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Reply to “Transesterification on imprinted silica”

[by W.R. Ahmad and M.E. Davis]

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In 1994 we published our observations on a selective transesterification with a new approach to molecular imprinting in inorganic materials [1]. In a recent publication in this Journal W.R. Ahmad and M.E. Davis (AD) expressed doubts concerning our imprinted silica catalyst [2]. Background of our procedure was the preparation of microporous amorphous silica with a narrow monomodal pores size distribution by our optimized sol–gel procedure. These pores are the transport pores of the alcohol released in the sol–gel procedure. Our original conclusion was that if a silica gel during its drying process can so precisely adjust its pore size to the transport requirements of the alcohol and solvent molecules, it may also be able to form molecular cavities capable of molecular recognition.

In analogy to catalytic antibodies a transition state analog was covalently connected to the gel by copolycondensation. Figure 1 shows the selected transesterification reaction, an associated transition state **1**, the transition state analog **2** and the actually used “imprint” molecule **3** with its $(EtO)_3$Si-anchor. Copolycondensation with TEOS resulted in a clear gel, which, after drying and calcination, provided the microporous amorphous silica **A**. A control material **B** was prepared under identical conditions in the absence of “imprint” molecule **3**. Both materials were of comparable porosity, pore size distribution and inner surface area, no deviation in the adsorption data could be associated with the “imprint” cavities. This was essentially reproduced by AD. What led us to postulate “imprint” catalysis was a competition experiment in which the original ethyl ester was transesterified with an equimolar mixture of *n*-hexanol, *n*-octanol and 2-phenylethanol. While all three esters were formed at comparable rates in homogeneous acid catalysis, with an H-zeolite as well as with acidified control silica **B**, the selective formation of the hexanol and octanol esters over the phenyl ethyl ester (7 : 8 : 1) was observed reproducibly only in the presence of “imprinted” silica **A**. Although these interesting experimental observations can be interpreted as the basis of the original working hypothesis (figure 1), the actual situation may be more complicated, as delineated in our full paper in 1995 on related systems [3].

Most of the experimental part of the publication by AD rests on a solid basis. In particular the narrow micropore size distribution claimed by us originally was fully reproduced by AD, while the pore diameter seems significantly smaller than the 1 nm reported by us [1]. Our novel procedure for the preparation of microporous amorphous oxides was reported in 1993 [4] and represents the basis of the “imprint” experiments and other applications in which unusual degrees of microporosity of amorphous oxides is the determining factor.

AD make a comparison of the volume occupied by the “imprint” molecule with that occupied by the templating agent in a ZSM-5 synthesis. Since they claim to have followed our preparation procedures closely, they should have used 123 mmol TEOS and 1 mmol **3**, which after hydrolysis and drying should have resulted in 124 mmol silica containing 1 mmol “imprint” molecule, which translates to 0.039 mg “imprint” molecule in 1 g of silica. Assuming a density of about 0.9 g/ml for the organic material, this results in a volume of $0.042\ cm^3/g$, little more than half the $0.07\ cm^3/g$ derived by AD. AD argue, that such a pore volume should be detectable, since they apparently assume, that the cavities should be of a different size than the micropores. However, they have not considered that for the catalyst to function, the “imprint” molecule must be able to leave the catalyst, i.e. to penetrate the pores. In the publication in Angewandte Chemie as well as in Heilmann’s thesis (chapter 7.2.1) we point out, that temperature-dependent MS-studies of the uncalcined catalysts show the MS-spectrum of the complete “imprint” molecule as the only evidence that the “imprint” molecule in the gel is still intact during calcination. In figure 2 details of the temperature-dependent MS data, obtained from a freshly prepared silica **A** catalyst, are presented. The typical masses for molecule **2** start to appear at about 180 and at 240°C this evolution is over. There is no release of **2** at lower temperatures. The associated spectrum marked 42 matches the spectrum of compound **2**. The data show, that some **2** is released undecomposed over a relatively narrow temperature range. From this information we have deduced our calcination temperature in the silica **A** preparation. This MS-spectrum has

