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Interoffice Communication

To W. J. Libbey

cc's - JWW 12/20/82

From R. J. Convers

Date December 13, 1982

Subject Results of Meeting with Kanegafuchi Representatives, December 8, 1982

During a December 8, 1982 meeting at the Conoco VCM Plant, various aspects of using Kanegafuchi ("K") oxy catalysts were discussed with K personnel. Attendees were the following:

J. A. DeBernardi	"Ken" Shiozaki (K R&D chief)
Ron Bryan	"Ken" Inoue (K overseas sales rep.)
Dick Davis	Garvin Fryar
Paul Fetzer	R. M. Owens
Johnny Cole	R. J. Convers
Peggy Marritt	

Major topics were (1) updated performance data from both K (air-based) VCM plants, (2) analytical data on the K catalysts, (3) data comparing Stauffer and K catalyst performance in K's O_2-based lab reactor systems and (4) potential legal problems associated with using K catalyst during the 1983 start of O_2-based oxy in the Conoco VCM Plant. Most of the details of topics (1) and (3) were summarized in handouts received by all attendees. Copies of those handouts are attached to copies of this letter sent to W. J. Libbey, C. M. Starks, R. J. Carlson, and D. A. Barclay.

(1) K Commercial Plant Data

The main news here was that K has produced a second generation of commercial oxy catalysts. The chemistries and properties of the new, ring-shaped catalysts for R301 and R302 are nearly identical to the corresponding K spherical models. The ring-shaped catalysts for R301 and R302 are used with the K pelleted graphite diluent. The ring catalyst for R301 has a higher $K^+:Cu^{++}$ mole ratio to counteract the activity gained from increased geometric (catalyst "skin") surface area per unit reactor volume. Shiozaki believes that the ring structure gives lower reactor pressure drops than the corresponding spherical catalysts.

Shiozaki said that efforts to produce the K spherical and ring catalysts were begun simultaneously about 15 years ago. The ring catalysts were more difficult to develop, although the eventual prices of corresponding spherical and ring catalysts should be the same. K will not make KOC-R1 available for sale until further K plant run data are obtained.

Inoue disclosed the following list of commercial VCM producers currently using K catalysts:

Company	K oxy Catalyst
Conoco	KOC-101
Shell (Deer Park)	KOC-101
Sumitomo	KOC-101, KOC-201
Formosa Plastics	KOC-101, KOC-201, KOC-R3
Keminord	KOC-101
BASF	KOC-101, KOC-201, KOC-R3 (pilot tests only)

Formosa Plastics is also using the K catalyst system for R304. Wacker, which has used a proprietary steam injection process in R301 since about 1975, has expressed no interest in the K catalysts.

Inoue heard from Stauffer that Shell has finally realized the impact of R302 catalyst on ethyl chloride selectivity in O_2-based oxy, and has changed out the traditional BASF loading for a new combination of Stauffer SCS206, SCS210, and SCS218 in R302 at Deer Park. If this hearsay is true, we should not be surprised if Deer Park experiences the first recorded case of major activity loss in R302 in commercial operations. KOC-R2 or even the standard Stauffer R302 pattern (SCS210 followed by SCS218) should be superior catalysts for that reactor, O_2-based, from activity and selectivity considerations.

(2) K Catalyst Analytical Data

At my request, Shiozaki provided the following catalyst analytical data (Table 1):

Table 1 - K Catalyst Data

Catalyst	$CuCl_2$, w/o	K Cl, w/o	Minimum Crush Strength, Kg
KOC-101	12	4	2
KOC-201	16	2.3	2
KOC-R3	16.5	2.3	1
KOC-R2	14	4	1
KOC-R1	12.5	4.5	1

The supports of the ring catalysts, KOC-R1, KOC-R2, and KOC-R3 (previously reported) are not the same. I got the impression that the porosity of the KOC-R1 and KOC-R2 supports were manipulated with the techniques used on the corresponding spherical supports (the supports for KOC-101 and KOC-201). I did not ask what technique was used to modify the support. I did not ask for the source of the support.

Shiozaki agreed to provide us with 1 liter samples of KOC-R1 and KOC-R2. When he asked for the results of our tests of the samples of KOC-101, KOC-201 and KOC-R3 (received last Spring), I told him that we had not run lab tests on those samples. We had been able to use analytical data from those samples in a proprietary oxychlorination model to predict successfully the performance of KOC-101 in our VCM Plant. Had the samples contained unusual elements, we would have run the lab tests.

Inoue and Shiozaki seemed surprised that such predictions could be (or were) made. Shiozaki asked if we were aware of the effects of the support on catalyst properties. I said yes.

In answer to further questions, I told Shiozaki that we had lab tested a variety of catalysts which we had made against Harshaw and Stauffer catalysts in an effort to improve the performance of R301, our most troublesome reactor. We had found some superior catalysts (different from K's) on which we filed patent applications. The best of those showed EDC selectivities slightly superior to that of KOC-101. We had tested none of our own catalysts in our VCM Plant. I remarked that Kanegafuchi was far ahead of us in catalyst development.

