Surface interaction model of γ-alumina-supported metal oxides

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An incorporation model has been proposed and used to discuss the interaction between various metal oxides and γ-alumina. The dispersion capacities of various metal oxides are predicted and the surface hydroxyl group density on γ-alumina estimated, based on the assumption that the (110) plane is preferentially exposed on the surface of γ-alumina. These results are in good agreement with the available experimental data.

Keywords: Incorporation model; r-alumina; hydroxyl group density; dispersion capacity; MoO_3, NiO, CuO

1. Introduction

Supported metal oxide catalysts have attracted much attention because of their wide application as oxidation catalysts and/or as precursors to the supported metal and sulfide catalysts used in a variety of industrially important reactions. Studies on the nature of the interaction between the dispersed metal oxide species and the support have been conducted as a key step in gaining a deeper insight into the catalytic behavior as well as in elucidating the optimum conditions for the preparation of these catalysts, and great efforts have been made in obtaining more information in this connection. It has already been established in the literature that the support influences strongly the nature and extent of metal oxide-support interaction. For example, on γ-alumina [1–4] many metal oxides have a much higher capacity for the formation of atomically dispersed species than on silica, and the physical and chemical properties of the highly dispersed surface species are usually drastically different from those of the corresponding bulk phases. Besides the effect of the support, the preparation conditions, especially the loading amount of metal oxide as well as the calcination temperature and time, also have a strong impact on the nature of the interaction between metal oxide and support. In fact, the existence of a strong metal oxide-support interaction has been detected even for silica-supported systems, especially when the oxide loading is low [5,6].

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Although supported metal oxide systems have been the subject of numerous discussions, the exact nature of the interaction between metal oxide and support in many systems is still not yet clearly understood; further, a diversity and apparent contradiction of results and interpretations can often be found in the literature and these discrepancies are commonly attributed to differences in the preparation conditions used. However, as reminded by Massoth [7], the basis of most of the techniques used in characterizing supported metal oxides is comparative in nature, which might lead to some misunderstanding. In these systems, one deals with indefinite and nonstoichiometric surface complexes which may have some properties similar to known compounds but others which are not. Hence, it is not surprising to see that with the emergence of better surface techniques some of the older explanations of supported oxide systems are being reconsidered and some models have been revised.

Several surface models concerning the interaction between metal oxide and γ-alumina have been proposed in the literature. For examples, Hercules et al. [4] have suggested a model for γ-alumina supported nickel oxide by assuming that the Ni^{2+} ions diffuse into the surface lattice vacancies of the spinel structure to produce Ni^{2+}(T) causing the inversion of Ni^{2+}(T) to Ni^{2+}(O) at the surface to replace a transition of Al^{3+}(O) to Al^{3+}(T). When the lattice near the surface is saturated with Ni^{2+}(O) and Ni^{2+}(T), both diffusion and inversion processes become slower and the growth of microcrystals of nickel oxide follows, and Cimino et al. [8] have mentioned that the nickel ions might occupy the tetrahedral and octahedral sites of γ-alumina, with the formation of what they called a surface spinel which has an average thickness about 0.1 to 0.4 nm. 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 [9], 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. An oligomer model has been proposed by Weigold [10], taking into consideration the fact that molybdate species react with hydroxyl groups on the support and undergo oligomerization. Xie and co-workers [11] have found that many oxides and salts can disperse spontaneously as a monolayer on the surface of supports and suggested that the utmost monolayer capacity, (C), for each metal oxide can be evaluated by a so-called close-packed monolayer model; the results calculated on this basis for the values of (C) as well as the corresponding experimental values (E) are shown in table 1. It has also been mentioned that it may be more appropriate to describe the structure as Mo^{6+} located in the first two or three surface layers of alumina [12]. In contrast, the penetration of Mo^{6+} ions into alumina subsurface has been argued to be almost impossible [7]. Hall and co-workers [13] have proposed that at Mo loadings close to monolayer capacity, the dispersed molybdena species are present in small clusters or islands containing presumably seven Mo atoms and being 2 layers thick, and part of the

