reactivity, etc.) should be taken into consideration. Reported in this paper are our recent results concerning the dispersion and site preference of some metal oxides on γ-alumina obtained by means of theoretical calculation/computational modeling on the basis of the incorporation model.

2. Cluster models and calculating method

The cluster model approximation, usually used in the molecular orbital and tight-binding calculations of solid surface, is employed to discuss the surface of γ-Al$_2$O$_3$ and its interaction with some metal oxides, see, e.g., Refs. [23,24].

To discuss the interactions between the dispersed oxide and support, the surface structure of the support is obviously one of the main factors needed to be taken into consideration. Usually different crystalline planes are exposed on a powder sample, however, to develop a detailed description it is very helpful to have models of possible surface structure of the support. The first approximation made by the incorporation model is to assume that there is a preferentially exposed crystalline plane in some of the supports. Indeed, we have found [5,21,22] that at least γ-alumina, ceria and titania are supports which the above approximation can be applied with in experimental errors of the measured dispersion capacities. Taking γ-alumina as an example, neutron diffraction studies of CD$_4$ adsorption [25] have indicated that its surface is consisting of (110) and (100) planes, with an area of ~ 40 and ~ 8 m^2/g, respectively, and, noteworthy, no trace amount of (111) plane was found. Moreover, it was concluded by the determination of lattice constants that most of the grains ($\sim 90\%$) of a γ-alumina thin film are oriented with the surface normal along the (110) direction [26]. Thus, it is proposed, as a first approximation, that the (110) plane is preferentially exposed on γ-alumina which consists of particles with one-dimensional stacking of its C–D–C–D $\cdots$ layers, and the exposure probability of these two layers is equal as suggested by Schuit and Gates [17]. Schematically shown in Fig. 1 are the structure and our cluster models of the C- and D-layer, respectively (C-layer—21 atoms, D-layer—17 atoms, and C + D-layer—38 atoms).

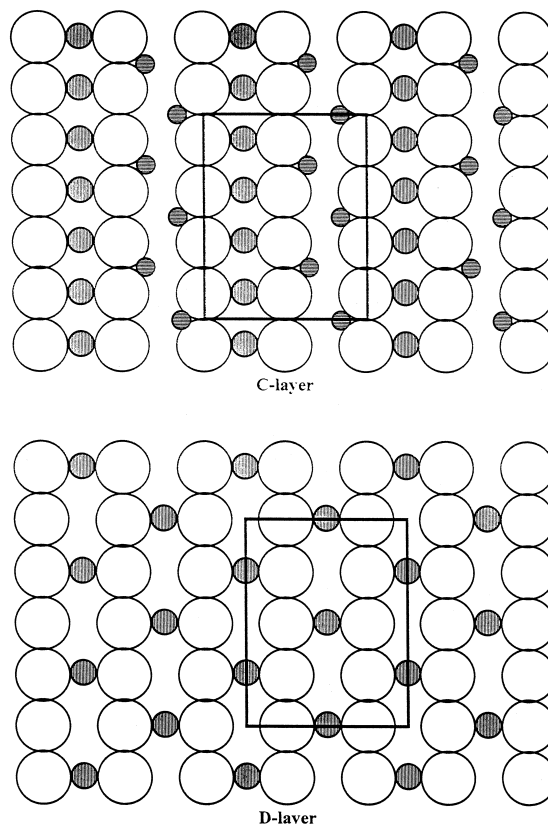In the present work, two layers, i.e., C- and D-layer, are considered together to model the

Fig. 1. The cluster model (as drawing in the framework) for C- and D-layer of γ-alumina (110) (C-layer—21 atoms, D-layer—17 atoms, and C + D-layer—38 atoms). (Large circle)—oxygens anions; (medium, lightly-shaded circle)—octahedral Al^{3+}; (small circle, fully shaded)—tetrahedral Al^{3+}.

