Reply to the comment A.J. Kassman and D.B. Losee on the "Effect of gallium ions and of preparation methods on the structural properties of cobalt-molybdenum-alumina catalysts"

Citation for published version (APA):

Lo Jacono, M., Schiavello, M., Beer, de, V. H. J., & Minelli, G. (1978). Reply to the comment A.J. Kassman and D.B. Losee on the "Effect of gallium ions and of preparation methods on the structural properties of cobalt-molybdenum-alumina catalysts". *Journal of Physical Chemistry*, 82(21), 2348-2349.
<https://doi.org/10.1021/j100510a021>

DOI:

[10.1021/j100510a021](https://doi.org/10.1021/j100510a021)

Document status and date:

Published: 01/01/1978

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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of surface impregnated species from the substrate. Thus, the formation of Co_3O_4 and/or CoMoO_4 may indeed be taking place, but as a distinct bulk phase rather than as a surface phase. This is supported by the fact that the absorption of the coimpregnated B-A γ GaMoCo (0.6:5:x) is linear, in comparison to the nonlinear absorption of the sequentially prepared A-A γ GaMoCo (0.6:5:x) which already contains molybdenum intimately bound to the substrate prior to cobalt addition. Some support for this hypothesis is obtained from the X-ray powder diffraction¹ results which suggest the formation of a discrete bulk CoMoO_4 phase in the B-A γ GaMoCo (0.6:5:x) series. In addition, experiments we have performed⁵ with A- γ GaCo (x:0.5), using Reynolds' RA-1 γ - Al_2O_3 and no grinding, have indicated no significant change in the relative absorption coefficients with $x = 0.7$ – 8.0% .

References and Notes

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Received November 28, 1977;
Revised Manuscript Received June 19, 1978

Reply to the Comment by A. J. Kassman and D. B. Losee on the "Effect of Gallium Ions and of Preparation Methods on the Structural Properties of Cobalt-Molybdenum-Alumina Catalyst"

Publication cost assisted by Consiglio Nazionale delle Ricerche, Italy

Sir: The more proper treatment of the reflectance spectra, done by Kassman and Losee (KL),³ allows confirmation of the effect of gallium ion addition.

First of all we wish to remark that both absorption bands at 578 and 1560 nm are strongly affected, but not to the same extent, by the presence of Co_3O_4 (Figures 1 and 6 of ref 1), a normal spinel, with Co^{2+} ions in tetrahedral positions.

Accordingly, in order to evaluate the effect of Ga^{3+} ions we must consider separately the low Co content specimens ($0 < \text{Co} < 3$) and the high Co content specimens ($\text{Co} > 3$), where the influence of Co_3O_4 is more strongly felt.

Thus, from Figure 1 (redrawn from ref 3) it can be observed that, in the low Co content region, the specimens containing Ga^{3+} ions have a higher absorption than the Ga^{3+} -free specimens despite the presence in the latter of a small amount of Co_3O_4 . Moreover, quite acceptable linearity was visible, even though peak heights were used instead of peak areas.

As for the high Co content region (Figure 1, ref 3), the presence of bulk phase Co_3O_4 does not allow one to make a meaningful comparison between A γ Co and A γ GaCo samples, since Co_3O_4 has a broad, very intense absorption over the whole range from 730 to 210 nm (see Figure 6, ref 1).

The same reasoning can be applied to the absorption at 1560 nm (see Figure 2, redrawn from ref 3) by taking into account the minor influence of Co_3O_4 . Indeed, the plots of Figure 2 are essentially linear at low Co content, for all

Figure 1. A plot of absorption (obtained by use of the Melamed conversion procedure and the optical density plots reported in ref 1 of KL) vs. concentration of cobalt (atom percent) at 578 nm: (Δ) A γ Co; ($\circ$) A γ GaCo (0.6:x); ($\bullet$) B-A γ GaMoCo (0.6:5:x); ($\square$) A γ GaCo (4:x); ($\odot$) A-A γ GaMoCo (0.6:5:x).

Figure 2. A plot of absorption (obtained by use of the Melamed conversion procedure and the optical density plots reported in ref 1 and 4 of KL) vs. concentration of cobalt (atom percent) at 1560 nm: (Δ) A γ Co; ($\circ$) A γ GaCo (0.6:x); ($\bullet$) A-A γ GaMoCo (0.6:5:x).

specimens. Moreover, it is still observed that the A γ GaCo specimens have higher absorptions.

At high Co content, while the specimens A γ Co₄ and A γ Co₅ show a jump in absorption due to the massive presence of Co_3O_4 , as visible by X-rays, magnetic susceptibilities, and reflectance spectra,¹ absorption for the Ga^{3+} -containing specimens are still linear. However, this linearity, as compared with the less linear plots of Figure 1, can be understood by considering the different influence of Co_3O_4 absorption in the two regions (578 and 1560 nm).

Furthermore, it is not surprising that KL have not found any significant differences in the relative absorption coefficients for their specimens, A γ Co and A γ GaCo, with a Co content of 0.5 at. %, since, as is seen in Figure 2, for this Co content the difference in absorption between A γ GaCo and A γ Co is very small (~ 0.02).

Finally, it must be pointed out that the conclusion about the effect of Ga^{3+} ions on the phase formation and cation distribution was based on the results obtained by several techniques, such as X-rays, magnetic susceptibilities, and reflectance spectra.