Table 1
Dispersion capacity of some metal oxides on γ-alumina

SYSTEM	Experimental value [a]		Estimated value [b]		E/C	E'/C'
	E (g/100m^2)	E' (cations/nm^2)	C (g/100m^2)	C' (cations/nm^2)		
MoO_3	0.12	5.0	0.12	4.5	1.0	1.11
WO_3	0.19	4.9	0.19	4.5	1.0	1.09
NiO	0.12	9.7	0.18	9.0	0.66	1.08
ZnO	0.13	9.5	0.20	9.0	0.65	1.05
CdO	0.20	9.4	0.31	9.0	0.65	1.04
MgO	0.07	10.5	0.10	9.0	0.70	1.17
CuO	0.058	4.4	0.19	9.0	0.30	0.49

[a] Data from ref. [11 and 14]; samples were calcined at ~ 770 K.

[b] C: Value estimated by close-packed monolayer model. C': Value estimated by incorporation model.

alumina surface remains uncovered. Raman spectroscopy and TDPAC (time differential perturbed angular correlation) results seem to confirm that adsorbed heptamer $Mo_7O_{24}^{6-}$ species are stable even under a calcination temperature of 770 K [1]. Apparently, it is possible that the interaction between molybdena and γ-alumina may be much more complicated, and the surface might be different from that depicted, and as concluded by Massoth in his review paper [7], although each of the models have their advocates, none can be considered definitely proven at present.

In spite of the fact that all the models discussed have taken into consideration some experimental evidence, surprisingly little attention has been given to explaining why different metal oxides have different dispersion capacities on the same support, e.g. γ-alumina, as shown in table 1. Also, it has not been explained why the same metal oxide has different dispersion capacities on different supports. For example, on silica both MoO_3 and NiO have tremendously lower dispersion capacities than on γ-alumina. Apparently, one needs to consider both the nature of the metal oxide and the surface structure of the support. The following discussion aims at obtaining more information in this connection, and the application of the incorporation model proposed by the authors [14] based on the surface structure of γ-alumina will be discussed in some detail, in particular for supported molybdenum, nickel and cupric oxide systems.

2. Surface structure and surface hydroxyl group density of γ-alumina

Many different crystal planes may be exposed on the surface of γ-alumina. However, neutron diffraction studies of CD_4 adsorbed on γ-alumina [15] have indicated that the surface consists of (110) and (100) planes, with an area of

~ 40 and > 8 m^2/g, respectively, and no trace of (111) plane has been found. In another recent work, it was concluded by determination of lattice constant that most of the grains (~ 90%) of γ-alumina thin film are oriented with the surface normal along the (110) direction [16]. In addition, it is known that the aluminas exist in the form of lamellae; therefore, at least as a first approximation, it seems reasonable to consider that the (110) plane is preferentially exposed, and alumina can be assumed to consist of particles formed by one-dimension stacking of C- and D-layers. The exposure possibilities of these two layers are equal, as suggested by Schuit and Gates [9].

It is well established that surface hydroxyl groups on γ-alumina are responsible for the interaction between molybdate anions and γ-alumina. Knözinger and Ratnasamy [17] have suggested that the detected five IR bands on γ-alumina can be related to the five possible configurations of the OH groups on the support, and the basicity of these OH groups can be evaluated individually by their net charge, which is determined by their configurations. Based on their description, there are at most four different kinds of OH groups on the surface if one supposes that only (110) and (100) planes are exposed. Accordingly, they have to assume that all the low index planes, viz., (111), (110) and (100) planes, must be exposed on the surface; however, this assumption is in contradiction with the recent experimental results as mentioned earlier. There is probably a weak point in their assignment of the OH groups on (110) plane due to neglect of the OH group formed by residing a proton on the exposed lattice oxygen. Generally, a freshly calcined alumina will be rehydrated and rehydroxylated at ambient temperature in the presence of moist air, due to the dissociative adsorption of water leading to the creation of OH groups [18], as pictured in fig. 1. By similar consideration, the hydroxylation should proceed on exposed (110) planes by attaching OH groups to Al^{3+} ions and residing protons on lattice oxygens until the surface is covered by the hydroxyl groups thus formed, as shown in fig. 2. Similar hydroxylation on the surface of MgO has been reported by Anderson et al. [19].