surface of γ-alumina. According to the atom arrangement of surface structure, the cluster consists of two repeated units of (110) surface-layer (C + D) (including 38 atoms, C-layer: Al9O12, D-layer: Al7O10) as included in the framework of Fig. 1. The termination of cluster has not used any atom to saturate. As the cluster is great enough and the interaction between metal oxides and support surface is localized, the strength of interaction may not be influenced much by the termination, non-saturation of cluster. The overall charge of cluster is +4. According to the partitioning rule of repeated unit of γ-Al$_2$O$_3$ (110) surface as shown in Fig. 1, there are 16 atoms in the two units of C-layer $[(7 + 2 \times 1/2)\text{Al} + (4 + 8 \times 1/2)\text{O}]$, and its charge is +8, but there are 12 atoms in the two units of D-layer $[(1 + 6 \times 1/2)\text{Al} + (6 + 4 \times 1/2)\text{O}]$, and its charge is −4, so the net charge in the two units of C + D-layer is +4, which equals to the overall charge of simulating cluster. The effect of charge will be alleviated much. Since the simulating cluster is taken from the two units of γ-Al$_2$O$_3$ (110), the tailoring of cluster is satisfied with periodical border condition of γ-Al$_2$O$_3$(110) surface.

In the following calculations, metal oxides themselves are always electroneutral, and two cases are discussed separately for the dispersion of metal oxides (MO) on the C- or D-layer as the first surface layer, namely: (i) at a rather low MO loading that the interactions between the dispersed MO species can be neglected, and the shielding effect of the capping anions, if there is any, is not significant; (ii) at a higher MO loading, both the interactions between the dispersed species and the shielding effect produced by the capping anions should be taken into consideration. Shown in Figs. 2 and 3 are the cluster models (the support surface is modeled by C + D two layers) of the incorporation of M^{n+} cations into the available octahedral and tetrahedral sites on the C- or D-surface layer of γ-alumina at low and high MO loading, respectively. The number of cluster atoms includes the 38 atoms of C + D-layer and metal
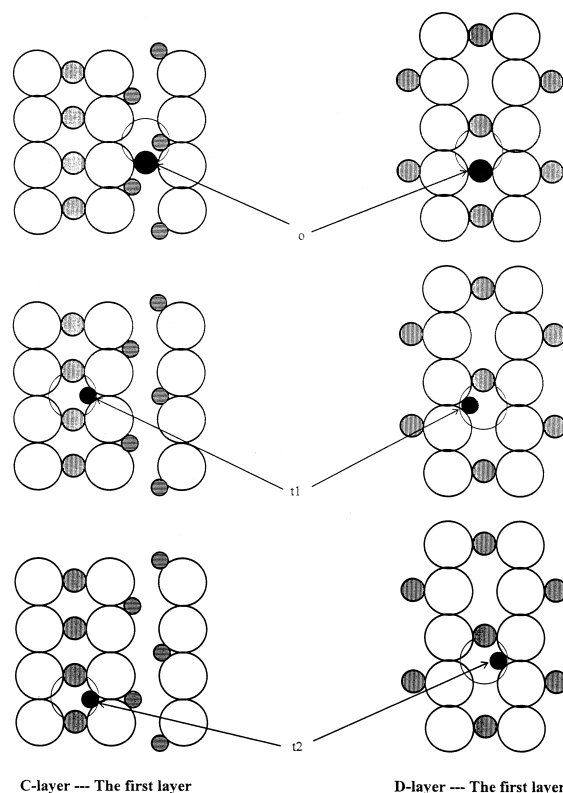

C-layer --- The first layer   **D-layer --- The first layer**

Fig. 2. The cluster model of the M^{n+} incorporating into the vacant site of γ-alumina (110) surface at low metal oxide loading. (The positions indicated by the pointer are the sites for the incorporation of metal cations investigated, C + D-layer as a modeling of support γ-alumina (110) surface—38 atoms, and metal oxides (MO)—2 atoms). (Large circle, boldly defined)—O^{2-}; (Large circle, lightly defined)—capping O^{2-}; (small, fully-shaded circle)—tetrahedral Al^{3+}; (medium, fully-shaded circle)—octahedral Al^{3+}; (small, lightly-shaded circle)—tetrahedral M^{n+}; (medium, lightly-shaded circle)—octahedral M^{n+}.

oxide atoms, the overall charge of cluster is the same as the modeling cluster of support surface.

