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Importance of surface science and fundamental studies in heterogeneous catalysis

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At Union Carbide Corporation, surface science and fundamental studies have played extremely important roles in the discovery, development, and diagnosis of several valuable commercial and developmental catalyst systems. Prior to the late '60s, it was very common among scientists and engineers to refer to catalysis, particularly heterogeneous catalysis, as either an "art" or "magic". Primary reasons behind these labels were our inability to understand the performance of "poor" and "good" catalysts nominally having the same bulk composition. With the development of surface science in the early '70s, heterogeneous catalysis field was relatively easy picking for diagnosis and improved understanding of many of these poorly understood catalyst systems. In fact, there were many "sad" stories across the chemical industry of catalysts that prematurely deactivated or essentially died and there was no known cause or relationship of performance with observable physical–chemical properties. In all such instances, the bulk characterization techniques failed to identify or uncover the cause or causes of such activity decline. However, through the use of surface science and fundamental characterizations, three such "sad stories" turned into "success stories" at Union Carbide. In addition, it will also be shown that the early use of surface science and fundamental studies led to the discovery, development and enhanced understanding of several catalyst systems. Many of the early surface science techniques along with the newly developed techniques continue to and will play a very important role in the future development of next generation catalysts and catalytic processes for the industrial use and environmental protection.

Keywords: ethylene oxidation, epoxidation, copper catalysts, silicones, methyl chlorosilanes, silver/alumina catalysts, mechanism and kinetics, synthesis gas, C_2 oxygenates

1. Discussion

Following the discovery and application of Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) to heterogeneous catalysis in the early 1970s, a number of other characterization techniques have been developed and found to be very useful as well. Several of these techniques, along with the bulk characterization techniques found to be useful in heterogeneous catalysis are listed in table 1. This is not an exhaustive list, but merely illustrative of some of the more common techniques. In addition to these surface and bulk characterization techniques, it is very important to use appropriate fundamental characterization techniques such as kinetic studies – employing unlabeled and labeled atoms of C, H, O, etc., in reactant/product molecules, chemisorption, temperature-programmed desorption or reaction, and heat and mass transfer studies, especially when dealing with commercially employed formed/shape catalysts.

The diagnostic use of some of these surface science and fundamental characterization techniques will be highlighted in section 1.1 through their application in three specific catalyst examples. Later on, in section 1.2, other catalyst examples will be discussed where the use of surface science and fundamental studies led to the discovery, development and enhanced understanding of commercially important catalyst systems.

Table 1
Catalyst fundamentals.

1. High-resolution spectroscopy	
SAM	scanning Auger microprobe
AEM/TEM	analytical and transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
SIMS	secondary ion mass spectroscopy
ISS	ion scattering spectroscopy
2. Other spectroscopies	
SEM	scanning electron microscopy
EDS	energy dispersive spectroscopy
XRD	X-ray diffractions
SSNMR	solid state NMR
3. Fundamental characterization studies	
• Kinetic studies including isotopically labeled molecules	
• Chemisorption, temperature-programmed desorption or reaction (TPD or TPR)	
• Heat and mass transfer studies	
• Bulk physical and chemical characterizations	

1.1. Application of surface science techniques for diagnosing poor catalyst performance

1.1.1. Surface lead poisoning of commercial copper catalysts

In the early 1970s, two commercial batches (Lots A and B) of copper catalysts that were otherwise identical by conventional analyses showed dramatically different catalytic activities for the reaction of methyl chloride with silicon metal to produce methylchlorosilanes [1]:

$$x\mathrm{CH_3Cl} + y\mathrm{Si} \xrightarrow[\text{catalyst}]{\text{copper}} \text{methyl chlorosilanes}$$

Known poisons for this reaction are As, Sb, Bi and Pb, while Al, Mg and Si are known promoters that enhance reaction rates to desired products.

Table 2 gives the detailed conventional analyses – both chemical and physical. From a comparison of analyses of "good" and "poor" batches, it is apparent that in comparison with "poor" batch (Lot B), "good" batch (Lot A) has lower surface area, larger particle size, somewhat higher amounts of poisons (Pb) and somewhat lower amounts of promoters like Cu_2O and Fe. Most of these differences are very likely not statistically significant. Thus, these batches should be essentially equivalent in performance. However, the two batches performed very differently.

