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# Polynuclear Metal Complexes as Model Mixed Oxide Catalysts: An Ion Exchange Support Interaction

## INTRODUCTION

Multimetal oxide catalysts have been studied to define unusual catalytic properties (*1*). Experimental difficulties in defining active surface area, turnover numbers, etc. have precluded direct application of the multimetallic theories (*2, 3*) to the problems of mixed oxide catalysis. Further advances in the theories of mixed oxide catalysis may result from progress in characterizing the microenvironment of model catalysts of these solids.

We reported (*4*) on the preparation and characterization of supported polynuclear metal complexes containing two types of metal ions ($Cu^{2+}$ and $M^{3+}$ where $M$ = Al, Cr, or Fe). The structure of the cation complex (charge = +3) is depicted in Fig. 1. These +3 complexes were balanced by three $ClO_4^-$ in the unsupported single crystal state. We showed that the strong ammonia sorption stoichiometry to each cluster depends upon the metal ion, $M^{3+}$; however, the sorption stoichiometry/cluster did not change when the cluster loading on Cab-O-Sil was increased from 10 to 30 wt%. We speculated the cluster interacted strongly with the Cab-O-Sil support to form a monolayer covering. In this note we report our studies of the cluster–support interaction.

The cluster–support interactions were studied by X-ray diffraction of the supported catalysts at different loadings and quantitative analysis for counterion concentrations, $ClO_4^-$, at each loading.

## EXPERIMENTAL

Bertrand (*5*) reported the synthesis, composition, crystal structure, and magnetic properties of polynuclear metal complexes of the form: $M[(\mu\text{-OH})\overline{\mathrm{Cu}(\mu\text{-OCH_2CH_2N}}R_2)]_6(\mathrm{ClO_4})_3$ where $M$ = Al, Cr, or Fe and $R$ = —$C_2H_5$ or —$n$-$C_4H_9$. Nitron [$N_4C_2H(C_6H_5)_3$, F.W. = 312.36] obtained from Aldrich, was used in the quantitative analysis for $ClO_4^-$.

Fumed, amorphous silica (200 $m^2/g$) obtained from the Cabot Corporation (M-5 Cab-O-Sil) was used as a support. XRD spectra were recorded on a GE diffractometer using Cu$K\alpha$ radiation.

*Procedure: supported clusters.* Cab-O-Sil-supported clusters (5 → 45 wt%) were prepared by dissolving the desired amount of cluster in 30 ml of dry acetonitrile (see (*6*) for drying procedure) to which was added 1 g of Cab-O-Sil. This mixture was allowed to stand overnight in a hood while all the solvent evaporated and the product was then dried for 12 h at 90°C.

The quantitative determination for $ClO_4^-$ on supported samples followed by procedure of Geilmann and Voight (*7*). As a check of the procedure, unsupported clusters were analyzed for $ClO_4^-$ content and compared to the known stoichiometry.

For the cluster–support study, a range of different loadings were prepared for examination by XRD and $ClO_4^-$ analysis. In this note, loadings are reported in terms of "molality" ($\mu$mole cluster/g Cab-O-Sil) and weight fraction (weight of initial cluster crystals added to impregnating solution divided by the sum of cluster and Cab-O-Sil weights).

*Theory: support–cluster interaction.* For this study, clusters of the form $M[(\mu\text{-OH})\overline{\mathrm{Cu}(\mu\text{-OCH_2CH_2N}}R_2)]_6(\mathrm{ClO_4})_3$ where $M$ = Al, Cr, or Fe were prepared with ei-