The semiempirical molecular orbital method (CNDO/2) had been employed to study the electronic structure of metal Mo and Ti cluster compounds [27], recently Rodriguezarias et al. [28] have used CNDO method to investigate the interaction between pyridine and partially hydrogenated MoS$_2$ surface, and now the method is applied for the following calculations with metal oxide atoms as adsorbates on γ-Al$_2$O$_3$ (110) surface, which results from the expensive efforts of the first principle calculations on the

NiO/γ-alumina(C+D) with C-layer as the first layer

CuO/γ-alumina(C+D) with C-layer as the first layer

NiO/γ-alumina(C+D) with D-layer as the first layer

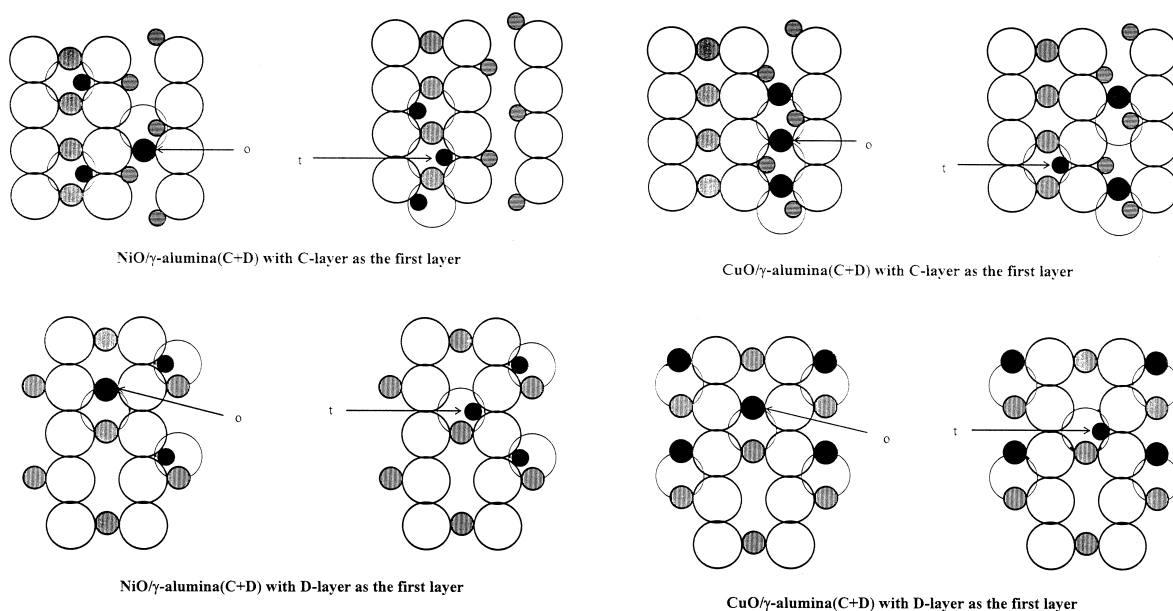CuO/γ-alumina(C+D) with D-layer as the first layer

Fig. 3. The cluster model of the M^{n+} incorporating into the vacant site of γ-alumina (110) surface at higher metal oxide loading. (The positions indicated by the pointer are the sites for the incorporation of metal cations investigated, and C + D-layer as a modeling of support γ-alumina (110) surface—38 atoms, but metal oxides (NiO) include 6 atoms, CuO include 6 atoms when C-layer of support as first surface layer, 10 atoms when D-layer as first surface layer). [The significance of symbols cf. Fig. 2].

great cluster models with the inclusion of many metal oxide atoms. Although the semi-empirical CNDO/2 method in accuracy is not so good as the first principle calculation, we here focus on some qualitative trends instead of accurate values. Meantime we discuss results in comparative ways to reduce the uncertain error of calculations. The basic functions of the ns, np, $(n - 1)$d and the ns, np valence orbital for metal and non-metal atoms are considered, respectively. Listed in Table 1 are the orbital exponents, electronegativities and bonding parameters of the atomic orbital (AO) of the metal atoms. The CNDO/2 parameters for the non-metal atoms are taken from Ref. [29]. The bond lengths of Ni–O, Cu–O and Mo–O are taken, respectively, as 2.10 Å, 1.95 Å, and 2.00 Å with the assumption that upon incorporation the M–O distances are almost unchanged, which is consistent with the EXAFS result on NiO/γ-Al$_2$O$_3$ reported in the literature [18,30]. The radius of oxygen anion is taken as 1.35 Å. Since the dispersion of metal oxides onto oxide support

surfaces is a very specific case, i.e., the interaction between metal oxides and support surfaces is not so strong as the chemical bond in compounds, the geometries of metal oxides and support surfaces are not changed much, it is better to use the above geometry than optimized