Auger analyses were performed on both catalysts – taking scans from several randomly chosen areas. Average analysis typical of Lots A and B are give in table 3. It was readily found that the Lot B catalyst of "poor" activity had large amounts of surface Pb, a known catalyst poison ($\sim$10% relative to surface Cu), apparently on top of the surface of Cu, while the "good" activity of Lot A catalyst had much lower surface Pb concentration of 0.033 or 3.3%.

Table 2
Conventional chemical analysis of two commercial copper catalysts.

	Lot A	Lot B
Copper metal	14.60%	18.80%
Cu_2O	48.20%	56.20%
CuO	31.10%	22.00%
Fe	0.98%	1.20%
Mg	0.20%	–
Pb	0.26%	0.20%
Soluble SO_4	1.52%	N.D.
Part. size	6.1 μm	5.5 μm
Surf. area	0.5 m^2/g	0.65 m^2/g
Performance	*Good*	*Poor*

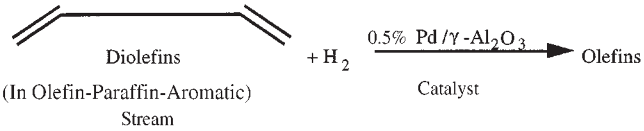
Table 3
Auger surface elemental analysis of copper catalysts.

Element	Surface (at%)	
	Lot A	Lot B
Sulfur	0.88	0.31
Chlorine	1.47	1.49
Lead	1.66	4.89
Carbon	N.D.	trace
Tin	0.33	0.45
Oxygen	38.64	39.30
Iron	2.43	2.23
Copper	50.34	49.16
Magnesium	1.52	0.56
Arsenic	0.55	0.56
Aluminum	1.35	0.71
Silicon	0.83	0.33
Lead/copper ratio	0.033	0.10
Performance	*Good*	*Poor*

The concentration of Pb on the top most surface layer may even be several fold higher, if all the Pb is enriched on the top layer only. The "good" activity catalyst Lot A was also found to contain larger amounts (2–3 fold) of Al, Mg, and Si – which can (and are known to) act as promoters. Additional diagnostic work revealed that the larger amount of surface Pb in "poor" sample is believed to have resulted from the migration of Pb to the grain boundaries of particles during a catalyst roasting step. These findings of surface Pb poison enrichment were also confirmed by ion scattering spectroscopy (ISS) – which is sensitive to top surface atomic layer.

1.1.2. Surface poisoning by iron of a commercial palladium on alumina catalyst

A commercial selective hydrogenation catalyst, 0.5% Pd/γ-Al_2O_3, lost most of its activity during normal plant use [2]. This catalyst is used for the selective hydrogenation of di-olefins in an olefin–aromatic–paraffin-containing liquid stream:



0.5% Pd/γ-Al_2O_3 – 3/16″ cyl. pellets
– $\sim$200 m^2/g
– Cr, Mo, Co promoters

Detailed investigation revealed that the loss in activity appeared to be associated with a change in feedstock that occurred a few days before. Conventional analyses including X-ray fluorescence spectroscopy failed to show significant differences between "fresh" and "spent" catalyst.

Only 0.16% Fe was found on spent catalyst by bulk analyses. This low level of Fe is not necessarily a poison for a $\sim$200 m^2/g support which contains only 0.5% Pd. On opening the reactor, the top of the catalyst bed showed some loose rust particles which were removed, but the catalyst still failed to rejuvenate. Auger analysis of "fresh" and "spent" catalyst (figures 1 and 2) was performed on the outer and inner, cleaved surfaces of 3/16″ (4.76 mm) pel-

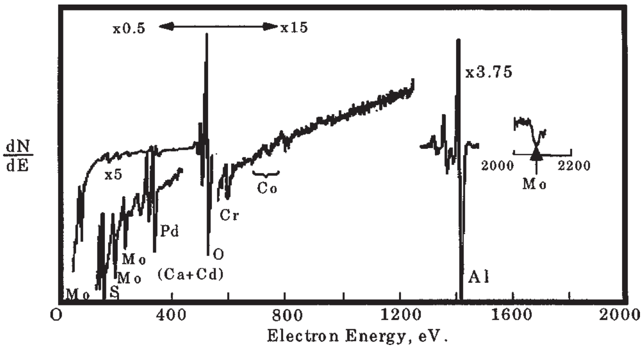


Figure 1. Auger analysis of fresh catalyst (outer surface).