It can be visualized in the above discussion that on the surface of the (110) plane, in addition to the three hydroxyl groups already suggested by Knözinger

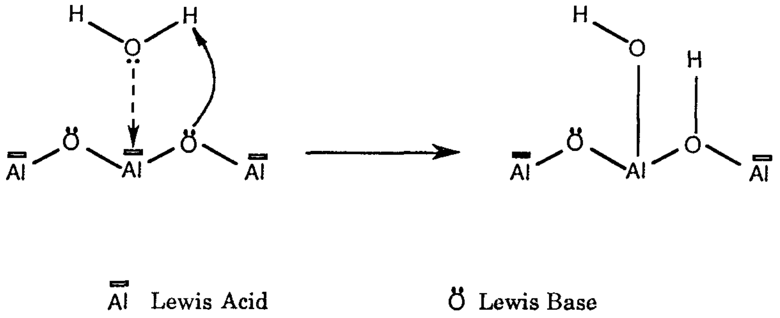
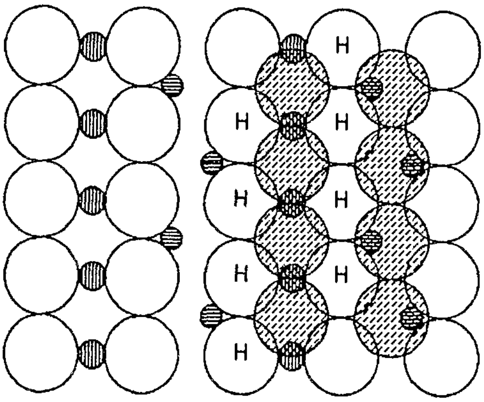
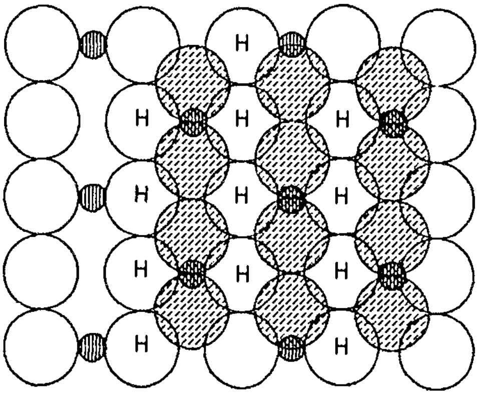


Fig. 1. Schematic representation of the hydroxylation of γ-alumina. Redrawn from ref. [18].



C-layer



D-layer

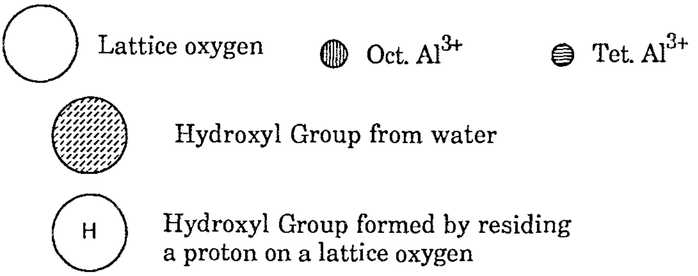


Fig. 2. Hydroxylated 110 plane.

and Ratnasamy [17], another three hydroxyl groups should exist as shown in table 2. Accordingly, the density of OH group on the (110) plane can be evaluated to be 18.0 OH/nm^2, which is excellent agreement with the result of ~ 17.5 OH/nm^2 measured by the maximum irreversible adsorption of water reported by Peri [20]; furthermore, as shown above at least six instead of five IR bands should exist on γ-alumina even if only the (110) plane is taken into

Table 2
Possible OH configurations on 110 plane of γ-alumina, the hydroxyloation of lattice oxygen anions considered

110 plane	Configuration *[a]	Net charge at O	Net charge at OH	$\tilde{\nu}$ (OH) cm^{-1}
	II$_b$  *[b]	−1.00	−0	3740 ~ 3745
C-layer	I$_a$  *[b]	−1.25	−0.25	3760 ~ 3780
	III$_b$ 	−0.25	+0.75	*[c]
	I$_b$  *[b]	−1.50	−0.50	3795 ~ 3800
D-layer	III 	−0.50	+0.50	3700 ~ 3710
	II$_a$ 	−0.75	+0.25	3730 ~ 3735

*[a] Large circle: Oxygen atom or hydroxyl group, and ●: Al^{3+}(O), O: Al^{3+}(T).
*[b] Configuration assigned to OH groups on 110 plane in ref. [17].
*[c] A band might be assigned at 3650–3550 cm^{-1} (ref. [21]) or at 3590 cm^{-1} (ref. [22]).

consideration. This expectation has been supported by the well-resolved IR spectra reported by Hall et al. [21] and Okamoto et al. [22], where one can see more than six OH bands in the IR spectra.