Table 1
CNDO/2 parameters for Cu, Ni, Mo

Atom	Orbital	Orbital exponents	$(I_f + A_f)/2^a$ (eV)	$\beta_f^0 X$ (eV)[b]
Mo	5s	1.710	3.250	−6.0
	5p	0.410	0.830	−4.0
	4d	2.050	2.580	−6.5
Cu	4s	1.950	4.567	−35.0
	4p	1.200	1.347	−35.0
	3d	3.733	6.590	−30.0
Ni	4s	1.530	4.306	−14.0
	4p	0.450	1.260	−6.0
	3d	2.120	6.184	−19.0

[a]I_f, ionization energy; A_f, electron affinity for f atomic orbital (e.g., f for Mo may indicate 5s, 5p and 4d).
[b]$\beta_f^0 X$, bonding parameters of the f atomic orbital of the metal atoms.

geometry. Furthermore, the optimized geometry will finally be corresponding to some compounds (composed of metal oxides and supports) instead of the above-mentioned dispersion.

3. Results and discussions

The incorporation model taking into consideration of the surface structure of the support has been used to explain some well known experimental facts, which can neither be answered by the monolayer dispersion model nor by the close-packed model. For example: (1) why an ionic compound (e.g., NiO, MgO, or NaCl, etc.) has different dispersion capacities on different supports, such as, the dispersion capacities of NiO on γ-alumina, on ceria and on silica are apparently different; and (2) why different ionic compounds have different dispersion capacities, on a same support, as it is well known that MoO_3 can form a so-called close-packed monolayer on γ-alumina, but NiO, MgO, Li_2O, NaCl cannot. However, if only the geometric factors are being considered, the incorporation model still cannot explain some other experimental phenomena, such as the preferential occupation of some surface sites on the support by the metal cations, for example, as it has been shown that Ni^{2+} cations prefer the tetrahedral sites on γ-alumina while Cu^{2+} the octahedral. Obviously, to get a deeper insight of the interactions between the ionic compound and support, besides the surface structure of the support and the valence type of the ionic compounds, attentions should be paid to the intrinsic properties (e.g., the electronic structure, bond length, bond strength, etc.) of the interacted species.

3.1. At low MO loading

This section focuses firstly on the situation that the loading amount of the ionic compound is so low that the interactions between the dispersed metal oxide species can be neglected.

Listed in Table 2 are the Wiberg bond order which is a measure of the bond strength between the corresponding dispersed species and support, and total energy (E_T) of the corre-

Table 2
Wiberg bond order, and total energy (E_T) of relevant species when the loading amount of the metal oxide (MO) is low

	o	t1	t2
CuO-D1C2			
O–S	0.9388	0.7522	0.7397
Cu–S	3.0604	3.1061	3.1371
(Cu+O)–S	3.9992	3.8583	3.8768
E_T (a.u.)	0.00	0.66	0.29
CuO-C1D2			
O–S	1.2629	1.0904	1.1301
Cu–S	3.2791	3.2092	3.2097
(Cu+O)–S	4.5420	4.2996	4.3398
E_T (a.u.)	0.00	0.44	−0.09
MoO₃-D1C2			
O–S	0.7859	1.0009	1.0645
Mo–S	1.0047	1.2261	1.2700
(Mo+O)–S	1.7906	2.2270	2.3345
E_T (a.u.)	0.00	0.11	0.06
MoO₃-C1D2			
O–S	0.9952	1.2466	1.4305
Mo–S	1.1948	1.3863	1.4030
(Mo+O)–S	2.1900	2.6329	2.8335
E_T (a.u.)	0.00	−0.04	0.06
NiO-D1C2			
O–S	1.0049	0.7054	0.6359
Ni–S	3.1496	3.8432	4.1557
(Ni+O)–S	4.1545	4.5486	4.7916
E_T (a.u.)	0.00	1.52	0.73
NiO-C1D2			
O–S	1.0920	0.9760	0.9962
Ni–S	3.6975	4.0478	4.1376
(Ni+O)–S	4.7895	5.0238	5.1338
E_T (a.u.)	0.00	1.95	1.39