Table 4
Surface atomic percent in Pd/alumina catalyst.

Element	Fresh catalyst		Spent catalyst	
	Dark area (outer surface)	Light area (interior surface)	Dark area (outer surface)	Light area (interior surface)
Mo	3.26	0.16	0.0	trace
S	1.51	0.11	1.40	trace
Ca	0.70	0.11	1.40	0.60
Pd	1.26	0.52	0.32	0.54
O	55.79	56.88	70.16	57.94
Cr	0.75	0.48	0.00	0.00
Fe	trace	0.00	13.68	2.53
Co	0.24	0.19	0.35	trace
Al	36.49	41.55	13.16	38.38 (est.)
	100.00	100.00	100.00	99.99

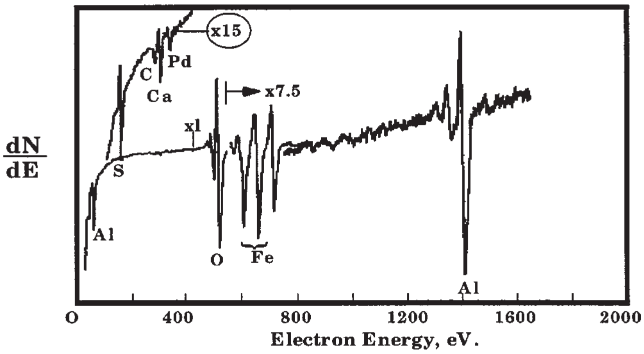


Figure 2. Auger analysis of spent catalyst (outer surface).

lets. Only the outer surface analyses are given here. These figures and data in table 4 clearly show that the "spent" catalyst got deactivated by a surface deposition of Fe (~80% coverage of Pd) on the active Pd surface. Very likely Fe entered the reactor dissolved in the liquid feedstream and deposited selectively onto the Pd catalyst surface. Typically, the iron concentration on the inside pellet surfaces was relatively small, but so was the Pd concentration as well. Hence, it was concluded that iron in a dissolved form in the feedstock was the main culprit responsible for catalyst deactivation by forming an overlayer on active Pd particles.

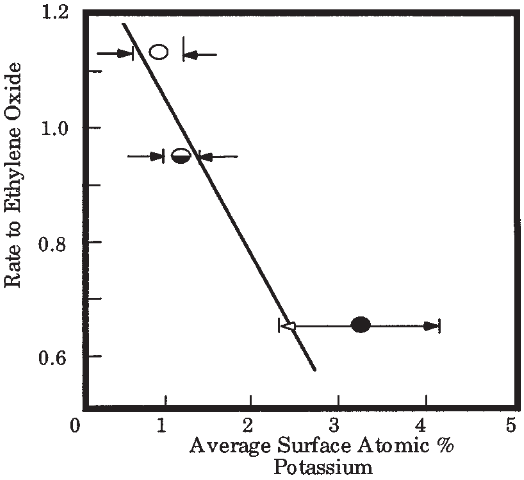


Figure 3. Oxide production as a function of surface potassium concentration.

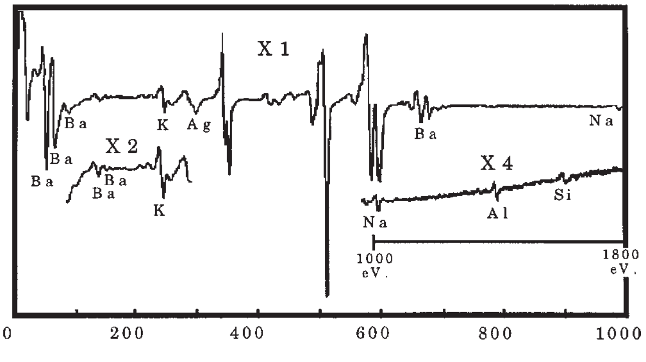


Figure 4. Auger spectrum of ethylene oxide catalyst.