3. Incorporation of metal cations into the surface lattice of γ-alumina

DISPERSION CAPACITIES ESTIMATED

NiO/Al_2O_3. Take NiO as a representative of $M^{2+}O$ type oxides. The surface structure of the (110) plane on γ-alumina, as shown in fig. 3, reveals that the distribution of Al^{3+} per unit mesh can be expressed as $[Al_2O_4]$ for the D-layer, and as $Al_{4/3}\star_{2/3}[Al_2O_4]$ for the C-layer, where ★ denotes the vacancies due to the defect spinel structure of γ-alumina. Apparently, it is reasonable to argue that the less dense surface structure of the (110) plane provides vacant sites for incorporating M^{2+} ions, provided that the size of these ions is similar to or less than that of Al^{3+} ions. Upon the incorporation of an M^{2+} ion into the surface lattice, an oxygen anion associated with the cation will stay at the top of the occupied site as a capping oxygen, cf. fig. 3, compensating the extra positive charge.

It should be noted that as a consequence of the shielding effect of the capping oxygen anions, only part of the available vacant sites are usable; thus, at most $4M^{2+}$ ions can be implanted in a unit mesh (~ 0.443 nm^2) of the D-layer and $(4-4\frac{2}{3}M^{2+})$ ions in a unit mesh of the C-layer, where the value of $4\frac{2}{3}$ comes from consideration of Al^{3+}(T) vacancies. Along these lines, the dispersion capacity, (C'), of $M^{2+}O$ type oxide can be estimated to be ~ 9–9.8 M^{2+} ions/nm^2. These results are consistent with the experimental values, (E'), shown in table 1. After the usable sites are occupied, the capping oxygen anions form an epitaxial layer on the top of γ-alumina surface, with a ratio of