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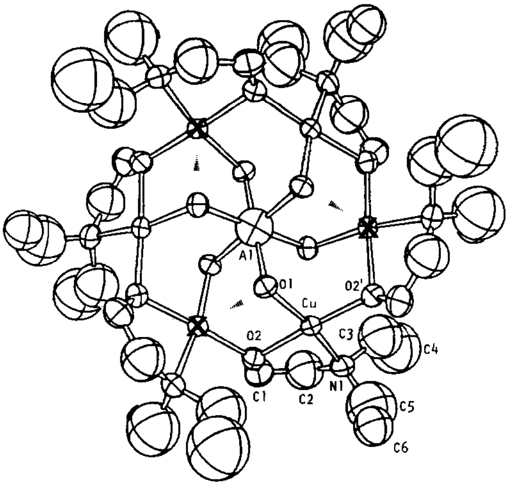

FIG. 1. Representation of polynuclear metal complex. Cation: aluminum–copper cluster. Al—aluminum ion; Ol—OH bridge; Cu—cupric ion; O2, O2′—alkoxide bridges; N1—nitrogen; C1, C2—methylene; $C_3$; $C_4$—ethyl groups; $C_5$, $C_6$—ethyl groups.

ther ethyl or *n*-butyl alkyl substituents on the ligand N. Scale models of the cation showed that the ethyl groups allowed close interaction of the cluster cation with the support whereas the *n*-butyl groups prevented such close interaction.

Consider a "cross section" of the cluster (Fig. 2). The Cab-O-Sil surface is modeled using the structure of cristobalite. One means of support–cluster interaction (Fig. 2A) with the surface is loss of protons from the support/complex followed by hydrogen bonding to the hydroxides. Implicit in this ion exchange mechanism is the replacement of $ClO_4^-$ by the hydrogen bond interaction with the silanol site, and formation of $HClO_4$ which can be easily volatilized by gentle heating. Figure 2B suggests a means by which the *n*-butyl groups prevent close approach to the OH groups.

## RESULTS

The XRD spectra of the samples are given in Fig. 3. The 35, 74, 117, 166, and 221 μmoles cluster/g Cab-O-Sil (5, 10, 15, 20, and 25 wt%, respectively) samples (Fig. 3B) gave only broad reflections characteristic of amorphous Cab-O-Sil (Fig. 3A) whereas the 262 molal (28.3 wt%) sample (Fig. 3C) gave two weak reflections at 2θ equal to 21.0° and 24.0°. The 285 molal (30 wt%) sample (full-scale deflection $\frac{1}{3}$ the sensitivity of spectra A, B, and C) gave a spectrum of strong and sharp peaks at $2\theta$ = 7.1, 8.75, 10.05, 12.38, 15.18, 16.0, 16.75, 17.5, 20.21, 21.55, and 23.8° (Fig. 3D). Unsupported Al–Cu crystals (same intensity as D) gave sharp reflections at $2\theta$ = 7.85, 9.85, 10.21, 15.90, and 23.75° (Fig. 3E).

The perchlorate ion analyses of the supported aluminum clusters (ethyl) are reported in Fig. 4 as molalities of perchlorate ion vs molality of cluster. No perchlorate was detected for samples having loadings of 221 μmoles cluster/g Cab-O-Sil and less (25 wt% and less). Samples having molalities of 262 μmoles cluster/g Cab-O-Sil (28.3 wt%) and greater show increasing $ClO_4^-$ molalities. These higher loading data were fit by a least-squares line showing a slope of 3.043

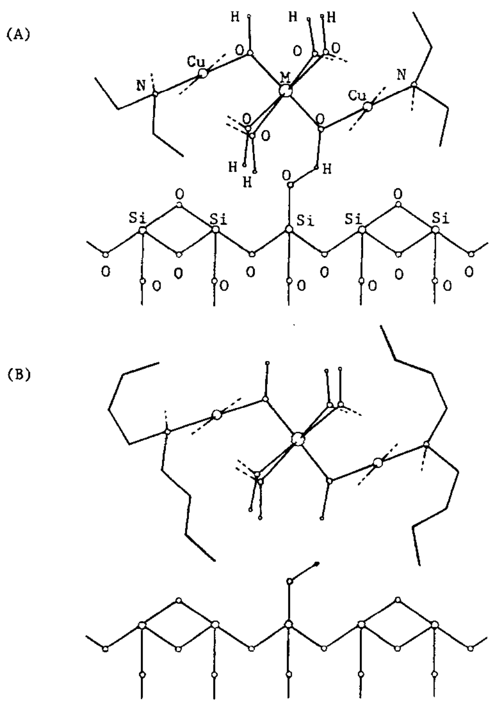

FIG. 2. Support–cluster interactions. (A) Ethyl cluster on Cab-O-Sil, (B) *n*-butyl cluster on Cab-O-Sil.