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Received January 31, 1978; Revised Manuscript Received August 8, 1978

Comments on "A Comparison of Manning's Polyelectrolyte Theory with the Cylindrical Gouy Model" by D. Stigter

Sir: The counterion condensation theory of polyelectrolyte solutions¹⁻⁷ is constructed on two fundamental tenets: (1) Linear charge densities greater than an unambiguously determined critical value are unstable; hence, the structural charge density of a polyelectrolyte chain, if greater than critical, is reduced to the critical value by association of counterions. (2) Residual electrostatic interactions of free counterions and coions with the unit composed of polyion and associated counterions may be accurately treated by the limiting form of the Debye-Hückel approximation. Stigter's paper⁸ calls both of these statements into question and asserts moreover that the Poisson-Boltzmann equation is a more accurate basis for polyelectrolyte theory. On the contrary, I believe that condensation and the Debye-Hückel interactions are soundly rooted in both experiment and theory, that Stigter's applications of polyelectrolyte theory to salt-exclusion and mobility require reinterpretation, and that his asserted higher accuracy of the Poisson-Boltzmann equation remains undemonstrated.

Counterion Condensation. Association of counterions to the extent predicted by condensation theory has been directly observed by experimental measurements.^{4,9-14} In particular, the predicted charge fraction of DNA has recently been confirmed by NMR techniques.¹⁵ It must be emphasized that these experiments are designed to detect *directly* the number of counterions that are in close proximity to the polyion chain (as defined, for example, by interpenetration of hydration layers or substantially increased relaxation rates). Indeed, had I been aware in 1969 of Ikegami's earlier index of refraction measurements, I would have viewed my theoretical argument (actually, Onsager's) as an attempt to explain Ikegami's experimental discovery of condensation⁹ rather than as the basis for a theoretical postulate. At any rate, those who wish to contest the reality of counterion condensation should now address themselves to the experiments.

Debye-Hückel Interaction. Justification for the use of Debye-Hückel theory to describe interactions after condensation has occurred is found in the enormous number of observations that agree with a priori prediction based on condensation (independently confirmed) and Debye-

Hückel theory.^{1-3,6} Of course, it is always possible that such agreement is the result of mutual cancellation of higher-order interactions, each of which is comparable to the Debye-Hückel term. Iwasa and Kwak¹⁶ have recently attempted to find a theoretical basis for this viewpoint in certain higher-order terms of polyelectrolyte cluster theory, but their calculations are so far inconclusive. Frequently observed discrepancies between observed and predicted coion activity coefficients¹⁶ and multivalent coion self-diffusion coefficients¹⁷ perhaps point to some difficulty; but, again, single-ion activity coefficients present experimental problems, and a transport property may not be a reliable guide to difficulties in the theory of the free energy and its derivatives.

A recent re-formulation of condensation theory⁴⁻⁷ shows that the correct extent of counterion condensation is obtained over a wide range of concentrations by minimizing a Debye-Hückel free energy with respect to arbitrary extent of condensation. It is possible, but undemonstrated, that some other form of the free energy would also give the correct value of condensation.

I interpret Stigter's Figures 4 and 5 as lending further support to use of the Debye-Hückel free energy. After condensation is considered, the value of ξ is unity. For $\xi = 1$, β departs from its Debye-Hückel value of unity by less than 20% over the entire concentration range portrayed. The quantity β is the ratio of the solution of the linearized Poisson-Boltzmann equation to that of the full equation for a given value of the surface charge density. Unlike β , the relevance of the quantity γ is not clear to me; nevertheless over the range of concentrations encountered in practice, $x_0 > 10^{-1}$, γ departs from its Debye-Hückel value of unity by less than 15%. By no means do I accept these figures as measuring the inconsistency of the Debye-Hückel term in condensation theory, since they may equally well reflect the inherent inaccuracy of the Poisson-Boltzmann equation itself (see below), but they do serve to suggest the kind of discrepancies with which we may be concerned. They are not large.

Bailey¹⁸ has utilized the cluster theory of ionic solutions, which is more rigorous than the Poisson-Boltzmann equation, to show that the Debye-Hückel free energy term is greater than the next higher-order terms by a factor of at least 70. His calculations apply to excess salt conditions, as do Stigter's.

Donnan Salt Exclusion. Stigter's Figure 1 seems to be straightforward. Data points are portrayed along with two solid lines, one representing the Devore-Manning theory,¹⁹ the other Stigter's calculation. It appears that the latter provides good agreement with the data, while the former is a rather poor description. Appearances, however, are sometimes deceiving.

The coefficient A_1 may be written as the sum of two terms²⁰

$$A_1 = A_1^{(0)} + A_1^{(1)} \quad (1)$$

where $A_1^{(0)}$ is an excluded-volume term, while $A_1^{(1)}$ is the electrostatic contribution. In Stigter's expression for A_1 , his eq 5, the second term in braces corresponds to $A_1^{(0)}$; in the Devore-Manning (DM) expression, eq 4b of Stigter, $A_1^{(0)}$ is absent, since we did not include excluded-volume contributions in our calculation. Therefore, for present purposes, Stigter should have quoted the DM result as

$$A_1 - A_1^{(0)} = -(4\xi)^{-1} \quad \xi > 1 \quad (2)$$

To compare eq 2 with experiment, values of the non-electrostatic term $A_1^{(0)}$ should be subtracted from observed values of A_1 and the result compared with the right-hand side of eq 2.