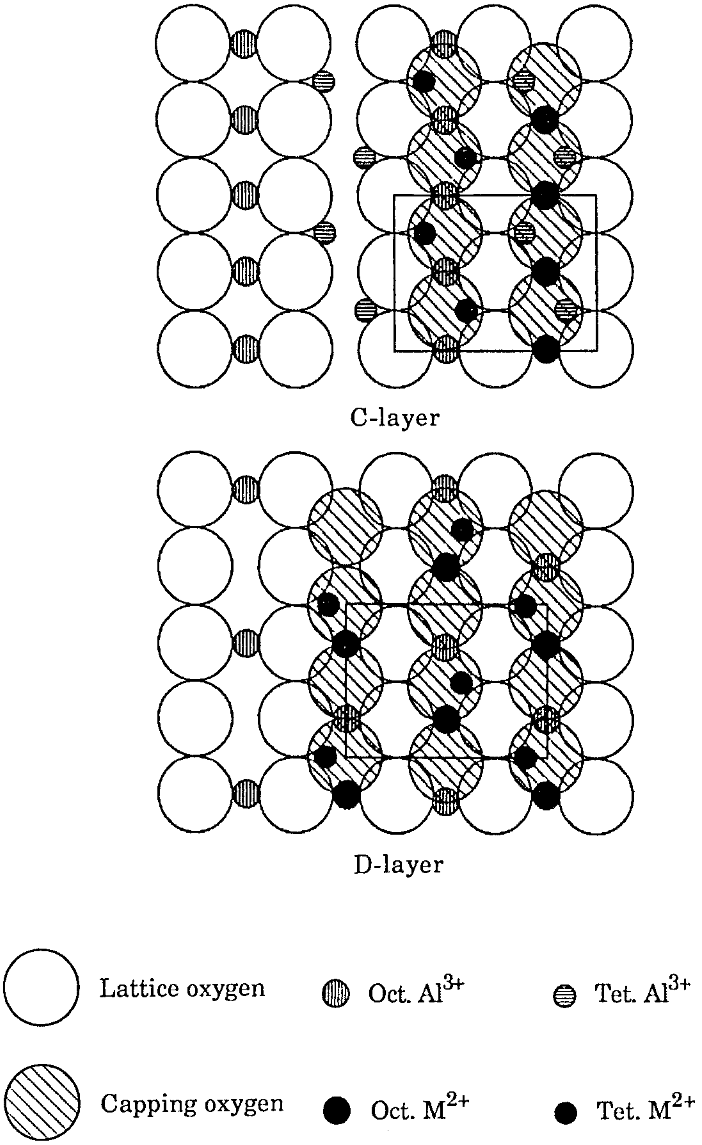


Fig. 3. The incorporation of M^{2+} ions into the 110 plane of γ-alumina.

$Ni^{2+}(O)/Ni^{2+}(T) \sim 50/50$. It is surprising to see that both the dispersion capacity and the ratio of $Ni^{2+}(O)/Ni^{2+}(T)$ predicted by this simple model are in excellent agreement with the experimental results of ESCA and ISS [14,23], EXAFS [24] and PAS (photoacoustic spectroscopy) [4] reported in literature.

CuO/Al_2O_3. As discussed in our previous paper and proven by ESCA results [14], Cu^{2+} ions in samples calcined at 723 K have a preference to occupy the usable octahedral sites in the surface lattice of γ-alumina; and, this behavior explains the fact that the experimental dispersion capacity is only about half of

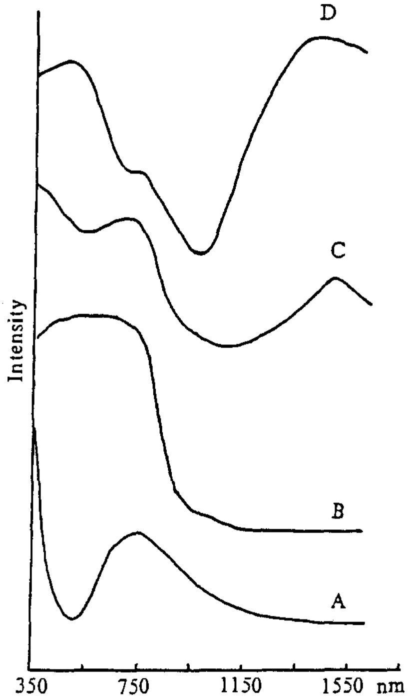


Fig. 4. Photoacoustic spectra of $CuO/\gamma\text{-}Al_2O_3$ samples: (A) 4.4 Cu^{2+} ions/nm^2, calcined at 723 K for 2 h. (B) 8.9 Cu^{2+} ions/nm^2, calcined as sample A. (C) 8.9 Cu^{2+} ions/nm^2, calcined at 1023 K for 2 h. (D) $CuAl_2O_4$ sample with the present of CuO.

the expected value. However, for another series of samples calcined at 1023 K, the experimental dispersion capacity has been measured to be ~ 9.0 Cu^{2+} ions/nm^2, which is close to the expected value. Moreover in these samples the occupation of Cu^{2+} ions in tetrahedral sites has been proven by photoacoustic spectroscopy with a peak at ~ 1500 nm, as shown in fig. 4.

MoO_3/Al_2O_3. MoO_3 is a representative of $M^{6+}O_3$ type oxides. Considering the fact that each M^{6+} ion is associated with 3 oxygen anions, a higher shielding effect will make the usable sites go down to 2 and 2–2$\frac{2}{3}$ Mo^{6+} ions per unit mesh of D- and C-layers respectively, and the estimated dispersion capacity goes to 4.5–5.3 M^{6+} ions/nm^2. The accompanied oxygen anions may arrange as an epitaxial capping layer with 4 oxygen anions per unit mesh and leave the other oxygen anions on the top of the capping layer, as suggested by Schuit and Gates [9], and the anions might also crowd into a close-packed capping layer to form a distorted surface structure as suggested by Xie et al. [11]. The dispersion capacity thus estimated is consistent with the experimental results listed in table 1. This model predicts the coexistence of Mo^{6+} in octahedral and tetrahedral sites and the existence of Mo-O-Mo bonds at full occupation; and moreover, the exposure possibilities of Mo^{6+} and Al^{3+} are not much different. These predictions are in good agreement with most of the experimental results. For example,