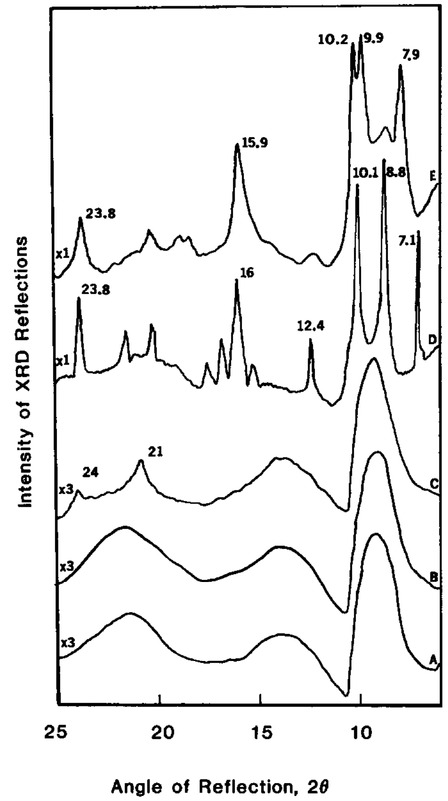

FIG. 3. XRD spectra of supported Al–Clu cluster (ethyl). (A) Cab-O-Sil; (B) 35, 74, 117, 166, and 221 μmole cluster/g Cab-O-Sil (5, 10, 15, 20, and 25 wt%, respectively); (C) 262 μmoles cluster/g Cab-O-Sil (28.3 wt%); (D) 285 μmoles cluster/g Cab-O-Sil (30 wt%); (E) unsupported Al–Cu cluster (ethyl). Reflection angles have been rounded off.

± 0.05 moles $ClO_4^-$ cluster and an intercept of 252 μmoles cluster/g Cab-O-Sil (27.6 wt%). Similar analyses for the Cr and Fe clusters yielded slopes and intercepts, respectively, of 2.97 ± 0.05 and 252 ± 2; 3.03 ± 0.05 and 261 ± 2. The unsupported clusters showed $ClO_4^-$ analyses of 2.97 ± 0.05 moles $ClO_4^-$/mole cluster. Samples of the supported aluminum clusters (*n*-butyl) at a molality of 45 μmoles cluster/g Cab-O-Sil (8 wt%) showed $8.52 \times 10^{-5}$ mole $ClO_4^-$/g Cab-O-Sil.

## DISCUSSION

Evidence of a strong support–cluster interaction comes from the XRD data of the Al–Cu (ethyl)/Cab-O-Sil samples at several loadings. That no sharp peaks are observed for loadings less than or equal to 221 μmoles cluster/g Cab-O-Sil (25 wt%) indicates that no long range order is established in these samples. It is interesting that the order appears over a narrow range over cluster loadings between 221 and 285 μmoles cluster/g Cab-O-Sil (25–30%). Moreover, some of the peaks in the 285 molal (30 wt%) sample appear to grow in registry with the amorphous peaks from the Cab-O-Sil (Figs. 3C, D) which is in contrast to those peaks of the unsupported cluster (ca., $2\theta = 7.1°$ and 12.4° in Fig. 3C; not present in the unsupported cluster, Fig. 3E). These XRD data suggest that no multiple-layered structures are developed on the surface of those catalysts having loadings of 221 molality (25 wt%) and less. Some multiple layers may be present on the 285 molal (30 wt%) sample.