(3) K O_2-Based Oxy Lab Tests

At our request, K ran 2 sets of O_2-based oxy runs in the K 3-reactor lab system. The runs compared Stauffer and K catalyst systems under O_2-based conditions which K feels might best simulate corresponding conditions in the K VCM plants. The K catalysts were from commercial batches. A drawback was the apparent inability of K to run the tests at pressures higher than atmospheric. At higher pressures, selectivity to by-products, particularly ethyl chloride, should increase. At higher pressures, the O_2 and HCl conversions should also increase.

K could and did sample products from each reactor in the lab test system. The data in Table 2, I believe, represent the selectivities of each, single reactor in the test system under the conditions shown on pages 11-13 of Shiozaki's report (handout). The data are averaged weight percent values.

Table 2 - O_2-Based Test Reactor Selectivities

Reactor:	R301		R302		R303	
Catalyst:	Stauffer	K	Stauffer	K	Stauffer	K
EDC	96.89	99.09	97.69	98.51	96.55	98.34
VCM + 112[a]	0.355	0.150	0.308	0.192	0.229	0.093
EtCl[b]	1.214	0.235	0.851	0.639	0.362	0.169
Chloral	0.0122	0.009	0.148	0.0119	0.0056	0.0044
CCl_4	0.0021	0.0012	0.0046	0.0019	0.0115	0.0077
$CHCl_3$	0.018	0.0065	0.0194	0.005	0.031	0.0114
CO	0.782	0.215	0.514	0.309	1.18	0.520
CO_2	0.641	0.248	0.525	0.285	1.52	0.815

[a] 1,1,2-Trichloroethane

[b] Ethyl Chloride

The data in Table 3 give a comparison of (weight percent) selectivities of K spherical and ring R302 catalysts under conditions similar to those used for Table 2. The ring catalysts showed superior EDC selectivity but slightly less activity.

Table 3 - O_2-Based Test Comparison of K R302 Ring & Spherical Catalysts

Catalysts:	Rings (KOC-R2 followed by KOC-R3)	Spheres (KOC-201)
EDC	98.70	97.86
VCM + 112	0.170	0.275
EtCl	0.585	0.821
Chloral	0.026	0.027
CCl_4	0.005	0.006
$CHCl_3$	0.008	0.012
CO	0.514[a]	1.028[a]
CO_2	0.465[a]	0.884[a]
Coolant Temp., C^o	230	245
Hotspot Temp., C^o	290	313
O_2 Conversion, %	92.75	93.32

[a]This value must be divided by 2 to calculate selectivity based on ethylene.

The conditions used for the data in Tables 2 and 3 correspond to extremely high ethylene recycle rates and/or very low residence times in the VCM Plant. Under practical O_2-based VCM Plant conditions, the O_2 conversions should reach 98% or more in R301 or R302. The differences in ethyl chloride selectivities from reactor to reactor in Table 2 should be exaggerated by increased reactor pressures and reactor pressure drops.

Useful insights on future Conoco oxy operations may be gained after the recent K data have digested.

(4) Potential Legal Problems

J. A. DeBernardi expressed concern that a choice of K catalyst for use in oxy next Spring may cause legal problems.

A strict interpretation of the K catalyst sales contract prohibits Conoco from discussing either K catalyst-related performance data or K

catalyst properties with either other K catalyst users (such as Shell), or non-users (such as Stauffer). Simultaneously, Conoco's choice of O_2-oxy start-up catalyst must be approved by Stauffer for the Stauffer process guarantee to be valid. DeBernardi expects Stauffer to require K catalyst performance and possibly even property data before it approves the use of K catalyst by Conoco next Spring. Inoue and Shiozaki said that Conoco could discuss K catalyst performance data (from both the Conoco VCM Plant and K lab tests) with Stauffer. J. A. DeBernardi asked for a written statement to that effect. Inoue said that he will pursue this matter when he returns to Japan around Christmas. He will send the written statement in time for a Conoco catalyst order to be made and shipped or will say that K cannot meet Conoco's April 15 catalyst delivery deadline.

(5) Miscellaneous Items

Shiozaki agreed to send us further K plant data several months from now, so that we can better evaluate the performance of KOC-R1 catalyst.

Shiozaki recommended a K catalyst "break-in" period of 10 days at 80% of full rates.

Shiozaki said that K has seen as much as ±6% absolute error in bulk ("mechanical") mixing of the 67% catalysts for R301 or R302. Alternatively, hand-mixing only enough material to charge one reactor tube at a time (in a polyethylene bag) essentially eliminates all diluent mixing errors and thus provides much more uniform reactor performance. He recommended the use of cut-off graduated cylinders to rapidly measure the volumes of catalyst and diluent needed to charge a reactor tube. He said that both bulk and hand mixing times were essentially the same. He provided the VCM Plant with a 35mm film record of K catalyst being mixed by the recommended method.

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cc: CMS:RJC:RMO:DAB:GJF:JADe:RB
DLD:JGC:MJM:MWC:PLF:HLH