The E values are related to those of the octahedral sites which are taken as 0.00.
1 a.u. = 2.63103×10^3 kJ/mol.
D1C2 and C1D2 representing respectively the surface D-layer of γ-alumina (110) with C-layer next to it and the surface C-layer with D-layer next to it.
o and t1, t2 represent the vacant octahedral and tetrahedral sites on γ-alumina, respectively.
M–S, O–S = Bonding between dispersed metal cation, accompanying oxygen anion and support.
(M+O)–S = Bonding between the dispersed metal oxide species and support.

sponding species formed by the incorporation of MoO_3, NiO or CuO into the C and D surface layers of γ-alumina at a very low loading amount. Notably, the total energy of CNDO/2 method has low accuracy, so we always use relative values to discuss in order to reduce uncertainties.

The capping O^{2-} anions might have several possible configurations on the surface, and we have made the calculations and comparison upon them. In Table 2 we only list the energetic preferable configuration for analysis.

As can be seen from the structure of the C- and D-layer of the (110) plane on γ-alumina, both octahedral and tetrahedral vacant sites are available on the surface. In addition, if taking the distribution of Al^{3+} cations in the nearest next layer into consideration, the vacant tetrahedral sites in both C (next to D) and D (next to C) layers can be subdivided into t1 and t2 sites. Comparatively t2 site is located further from the Al^{3+} cations in the second layer, consequently t2 should be preferentially occupied by the dispersed metal cations in competition with site t1. For instance, NiO dispersed on the surface D-layer of γ-alumina with C-layer as the nearest underneath layer, which is denoted as D1C2 in Table 2, the total energy (E_T) for the occupation of t1 site is 1.52 a.u. (relative to that of octahedral sites which is taken as 0.00), and that of t2 site is 0.73 a.u., i.e., there is 0.79 a.u. difference in their total energy predicting that t2 sites should be preferentially occupied by the Ni^{2+} cations. In addition, the Wiberg bond orders listed in Table 2 indicate that the surface bonding on t2 site either formed by the incorporated Ni^{2+} cation and support (S) which has a bond order of 4.1557, or formed by the nickel oxide species (i.e., Ni^{2+} incorporated and O^{2-} capping oxygen) and support (S) with a bond order of 4.7916, is stronger than its counterparts formed on t1 site, which has a bond order of 3.8432 or 4.5486, respectively. Similar conclusions can be derived for the other two metal oxides listed in Table 2. The above discussions point to the conclusion that the occupation of

tetrahedral sites on γ-alumina t2 site is preferred in comparison with t1.

Similar comparison between the occupation of the octahedral and tetrahedral sites can also be derived from the data in Table 2. Generally speaking, octahedral site is more favorable than tetrahedral sites from the total energy point of view. One can see for the case of supported cupric oxide samples, both the total energy and the bonding strength terms are favorable for copper cation to incorporate into the octahedral site on the surface. For the case of MoO_3/alumina as the difference in the total energy of the incorporated tetra and octahedral sites is rather small and, in contrast, the difference in bonding strength is apparent, the conclusion that Mo^{6+} cation prefers the tetrahedral site when its loading is low can be withdrawn. The above predictions i.e., Cu^{2+} and Mo^{6+} prefer to incorporate into the octahedral and tetrahedral site, respectively when their loading amounts are low consistent with the experimental results reported in the literature [22,31]. The in situ Raman and XANES studies [31] have revealed that the structure of the molybdenum oxide species dispersed on different oxide supports depends on the nature of the specific support and the loading amount of molybdenum oxide, i.e., the coverage of the surface. Under ambient or dehydrated conditions, the surface molybdenum oxide species on γ-alumina are primarily isolated, tetrahedrally coordinated at low loading, octahedrally coordinated species appear with the increase of loading, and finally there is a mixture of tetrahedral and octahedral coordinated species when the loading amount is approaching its dispersion capacity. These facts are consistent with the above conclusions. While for the case of supported nickel oxide sample, the bonding strength is apparently stronger for its incorporation into the tetrahedral site, but the total energy prefers to take over the octahedral. Thus, it is hard to make prediction about the site preference based on these data alone. However, as it is reported by Bruggraf et al. [13], photoacoustic spectra for selected Ni catalysts calcined at