1.1.3. Understanding relative activity performance of three experimental ethylene oxide catalyst batches

In the early development of ethylene oxide catalysts, there were three experimental batches of ethylene oxide catalysts (of same catalyst composition) that were produced under somewhat different preparation conditions that gave dramatically different rates to ethylene oxide production. The rates were different by almost a factor of 2 for the best and the poorest catalysts (figure 3). These three catalysts showed no significant difference in their physical and chemical properties measured by various standard bulk characterization techniques including surface area, chemical composition, etc.

Figure 3 clearly demonstrates the power and utility of the surface analysis techniques in identifying the cause and the relationship of surface composition to performance of these three catalysts. Ethylene oxide rate was found to be inversely proportional to the surface potassium concentration.

In addition, Auger spectrum identified the presence of sodium, aluminum and silicon on the catalyst surface (figure 4). These elements are the components of the catalyst support used in the manufacture of ethylene oxide catalyst support. The surface concentration of these elements also correlates very well with the potassium and, hence,

Table 5
Effects of iron additions on selectivity.

Fe	CO	Efficiency (carbon at%)				
(wt%)	conversion	Total CH_4 + HC + oil	Methanol	Ethanol	Acetaldehyde + acetic acid	C_2 chemicals
0.00	3.1	55.4	0.3	17.0	26.1	43.1
0.05	3.5	52.5	2.8	31.4	13.2	44.7
0.20	3.3	44.2	21.1	29.2	4.5	33.7
0.50	1.8	38.3	35.2	23.7	2.0	25.7
5.00	4.8	76.9	9.4	4.0	7.6	11.6

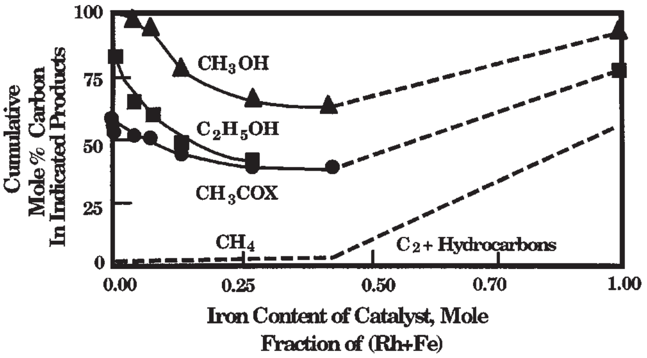


Figure 5. Selectivities of rhodium–iron/silica gel catalysts.

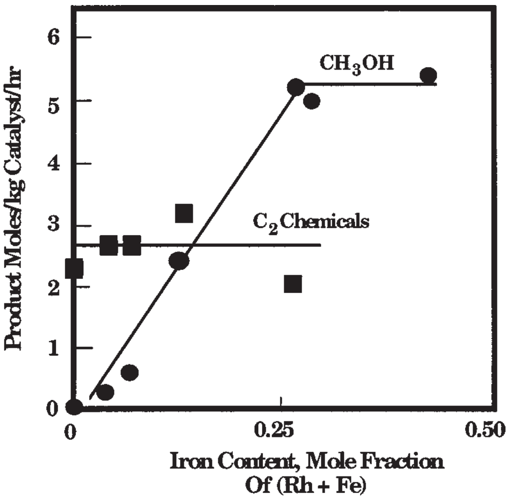


Figure 6. Effects of iron on rates of product formation.

Table 6
Effects of iron additions on rates.

Fe	Initial Rh	Rate (mol/kg h)		
(wt%)	dispersion	CH_4	CH_3OH	C_2 chemicals
0.00	35.4	5.46	0.04	2.29
0.05	30.9	5.75	0.26	2.63
0.10	29.6	6.01	0.59	2.67
0.20	NA	4.72	2.34	3.20
0.50	14.6	5.60	5.19	1.96
5.0	NA	4.36	1.60	0.89

inversely with catalyst activity. Thus, the performance of these three experimental batches was found to vary as a result of the varying amounts of these impurity elements coming out of the support and later getting deposited on the surface of silver and thereby acting as catalyst poisons in excessively large amounts. Some of these elements, i.e., Na and K, are also known to be promoters for ethylene epoxidation when present in near-optimum amounts.