IR [13,25] and 1H-NMR [26] provide evidence that alumina hydroxyl groups are still present on the surface of a γ-alumina-supported molybdena catalyst with Mo loading near to the monolayer capacity; EXAFS [27] shows that a single well-defined molybdenum-containing compound does not exist, and in the calcined catalysts molybdenum is present as isolated ions, chains, or small disordered patches. LRS evidences the existence of Mo-O-Mo bound; ESCA and ISS prove presence of both tetrahedrally and octahedrally coordinated molybdenum and the coexistence of Mo^{6+} and Al^{3+} ions on the utmost surface [28].

The proposed model points to the fact that the dispersion capacity of a metal oxide on a support is mainly determined by the surface structure of the support, the valence type of the metal oxide and the calcination conditions, and whether the oxygen anions are close-packed or not is not of importance.

SPECULATIONS ON THE INCORPORATION PROCESS

The microscopic mechanism of the incorporation process is not clear. γ-alumina-supported transition metal (Ni, Co, or Cu) oxide catalysts are often prepared by impregnating γ-alumina with corresponding metal nitrates, drying and calcining at ~ 770 K. Many authors [4,8,12,29] have concluded that mainly the so-called surface spinel can be formed in these systems, provided that the loading amount is less than the dispersion capacity of the cation. It is reasonable to suggest that the first step is the decomposition of the nitrate with the formation of amorphous metal oxide on the surface, followed by diffusion of the metal ions into the surface lattice of γ-alumina. Recall the following facts: (i) The arrangement of oxygen anions in the (110) plane is less dense as compared with (111) or (100) planes, and there are numerous vacant sites on the (110) plane to act as acceptors for the cations; and, (ii) The Tamman temperature for the surface mobility in γ-alumina is only ~ 680 K, which is lower than the common calcination temperature. If the loading amount is lower than the dispersion capacity of the cations, then the counter diffusion of M^{2+} and Al^{3+} cannot happen, and the M^{2+} can stay in the first layer leaving the associated oxygen anion on the top to maintain charge equilibrium. However, if the loading amount of metal oxide and the calcination temperature increase, one might expect to form the bulk spinel structure as the Tamman temperature for bulk lattice mobility of γ-alumina is about 1150 K. Therefore, the formation of a so-called nonstoichiometric surface spinel is actually controlled by the diffusion of M^{2+} into the surface lattice [30].

γ-alumina-supported molybdena catalysts can be prepared by different methods, e.g., by impregnating γ-alumina with a solution of ammonium heptamolybdate, by adsorption of molybdates from solution or from the gas phase [31], or by the calcination of a mechanical mixture of MoO_3 and the support in ambient atmosphere [11]. It is interesting to note that the different preparation methods

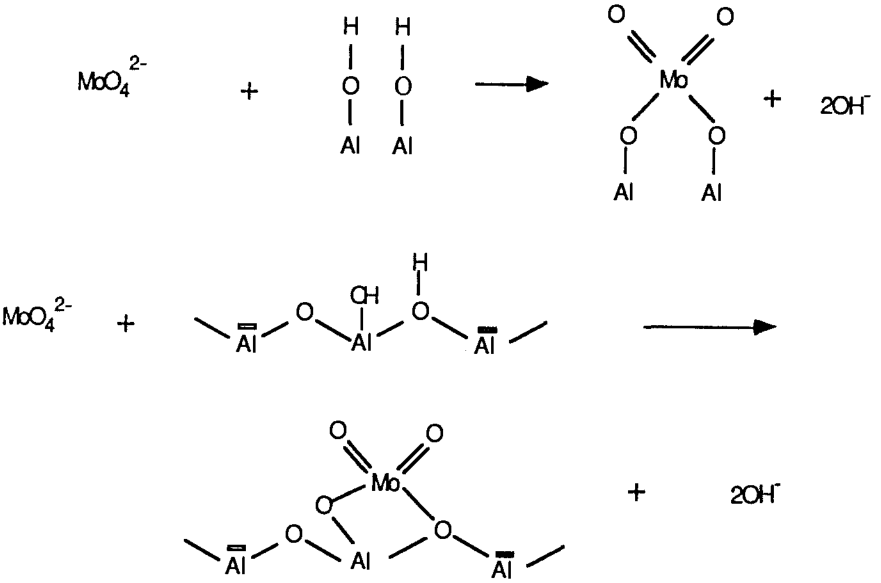


Fig. 5. Interaction between molybdate and surface hydroxyl groups on γ-alumina.