500°C indicates that octahedral nickel species make a substantial contribution even at 1.25% nickel loading, and at 4% nickel loading the spectrum is dominated by absorption of octahedral species. These data show that the ratio of Ni(Octa) to Ni(Tetra) increases with decreasing calcination temperature in comparison to those calcined at 600°C, and Wu and Hercules [32] from ESCA studies also have same conclusions. Hence, the octahedral sites seem to have energy preferences over tetrahedral sites at decreasing calcination temperature. There might be an energy barrier existed which prevents the lowest local energy (corresponding to the bond strength) sites from being occupied. Along this line one would expect if calcination was carried out under an adequate high temperature the energy barrier might be overcome, i.e., the dispersed species might have a mobility which is high enough to move them to the site of the lowest local energy, i.e., to incorporate into the tetrahedral site.

As listed in Table 2, the Wiberg bond orders of $(Ni + O)–S$ on the t2 site of surface D- and C-layer of γ-alumina are 4.7916 and 5.1338, respectively, and in comparison, for $(Cu + O)–S$ on (o) sites of surface D- and C-layer the corresponding values are 3.9992 and 4.5420, respectively. It seems reasonable to argue that the bondings between the dispersed NiO species and surface of the support are stronger than that of dispersed CuO.

Moreover, the bonding strength between metal cations and support can also be estimated from Table 2. For MoO_3 and NiO, their M–S bonding on t2 is stronger than on (o) site, which has a similar trend as the interaction between the corresponding $(M + O)$ and support. In contrast, for CuO when Cu^{2+} is dispersed on the surface C-layer its M–S bonding on t2 site is weaker than on (o) site, and the situation is reversed when Cu^{2+} is dispersed on the surface D-layer, i.e., bonding on t2 site is stronger, the differences in their Wiberg bond order values are small but still can be seen in Table 2. Noticeably, when the accompanying oxygen an-

ion is taking into consideration, the stronger bonding of $(Cu^{2+} + O^{2-})$ species with the (o) site on either C- or D-layer of γ-alumina can be clearly seen. The results are consistent with the experimental facts, i.e., the octahedral sites are preferentially occupied by Cu^{2+} cations when CuO is dispersed on the surface of γ-alumina. The results also reveal that the influence of the accompanying oxygen anion on the dispersion of the Cu^{2+} is more pronounced than that of Ni^{2+}.

Both Cu^{2+} and Ni^{2+} are divalent cations, the differences in their behaviors should be correlated to the differences in their electronic structures. It is known that Ni^{2+} cation has two unpaired electrons with $3d^8 4s^0$ configuration, and Cu^{2+} cation has only one unpaired electron with $3d^9 4s^0$ configuration, there are stronger covalent contributions in Cu–O bond of dispersed cupric oxides, which might lead to the different bonding ability and site preference (i.e., preference in different coordination environment) of these two divalent cations.

3.2. At higher MO loading

With the increase of the loading amount of metal oxide, the interactions between the dispersed MO species should be taken into consideration, The cluster models designed for this purpose are shown in Fig. 3, which mimics a higher MO loading amount by considering the implementation of a metal cation to a site which has its nearest available sites being preoccupied by metal cations. As each Mo^{6+} cation is accompanying with three O^{2-} anions, to modeling, at a higher loading amount, the interaction between dispersed MoO_3 species and support to a very large cluster is needed, and the calculation would be much more complicated, thus as representatives only of the dispersion of NiO and CuO are chosen in this section to show that the site preference might relate to the loading amount of the metal oxide. Based on the models shown in Fig. 3, the site for the incorporation of metal cation has been marked by the pointer

signs and the calculation results are listed in Table 3.