1.2. Application of surface science and fundamental techniques to discovery and development of new catalyst systems and enhanced understanding of commercial catalysts

1.2.1. Importance of surface science in the discovery of new rhodium–iron catalyst

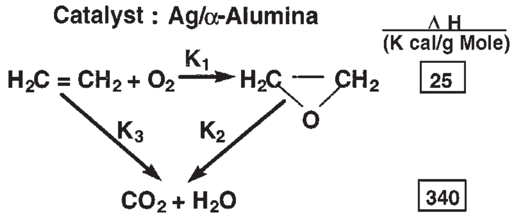
In this example, the discovery of a rhodium–iron catalyst for the selective synthesis of C_2 chemicals (particularly ethanol) from synthesis gas was made possible through the use of surface science techniques in a research project in the mid-70s [3]. While investigating the conversion of synthesis gas to C_2 chemicals, it was observed that selectivity to alcohols (methanol and ethanol) increased as the rhodium/silica gel catalyst operated for a day or so before stabilizing. Depending on the temperature and reaction conditions of each run, this observation was repeatedly made on several occasions. By investigating the surface composition of "fresh" and "used" catalysts, it was quickly found that the "used" catalyst was picking up iron on the surface of rhodium/silica gel catalyst. Incidentally, even in the mid-70s, these surface analyses took only a few hours to perform. Following these observations, several deliberately added iron-containing rhodium/silica gel catalysts were made (figure 5 and table 5) and it was found that both methanol and ethanol selectivity increase on addition of even 0.1 mol fraction of iron to rhodium/silica gel catalysts. However, from a more detailed look at the production rate for methanol and C_2 chemicals it is quite evident (figure 6 and table 6) that methanol rate increases more dramatically up to 0.25 mol fraction iron in the catalyst, while ethanol rate increases relatively modestly.

Another important use of surface science was the early discovery of various impurities, i.e., Fe, Ca, and Na, in silica gels – in so-called high-purity silica gels. This led to the oxalic acid washing of these gels to remove these impurities. This was a key in determining the "true" catalyst and promoter effects. The work report here is all based on oxalic-acid-washed, contaminant-free silica gel.

These observations certainly attest to the power and importance of surface science studies of "fresh" and "reactor-used" catalyst systems. The source of iron, somewhat expectedly, is from the stainless-steel material of construction of the high-pressure autoclave – very likely coming in as iron carbonyl formed in the inlet piping leading to the autoclave as a result of carbon monoxide attack on the stainless steel. The discovery of the Rh–Fe system led us to investigate other mixed metal oxide systems. From these investigations evolved the extremely active (by an order of magnitude) and selective Rh–Mn catalyst system [4].

1.2.2. *Application of surface science and fundamental studies to enhance understanding of EO catalysis*

Ethylene epoxidation catalysts have employed silver as catalyst supported on an inert support like alpha-alumina and silicon carbide, etc. Shown in scheme 1 are the kinetic reactions involved along with heats of reaction for EO synthesis and combustion reactions.



Scheme 1.

The combustion reaction is exothermic by a little more than an order of magnitude in comparison with the synthesis reaction. Promoters/inhibitors can accelerate or inhibit K_1, K_2 and/or K_3 – the three important rate constants in ethylene oxide catalysis.

Surface science and fundamentals have been very valuable in not only diagnosis of catalysts showing different activities though otherwise identical (see section 1.1.3), but also in understanding the mechanism of alkali promoter synergism as well as in breaking the so-called 85.7% efficiency limit.