The $ClO_4^-$ analyses of the unsupported clusters established the reliability of the technique to determine the $ClO_4^-$ content of a sample (2.97 ± 0.05 vs a theoretical value of 3). The samples having loadings less than or equal to 221 μmoles cluster/g Cab-O-Sil (25 wt%) showed *no* $ClO_4^-$ present indicating that an ion exchange process had occurred to support the cationic clusters. Qualitative tests of the solvent washes after

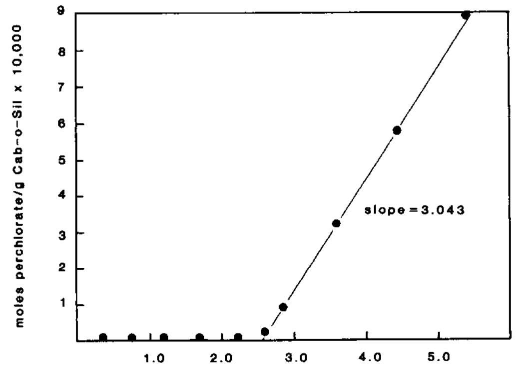

FIG. 4. Perchlorate analysis of supported Al–Cu cluster (ethyl).

impregnation were positive for $ClO_4^-$ thus indicating the counterion could be removed during the preparation. For other samples (<25 wt%) which were not washed during preparation, the $ClO_4^-$ counterion could be completely removed simply by heating at 90°C for 12 h. The counterion probably left as a volatile hydrate of perchloric acid. For samples of loadings greater than a molality of 252, the $ClO_4^-$ per gram of Cab-O-Sil in the sample increased linearly with a slope of $3.043 \pm 0.05$ (Fig. 4).

These higher loading samples show long range order to produce XRD peaks; thus, we conclude that multiple layers of the cluster are present. For the first layer of cluster on the support we speculate the support/complex protons are activated such that the complex becomes hydrogen bonded to the support. The population of silanols on the Cab-O-Sil (4 SiOH/nm$^2$) (*8*) is more than adequate to meet the demand for three hydrogen bonding sites per cluster (0.9 $SiO^-$/nm$^2$). The second and subsequent layers probably form by employing $ClO_4^-$ as the counterion as with the unsupported cluster.

It is remarkable for the Al–Cu (ethyl/Cab-O-Sil) samples that the occurrence of X-ray peaks and measurable amounts of perchlorate ion appear over a very narrow range of cluster molalities (near 250 $\mu$moles cluster/g Cab-O-Sil, or 27.3 wt%). We interpret these data by a model which calls for completion of a monolayer before multilayers of the cation complex form. This model demands the cluster–support interaction be very strong. Additional studies show that a sample loaded in excess of a monolayer loading (285 $\mu$moles cluster/g Cab-O-Sil) could be washed with solvent to remove cluster and $ClO_4^-$ (detected by qualitative tests of solvent wash for $Cu^{2+}$ and $ClO_4^-$). The resulting sample was found to contain 243 $\mu$moles cluster/g Cab-O-Sil. Repeated washings could not remove cluster as the solvent washes tested negative for $Cu^{2+}$ ion and $ClO_4^-$. The *n*-butyl modification shows significant amounts of $ClO_4^-$ even at low loadings (45 $\mu$moles cluster/g Cab-O-Sil, or 8 wt%). Thus, we conclude the steric hindrance prevents sufficiently close interaction to facilitate total ion exchange.

## CONCLUSIONS

These data show the ethyl clusters ($M$ = Al, Cr, and Fe) to be attached strongly to the surface probably through the siloxide ions of the Cab-O-Sil and the cluster OH bridges. The *n*-butyl cluster is an example of how the attachment may be frustrated by steric hindrance. The ethyl clusters exhibit an unusual affinity to a somewhat "neutral" support arising from properties unique to the cluster. The rather surprising conclusion is that strong support/catalyst interactions leading to monolayer dispersion of the cations may be developed by altering the properties of the catalyst rather than judicious choice of support.

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