As shown in Table 3, for the dispersion of NiO at a higher loading amount, the total energy E_T of the occupation of a tetrahedral site on C-layer is smaller than that of octahedral site (-1.96 vs. 0.00), while on D-layer the situation is reversed, i.e., E_T of tetrahedral site is larger than that of octahedral site (0.98 vs. 0.00). Accordingly, from the E_T values alone, it is hard to decide which site is favorable of the dispersion of NiO. Similar results can be found for the case of the dispersion of CuO, on both C and D layers of γ-alumina. Notably we discussed in Section 3.1, if calcination was carried out under an adequate high temperature the site energy barrier might be overcome, i.e., the dispersed species might have a mobility which is high enough to move them to the site of the lowest local energy, which should correspond to the bonding strength (Wiberg bond order). Thus as can be seen in Table 3, the Wiberg bond orders of metal oxide species and support, i.e., (M + O)–S, on octahedral sites are all larger than that of tetrahedral sites for the dispersion of CuO or NiO on both C and D layers of γ-alumina, e.g., $(Ni^{2+} + O^{2-})$–S Wiberg bond order on the o and t sites of D-layer of γ-alumina is 4.7956 and 4.6164, respectively; $(Cu^{2+} + O^{2-})$–S on the o and t sites of D-layer of γ-alumina is 4.2301 and 4.0167, respectively.

These results suggest that the surface bonding strength of the above metal oxide species interacted on octahedral sites are stronger than that on tetrahedral sites, and both NiO and CuO will preferably occupy the vacant octahedral sites when their loading amounts are high. The above results are consistent with the fact, that with the increase of their loading amount the dispersed CuO species still prefer the octahedral sites on γ-alumina, but the dispersed NiO species, which prefer the tetrahedral sites at low NiO loading, gradually change their site preference to take over the octahedral sites instead, accordingly, when the loading of NiO is high, a mixed occupation of the tetrahedral and octahedral sites is observed. In addition, using the simple models as shown in Fig. 3, by adding the preoccupied Ni^{2+} cations into the available vacant tetrahedral sites, one can estimate that, the implementation of Ni^{2+} cations into the available vacant octahedral does not occur until the incorporation of about $1/4$ Ni^{2+} cations in the tetrahedral site of each unit mesh. As $1/4$ preoccupied Ni^{2+} (tetra) cations are followed by the preferred incorporation of Ni^{2+} cations into the available octahedral sites, the reachable maximal ratio of octahedral and tetrahedral Ni^{2+} cations is about 2:1. But after the full incorporation of octahedral and tetrahedral Ni^{2+} cations into each unit mesh, the final ratio of octahedral and tetrahedral Ni^{2+} cations is 1:1.

UV reflectance spectra results of Jacono et al. [14] have demonstrated that following the calcination of NiO/γ-alumina samples at 450 or 600°C for 24 h, nickel ions diffuse into the surface tetrahedral and octahedral sites of γ-alumina, and increasing nickel oxide loading favors the formation of octahedral coordination species. The PAS results of Bruggraf et al. [13] show that the ratio of tetrahedral and octahedral species of NiO/γ-alumina calcined at 600°C, varied from 1:0 for nickel loading less than 3% to 0.3:0.7 for 20% nickel loading. ESCA results [22] have shown that Cu^{2+} ions in samples calcined at 723 K have a preference to occupy the available vacant octahedral sites in the sur-

Table 3
Wiberg bond order, and total energy (E_T) of the relevant species when metal oxide (MO) loading is high

CuO-D1C2	o	t	CuO-C1D2	o	t
O–S	1.0664	0.8430	O–S	1.2979	1.1265
Cu–S	3.1637	3.1737	Cu–S	3.1589	3.1553
(Cu + O)–S	4.2301	4.0167	(Cu + O)-S	4.4568	4.2818
E_T (a.u.)	0.00	−0.04	E_T (a.u.)	0.00	1.45
NiO-D1C2	o	t	NiO-C1D2	o	t
O–S	1.1741	0.6759	O–S	1.1558	0.9909
Ni–S	3.6215	3.9405	Ni–S	4.1136	4.1283
(Ni + O)–S	4.7956	4.6164	(Ni + O)-S	5.2694	5.1192
E_T (a.u.)	0.00	0.98	E_T (a.u.)	0.00	−1.96