1.3. *Study of mixed alkali promoter synergism in selective oxidation*

At the International Congress on Catalysis in Budapest, the author presented Union Carbide's results on the synergistic improvement of efficiency in silver catalysts containing mixtures of Cs with other alkalis, i.e., Li, Na, K and Rb [5]. One of the most striking examples of mixed alkali promoter synergism was that disclosed with a Li–Cs binary promoter (table 7). The experimental data with a very high cesium concentration of 0.03 wt% (catalyst 2G), showed that this catalyst was totally inactive. However, addition of 0.03 wt% lithium (catalyst 2E) to this catalyst makes the performance of the binary promoted Li–Cs catalyst about as good as the best observed in the binary mixed alkali promoter systems. However, these results are even more noteworthy, since lithium by itself is not a desirable promoter, since it does not increase the efficiency significantly over an unpromoted silver catalyst (compare no-alkali-promoter catalyst 2F with 2B, table 7). Another noteworthy synergistic system is the binary cesium–potassium promoter system. Key findings are shown in figure 7. It is clearly evident that efficiency of ethylene epoxidation for a cesium-only catalyst when plotted as a function of the alkali content (for 7% Ag catalysts) has a very sharp maximum at 75.5% efficiency. Potassium, on the other hand, has a very broad efficiency maximum of around 74% at nominally 5–6 times the atomic concentration. However, it is noteworthy that mixtures of cesium and potassium have an efficiency optimum that is even higher than the best obtainable from the optimum cesium-only catalyst (best individual alkali promoter). The efficiency for the optimum mixture is little over 1% higher and has a very broad efficiency optimum. Generally, a broad optimum is more desirable than a very sharp narrow optimum, especially in catalyst manufacture. This is an added beneficial feature of the mixed synergistic alkali promoter system.

The mechanism of synergistic alkali promotion is somewhat complex and not fully understood. However, one possible mechanistic explanation is as follows. Cesium and potassium (and/or Rb, Na and Li) salts, when added as promoters to silver catalysts, wind up on both the silver and the support surfaces of alpha-alumina. Alkali ions are well known to tie-up acid sites and reduce EO isomerization and burning. Furthermore, the work of Professor Lambert has shown that bulky cesium ion sits on the surface silver

Table 7
Catalysts containing synergistic combinations of silver, cesium, and lithium.

Catalyst	Ag (wt%)	Cs (wt%)	Li (wt%)	Eff. (%)	Temp. (°C)
2A	12.8	0.0052	0.000	72.6	257
2B	13.1	0.000	0.0030	65.9	257
2C	12.8	0.00521	0.0030	76.0	257
2D	13.1	0.0300	0.0300	72.8	258
2E	13.0	0.0300	0.0300	78.6	258
2F	13.0	0.000	0.000	65.4	263
2G	13.0	0.0300	0.000	Inactive[a]	

[a] No measurable ethylene oxide was produced.

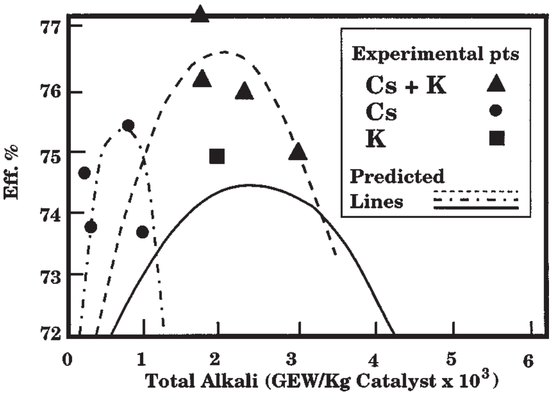
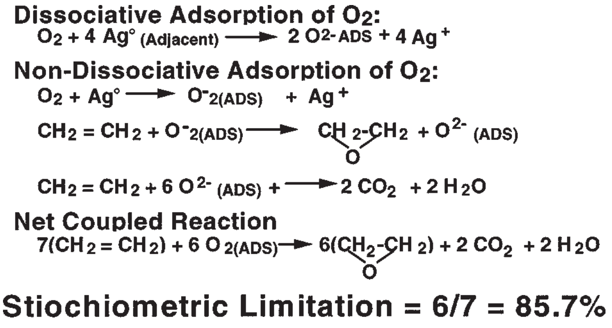


Figure 7. Cs–K synergism at 7% silver.

atoms, while the smaller potassium ion goes into the silver sub-surface [7]. This leaves coordination sites available on a K-promoted catalyst more so than on a Cs-promoted silver catalyst. Smaller ions Na^+, Li^+ and even Rb^+ also would be expected to behave similarly. Thus, Cs is more effective in reducing EO burning than any of the other alkali. However, Cs is modifying the surface much differently than the smaller alkali ions, thereby providing enhanced efficiency in a mixed Cs–alkali synergistic catalyst system over that obtainable with the optimum cesium-only promoter system.