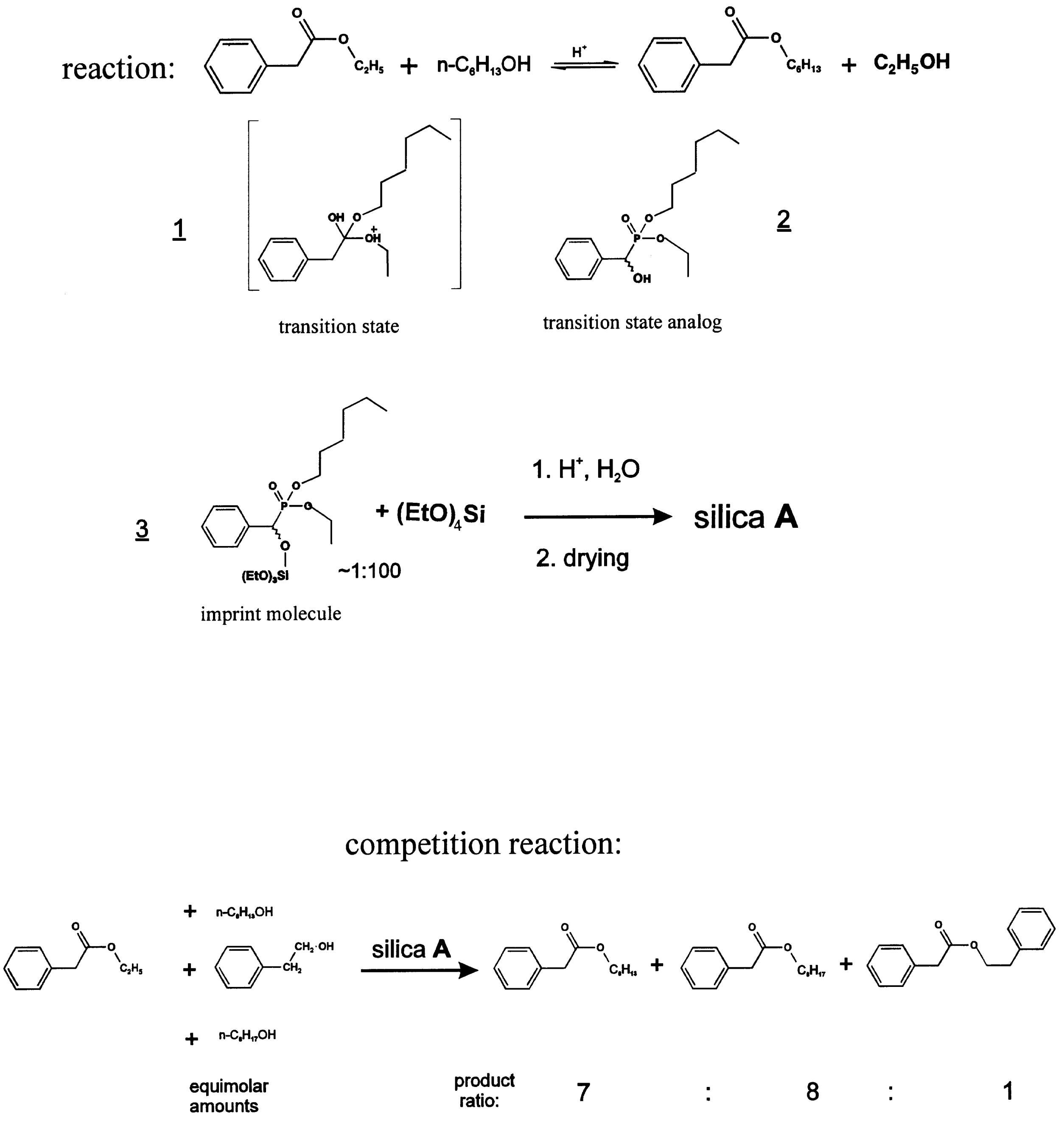

Figure 1. Selected reaction, transition state structure, transition state analog, preparation of silica **A** and competition reaction of refs. [1,2].

been taken as a first indication of a proper "imprint" catalyst. There is no mentioning of MS-studies of **A** in the AD work.

In our original publication as well as in the thesis of Heilmann we already stated the lack of inhibition of the catalyst **A** with two "imprint" molecules, one of which was compound **2**. AD have repeated this inhibition experiment with compound **2**. AD also observed the lack of inhibition without referring to our work.

Of much greater concern to us are the data reported by AD in section 3.3, concerning the attempted reproduction of the competition experiments. Here the selectivity of transesterification of phenyl acetic ethyl ester with an equimolar mixture of *n*-hexanol, *n*-octanol and phenylethanol to preferentially form the hexyl and octyl ester "imprinted" silica was interpreted by us as sole evidence for "imprinting". A serious problem with AD's work is the purification of the organic starting materials for the competition reaction. AD report that they have not been able to reproduce the inhibition of autocatalysis for the transesterification reaction by "imprint"-free reference silica **B**. This indicates, that their starting mixture is not of sufficient purity. There is little point in studying this reaction under conditions where autocata-

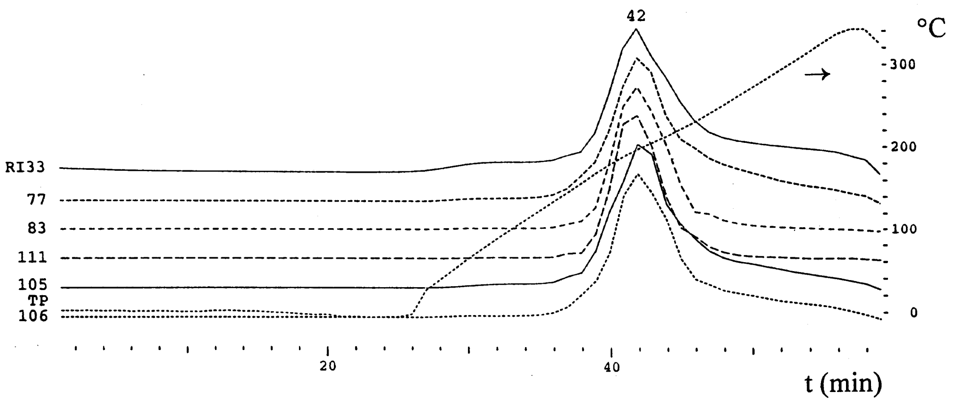

Figure 2. Temperature-dependent MS of silica **A**. RI is the total ion intensity, the other lines are ion intensities of selected masses, typical for compound **2**.