The significance of symbols is the same as in Table 2.

face lattice of γ-alumina, while at 1023 K, the occupation of Cu^{2+} ions in tetrahedral sites has been proven by photoacoustic spectroscopy with a peak at ~ 1500 nm [21]. Recently, Hao and Cooper [33] have reported that the modeling and calculation by FLMTO method lead to the conclusion that copper cations are adsorbed at the surface octahedral vacant sites of the alumina. It has also been reported in the literature [13] that the relative apparent activation energy of the formation of Co(Tet.) (designated Co^{2+}) to the formation of Co(Oct.), (designated Co^{3+}) is approximately 2.3 ± 0.5 kcal/mol, and the Co(Tet.) to Co(Oct.) ratio in Co/γ-Al_2O_3 catalysts is consistently larger for catalysts calcined at 600°C in comparison to those calcined at 400°C, but diminishes steadily with the increase of cobalt loading.

All the above experimental results seem to support our results of calculation, and are consistent with the incorporation model [21,22].

Data of Table 3 have also shown that the bonding strength between Ni^{2+} and support, i.e., Ni^{2+}–S, on the tetrahedral sites is stronger than that of octahedral sites, however, after taking the accompanied oxygen anion into consideration, one can see that the bonding strength between the dispersed nickel oxide species and support, i.e., $(Ni^{2+} + O^{2-})$–S, on the tetrahedral sites is changed to become weaker than that of octahedral sites. Therefore, it seems evident from the above results that the accompanied oxygen anion can influence significantly the occupation of the octahedral sites at high nickel oxide loading. Similar results are obtained for the dispersion of CuO on γ-alumina, although the influence of oxygen anion is comparatively small.

4. Summary

Cluster models based on the incorporation model are proposed to understand the site preference upon the dispersion of some metal oxides, i.e., MoO_3, NiO and CuO, on γ-alumina through semiempirical molecular orbital (CNDO/2) calculation method. The results can explain the experimental observations which could not be interpreted by most existing models (e.g., overlayer or close-parked monolayer models). It is the first theoretical analysis based on the incorporation model, which can explain: (1) as can be seen from the structure of the C- and D-layer of the (110) plane on γ-alumina that both octahedral and tetrahedral vacant sites are available on the surface. If taking the distribution of Al^{3+} cations in the next layer into consideration, the vacant tetrahedral sites in both C (next to D) and D (next to C) layers can be subdivided into t1 and t2 sites. Comparatively t2 site is located further from the Al^{3+} cations in the second layer, consequently t2 should be preferentially occupied by the dispersed metal cations in competition with site t1; (2) the dispersed CuO species always prefer the octahedral sites on γ-alumina; (3) if calcination is carried out under an adequate high temperature, the dispersed NiO or MoO_3 species prefer the tetrahedral sites when its loading amount is low but octahedral sites when loading is increased to a certain extent; (4) for the case of NiO, the incorporation of the octahedral sites does not occur until the incorporated tetrahedral nickel cations reach to the amount of about $1/4$ Ni^{2+} cations in each unit mesh, and the reachable maximal ratio of Ni^{2+} (o) to Ni^{2+} (t) is about 2:1, but the ratio is 1:1 when all the available vacant sites on γ-alumina are being occupied. The differences between the behavior of dispersed NiO and CuO species should be attributed to their electronic structures. Ni^{2+} cation has a $3d^8 4s^0$ electronic structure with two unpaired electrons, and Cu^{2+} cation is $3d^9 4s^0$ and has only one electron. Ni^{2+} cations have a stronger bonding ability with the surface of γ-alumina than that of Cu^{2+}, and there are stronger covalent contributions in Cu–O bond of dispersed cupric oxides. In addition, the accompanying oxygen anion also produces some influence on the site preference of the $Ni^{2+} + O^{2-}$ or $Cu^{2+} + O^{2-}$ species. Generally speak-

ing, the incorporated NiO species have a stronger bonding strength with γ-alumina than CuO species do.

Acknowledgements

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