1.4. *Mechanistic efficiency limit of 85.7% has been exceeded!*

This should come as no news to technologists actively working in ethylene oxide catalysis. However, the question of 85.7% mechanistic limit (at times erroneously called the "theoretical limit") has been frequently raised by many scientists. The simple answer is unquestionably "yes". However, it is important to note that surface science and fundamentals played a very important role in discarding this mechanistic limit or barrier [6]. The mechanism, as proposed by Sachtler over a decade ago, is shown in scheme 2.



Scheme 2.

It may come as somewhat of a surprise that in Union Carbide Corporation a similar mechanism was independently proposed by Young and co-workers which predates Sachtler publication by many years. According to Sachtler's mechanism, it is the isolated Ag sites that give rise to the selective O_2^- sites, while the adjacent Ag atom sites give the non-selective O^{2-} sites that lead to combustion products. The mechanistic efficiency limit comes in because of stoichiometric necessity of having to use up ethylene to burn these non-selective O^{2-} sites so as to regenerate isolated Ag^0 sites. However, there are no theoretical or thermodynamic reasons for this limit. For many years this mechanism was accepted and justified since efficiency greater that 85.7% could not be obtained even at zero conversion (by changing space velocity or temperature). It is no longer true for many years, since there have been numerous patents and some publications reporting much higher selectivities into the 90–95%, at good reaction rates [7,8].

In discarding this well known mechanistic limit, important roles were played by both the discoveries by experimentalists [7,8], as well as surface science/fundamental studies. The importance of the latter approach was demonstrated by Professors Lambert, Bell and others [9,10] that a monoatomic oxygen can indeed mechanistically be shown to synthesize as well as burn EO. Hence, if one can poison the undesirable type of oxygens, then it is entirely feasible to reach 100% efficiency. Yet another alternate mechanism the author has proposed is that very high efficiencies approaching 100% can be achieved (even assuming the Sachtler/Young mechanism is valid) if the undesirable O^{2-} can recombine at a high enough rate such that the desirable O_2^- species always dominates on the surface, as highlighted in scheme 3.

$$2\,O_{(ads)} \xrightarrow{r_1} O_{2(ads)}$$
$$E + O_{2(ads)} \xrightarrow{r_2} EO + O_{(ads)}$$
$$r_1 >> r_2$$

Scheme 3.

Finally, the author would like to clarify that at times, many technologists lost sight of the fact that it is a mechanistic limit and incorrectly started to advocate it as a theoretical limit-stifling innovation. Hence, surface science and fundamental studies have played an important role in discarding the mechanistic 85.7% efficiency limit.

2. Summary

In summary, it has been amply shown that:

1. Heterogeneous catalysis has evolved into much more of a "science" than the "art" it used to be only two decades ago. This has been made possible through the application of surface science and fundamental characterization studies.
2. Early development of surface science that had its origin in the late '60s to early '70s was key to quick diagnosis of the cause(s) of catalyst performance in "fresh" as well as "used/abused" catalysts. This indeed resulted in a quick payout for many industrial catalysts.
3. Surface science studies of "fresh" and "used" catalysts were responsible for the discovery of novel catalyst systems, e.g., Rh–Fe and other mixed metal oxide systems for the selective synthesis of C_2 chemicals from synthesis gas.
4. Surface science characterization techniques were key to understanding the variable activity of several batches of ethylene oxide catalysts.
5. The use of surface science techniques in combination with kinetic studies enhances the quality of the information obtained on catalysts. Certainly, these studies contributed significantly to the discovery and understanding of synergistic action of mixed alkali promoters as well

as in removing the 85.7% efficiency limit of a mechanistic proposal for the important commercial epoxidation of ethylene to ethylene oxide.

3. Conclusions

In conclusion, surface science and other new techniques, some in infancy and some yet to be developed, shall play even a greater role in the discovery and development of novel catalysts and catalytic processes for the many industrial and environmental challenges facing the scientific community and the world as we try to make our planet earth a better, healthier, and a safer place to live for centuries and generations to come. Indeed, this is what Responsible Care is all about and all of us at Union Carbide are committed to it.

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