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Professor

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September 26, 2006

Dr. F. Ann Walker
Associate Editor, JACS
Department of Chemistry
University of Arizona
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Re: MS No. ja065497c

Dear Professor Walker:

We are generally very pleased with the reviewers' comments on our paper, "Chemistry of the Silica Surface: Liquid-Solid Reactions of Silica Gel with Trimethylaluminum," especially the detailed comments of Reviewer 2, who clearly read our manuscript very carefully and whose comments offer us an opportunity to clarify and/or correct the issues raised.

As requested, we have faxed a Copyright Status Form, and our revision contains a Table of Contents figure on the last page (p. 31) and, of course, an abstract. The status of Reference 53 has not changed, so we have removed it from the list of references. Our responses to reviewers' specific comments follow.

Reviewer 1.

1. The reviewer's point is a good one. Accordingly, we have added a new paragraph after equation (16) in the main text to clarify this point.
2. The reviewer's point is now made in the parenthetical clause added just before eq. (16).
3. Although we agree that the toluene-vs-cyclohexane comparison made by this reviewer might be relevant, we are not especially enthusiastic about it. Nevertheless, we have added a short paragraph on this point just before the Summary.

Reviewer 2.

General

- a) In order to accommodate this reasonable opinion of the reviewer, we have added the words “hypothetical and speculative” in the 16th line of p. 17.
- b) Our reason for exposing the initial $\text{Al}(\text{CH}_3)_3/\text{silica}$ product to a diethyl ether wash is now given in the beginning of the section on Effects of Diethyl Ether on Initial Reaction Products (p. 13).
- c) The reviewer’s wording regarding our treatments with “controlled amounts of water (for unstated but obvious reasons for those familiar with these materials)” implies that most readers will not know the purpose of this part of our experimental strategy. Consequently, we have added two new sentences at the beginning of the section on Limited Hydrolysis (p.13).

Specifics

- a) The reviewer is completely correct on this point concerning the redundancy in Equations (1) – (3). We were simply trying to be faithful to what previous authors have placed in the literature. In any case, we have now eliminated what was initially eq. (3).
- b) The words “are identified” have been replaced by “are tentatively identified (structures proposed)” in the last paragraph of the Introduction.
- c) In the second line of Sample Preparation, “of” has been inserted between “suspension” and “dry”, as requested.
- d) In order to accommodate the reviewer’s opinion, we have changed “in elucidating the structures present” to “to provide structural information on the species present” in the 2nd line of NMR Spectroscopy in the Results section.
- e) We agree that, referring to the $\text{Si}(\text{CH}_3)_3$ groups, 1) “It is difficult to formulate a reaction whereby such groups are formed” and 2) “Later, when exposing these samples to water, these groups are found to be easily hydrolyzed.” Nevertheless, a small, but reproducible peak *is* observed at 25 ppm in the ^{29}Si spectrum. It is not clear why a $\text{Si}(\text{CH}_3)_3$ species would be unstable to an aqueous environment, but one should note that there is only one Si-O-Si linkage to the surface for this species, whereas $\text{Si}(\text{CH}_3)_2$ and SiCH_3 moieties may have two or three such linkages. In any case, the word “tentatively” has been inserted before “(-O₃SiOSi(CH₃)₃)” in the sentence on peak assignments (line 5 of p. 11).
- f) The uncertainties regarding Table 1 are now clarified as follows: As now stated in footnotes in Table 1, the results are averages of six replicate reactions for each solvent, with uncertainties given as estimated standard deviations. The sample sizes were not identical for the individual runs or for both solvents (which is why the numbers of silanols of the silica reactant differ). “Unreacted Al-CH₃”, as now

specified in footnote d, is measured in the supernatant liquid (including the initial wash). The “silica surface methyl product,” as now specified in footnote e, refers to *all* of the methyl groups attached via a variety of linkages to the surface in the initial reaction product.

- g) Concerning the apparent discrepancy pointed out by this reviewer on the $\text{AlCH}_3/\text{SiCH}_3$ ratio, we don't think there is a real discrepancy. If 70% of the surface-attached methyl groups are in the AlCH_3 form, then 30% are presumably SiCH_3 and SiOCH_3 . Suppose this 30% is split evenly between SiCH_3 and SiOCH_3 ; in this case the $\text{AlCH}_3/\text{SiCH}_3$ ratio is $70\%/15\% = 4.7$ - - close to 4.5.
- h) We think there is some misunderstanding regarding the concerns expressed regarding the “detection of Si-OCH_3 groups.” As stated on p. 2 (and now emphasized with italics), “Equations (1) through (6) represent a consensus of chemical understanding *embodied in the prior work*.” A subsequent equation does indeed include Si-OCH_3 groups among the products (eq. 7, now eq. 6). What is probably the ‘offending sentence’ has now been modified to include Equations 1 – 10.
- i) The reviewer's concern at not seeing a conversion of AlCH_3 ^{13}C intensity to Si-OCH_3 intensity upon ether treatment (top of p. 13) is understandable. This small conversion is more apparent in some of the other replicate experiments and in ^{13}C spin counting, as now reflected in new wording of the first half of the paragraph on Effects of Diethyl Ether on Initial Reaction Products (p. 13). Regarding the reviewer's concern regarding methane generated during the ether-treatment step, we did not mean to imply that there was *any* methane generation during this step. It is true that a measurement of methane evolution was made during this step, but the measured amount was *zero*. This fact is now clarified by the addition of “nor CH_4 evolution” in the last sentence of “Effects of Diethyl Ether on Initial Reaction Products (p. 13).
- j) Reference 53 has been eliminated.
- k) The reviewer raises an interesting point regarding hypothetical structures on pages 17 and 18 that include Si-O(H)-Al moieties. The protons of such moieties are included in these hypothetical structures primarily to render the net electrical charge of the structures zero. Furthermore, the protons of such structures, if they exist, are likely to be rather mobile in these structures, and we have no idea how one might observe them.

It is true that the *atomic building blocks* of the corresponding silanols are “not truly lost” but the *chemical identity* of such a silanol is certainly lost (changed).

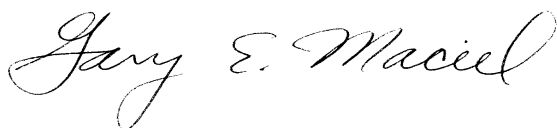
- l) This reviewer's concern regarding “three bonds to the surface” (referring to $-\text{O-Si}$ linkages) is valid and has been addressed, as described in response to Reviewer 1's first comment (the new paragraph following eq. 16 on p. 19).

Reviewer 4.

We are delighted that this reviewer had no scientific criticisms at all. His/her comment that "The abstract is that of a 'synthesis and characterization' paper..." has caused us to re-examine and refine the Abstract. Our view of a "synthesis and characterization paper" is one that describes a study aimed at the preparation of a specific species or class of species and the characterization of the various products and intermediates obtained. That was certainly not the intent of our paper. We had no synthetic goal; we simply wanted to illuminate the chemistry that occurs when trimethylaluminum in solution is mixed with dry silica. We have also taken to heart this reviewer's suggestion of "highlighting in their paper the new insights into TMA derivatization" by adding some new wording in the revised Abstract and in the Summary.

We believe we have addressed all of the reviewers' concerns successfully and trust that the revised paper will now be deemed acceptable for publication in JACS. Please let me know if you need any additional information or action from me.

Sincerely,

A handwritten signature in cursive script that reads "Gary E. Maciel". The signature is written in black ink and is positioned below the word "Sincerely,".

Gary E. Maciel
Professor of Chemistry

GEM/eam