lysis is still dominating. We have stressed, that the alcohol mixtures and the ester had been purified. It should be trivial, that such a purification is only adequate when autocatalysis is suppressed to a level not to interfere with the expected catalyst activity. Apparently AD have not purified their starting materials sufficiently and all they report is the autocatalysis. To us it was no problem to purify the alcohols and the ester by standard methods (40 cm Al_2O_3-column) in order to suppress the autocatalysis. In fact, when properly purified, autocatalysis is not detectable for at least 8–24 h at 140°C.

Other parts of the AD paper are beyond criticism. Their results obtained from ^{31}P/MAS-NMR nicely confirm our initial assumption (2) that the catalytic activity is due to the presence of phosphorous sites. However, it is not clear how much of the "imprint" molecule is actually removed by calcination, since AD report the presence of a large peak at -22 ppm in the presence of the "imprint" molecule and of a large peak at -19 ppm directly after calcination (silica **A**). We assume that the minus signs are misprints of AD, since for our uncalcined silica **A** the ^{31}P-NMR signal is found as a single large broad peak at $+22$ ppm with a shoulder at $+19$ ppm. In contrast to AD, after calcination of our silica **A** (an active catalyst) we observed not the large signal at 19 ppm described by AD, but already the weak signals at -37, -11, 0 ppm, and a strong signal at -23, described by AD to appear only after few hours of exposure to ambient atmosphere. Furthermore, the same signals are detected by us in a used catalytically active silica **A** after the reaction. The single peak at 0 ppm, described by AD to appear after exposure to the atmosphere over night, is present in our used catalytically active silica **A** together with the peak at -11 ppm in comparable intensity. The resonance at -23 ppm becomes much smaller in this material. After exposure of our sample to the atmosphere over night we found, similar to AD, a sharp resonance without side bands at 0 ppm as a dominating signal. However, in order to probe the nature of the "imprint" molecule during the preparation of silica **A** we have studied the ^{31}P/MAS NMR spectra of an untreated gel of **A**, of the gel predried at 130°C, which according to MS contains still the "imprint" molecule, and of reference silicas impregnated with "imprint" molecules **2** and **3** respectively and predried at 130°C. To our surprise, the untreated gel as well as the predried sample showed a rather sharp signal at $+22$ ppm (halfwidth 110 and 400 Hz respectively). While the signal in the untreated gel is accompanied by negligible bands the ^{31}P-MAS signal of the predried sample showed small first order side bands only. These facts together with the observation that the cross-polarization did not operate for the untreated sample and is very ineffective for the predried gel, indicates free movement of the "imprint" molecule in both samples. It confirms that the "imprint" molecule **3** is not covalently bound to the polymer network but only physically adsorbed as stated by AD. Therefore the cavity as anticipated originally by us could never have formed and therefore the selectivity observed cannot have been the result of imprint catalysis. The impregnated samples show a slightly broader peak (halfwidth 560 Hz) with typical side band patterns. The unexpected lack of copolycondensation of **3** must be due to a hindered hydrolysis behavior of **3**, the origin of which is not clear yet. The free movement of **3** also explains the MS-trace shown in figure 2.

Furthermore, despite proper catalyst production and catalytic reaction conditions, we have not been able to reliably reproduce the original selectivities, indicating that there are important experimental details we are not aware of. Significant may be that we have not been able to reproduce the original pore sizes of 1 nm. Our pore sizes of about 0.8 nm are larger than those reported by AD and larger than those of a Na-Y-zeolite, but smaller than the original pores. Thus it remains unclear whether the "imprinted" material by AD or by us is identical with our original material reported in 1993. The problem of interpretation of our original results remains. Other explanations, such as different rates of diffusion of the alcohols or esters in the specific micropores of the original silica materials need to be considered.

Conclusion

Some of the experiments reported by AD are correct, while others have not been conducted properly, leading to improper conclusions. Most importantly, the conclusion of AD that we do not have an "imprint" seems correct, since the copolycondensation of the "imprint" molecule with the bulk matrix apparently never took place. The original transesterification selectivity, which we are now unable to reproduce, may have been the result of diffusion phenomena due to the specific pore sizes obtained originally.

Acknowledgement

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References

[1] W.F. Maier and J. Heilmann, Angew. Chemie 106 (1994) 491; Angew. Chem. Int. Ed. 33 (1994) 471.
[2] W.R. Ahmad and M.E. Davis, Catal. Lett. 40 (1996) 109.
[3] J. Heilmann and W.F. Maier, Z. Naturforsch. B 50 (1995) 460.
[4] W.F. Maier, I.-C. Tilgner, M. Wiedorn and H.-C. Ko, Adv. Mater. 10 (1993) 726.