as well as different sources of γ-alumina result in a similar dispersion capacity of molybdena on γ-alumina, provided that the calcination temperature is close to 723 K. Accordingly, the dispersion capacity of molybdena on γ-alumina must be controlled by some intrinsic factors.

It is generally accepted that for samples prepared by impregnation methods, the surface OH groups on γ-alumina are considered to be responsible for the interaction between the molybdates and alumina. However, there is still disagreement on which species, e.g., $Mo_7O_{24}^{6-}$ or MoO_4^{2-} is actually adsorbed on the surface. We note that according to the possible OH configurations on the (110) plane suggested in table 2, there are three different OH groups with different net charges on either the C- or D-layers. Probably the typical interaction model between MoO_4^{2-} species and OH groups should be described as the schema in the lower part of fig. 5 instead of by those models commonly used in the literature. Thus, as MoO_4^{2-} species interact with the OH groups, a distorted tetrahedral site partially incorporated into the surface lattice is formed, and the three oxygen anions associated with Mo^{6+} can also be seen.

Atomically dispersed molybdena on γ-alumina can also be prepared by calcining a mechanical mixture of MoO_3 and γ-alumina et ~ 770 K. In ambient atmosphere, Knözinger and co-workers have described this phenomenon as the support wetted by MoO_3, and they attributed the driving force for this process to the following change of surface free energies [1]: $\Delta Fs = \gamma_{AM}\Delta A_{AM} + \gamma_m \Delta A_M - \gamma_A \Delta A_A$, where γ_A, γ_M and γ_{AM} are the specific surface or interface free energies of alumina, MoO_3 and the interface of these two oxides, respectively, and ΔA_A, ΔA_M and ΔA_{AM} are the corresponding changes in surface or interface area. The process will occur if $\Delta Fs < 0$. These descriptions perhaps can fit the predried systems reported by Hayden et al. [32], and recently by Knözinger [33], while for normal situations commonly used for the preparation of catalysts, there are probably several weak points in this explanation. First, if the process is carried out in ambient atmosphere, the surface of the oxides will be usually covered by OH groups, and the experimental surface free energy data measured at elevated temperature are far from the real situation used for catalyst preparation; second, as reported by Xie et al. [11], the spontaneous dispersion of MoO_3 on γ-alumina can form only a close-packed monolayer. If the driving force is simply due to the change of free energies, why are second or third layers not formed? Since the Tamman temperature for the bulk phase mobility of MoO_3 is as low as 534 K, and MoO_3 starts subliming at ~ 800 K, it seems reasonable to suppose that the probability of the dismantlement of MoO_3 bulk phase into ion pairs or molecules is high at the calcination temperature. The underlying fairly open structure of the (110) plane will provide a favorable environment for incorporation of Mo^{6+} ions. In addition, the low Tamman temperature for the surface mobility of γ-alumina will stimulate the diffusion process. In contrast, SiO_2 has a saturated structure, which explains the very low dispersion capacity of MoO_3 on silica.

4. Conclusions

1. The interaction between γ-alumina and various metal oxides, in particular MoO_3, NiO and CuO, has been discussed by an incorporation model, and the dispersion capacities of various metal oxides on γ-alumina predicted by the model are in good agreement with the experimental results.
2. The model emphasizes that the dispersion capacity is dependent mainly on the surface structure of the support and on the valence type of the metal oxide, while the close-packing of the oxygen anions is not a key factor.
3. According to the proposed surface hydroxyl group configurations, there are at least six IR bands on the (110) plane, and at full coverage the density of the hydroxyl groups is 18.0 OH/nm^2. Both predictions are consistent with the experimental results.
4. At an appropriate calcination temperature, the dispersion of metal oxides on γ-alumina is controlled by an incorporation and/or a surface diffusion process.

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