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Carbon–carbon bond formation on metal oxides: from single crystals toward catalysis

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Previous work in our laboratory indicated that carbonyl metathesis of aldehydes can be accomplished as a gas–solid reaction on a reduced $TiO_2(001)$ single crystal under ultrahigh vacuum (UHV). This reaction requires the presence of cations in lower oxidation states on the surface, but does not require Ti^0 as suggested by previous studies in the liquid phase. In the course of attempts to carry out this reaction catalytically, TPD experiments on TiO_2 single crystals and powders were conducted. In addition to the aldolization of acetaldehyde to crotonaldehyde, carbonyl metathesis of acetaldehyde to butene was observed. Benzaldehyde TPD on reduced TiO_2 powder gave substantial amounts of styrene ($PhCH{=}CH_2$) which is most likely formed by disproportionation of stilbene (PhCH=CHPh), the metathesis product observed in single crystal studies. Addition of Ti metal to titania resulted in the formation of large amounts of toluene (by unimolecular reduction) rather than stilbene or styrene (by bimolecular reductive coupling). More importantly, it was possible to form 1-phenylpropene ($PhCH{=}CH{-}CH_3$), a cross-coupling product, by the co-metathesis of benzaldehyde and acetaldehyde on reduced titania, ceria and iron oxide powders during TPD at atmospheric pressure. These studies represent an extension of stoichiometric reactions observed on single crystals in UHV toward novel catalysis. While carbonyl metathesis has still not been accomplished catalytically, its observation during TPD of aldehydes on dihydrogen-reduced oxides has demonstrated the feasibility of each of the steps required to close a catalytic cycle.

Keywords: Reductive coupling; aldehydes; olefins; carbonyl metathesis; metal oxide catalysts

1. Introduction

Efficient and economical carbon–carbon bond formation is one of the triumphs of catalysis. Examples practiced on a large scale include olefin polymerization, methanol carbonylation, olefin hydroformylation and Fischer–Tropsch synthesis. With the exception of the last of these, the above processes conserve

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the atoms of the reactants in the target products, i.e. these reactions can be described as the net assembly of reactants without elimination (waste). As recently pointed out by Trost [1], "methods that involve combining two or more building blocks with any other reactant needed only catalytically constitute the highest degree of atom economy". He further suggests that atom economy, minimizing both raw material consumption and waste production, is a worthy goal for organic synthesis [1]. It is perhaps ironic, given the dominance of catalysis in industrial practice, that its inherent efficiency should have escaped the notice of such a large community. The importance of reactant assembly processes in general, and C–C bond formation in particular, has not been lost on those pursuing principles of catalysis via ultrahigh vacuum surface science approaches, but the direct study of these reactions is generally blocked by thermodynamics. Simple association of reactants must reduce the number of moles from reactants to products, and is disfavored by low pressures. Thus there are only a handful of examples of assembly of C–C bonds in the surface science literature. These generally belong to one of two types, outlined below. Examples of net bimolecular or termolecular assembly reactions on single crystal metal surfaces are cyclizations, including acetylene trimerization to benzene [2,3], and heterocyclization of acetylene or butadiene to thiophene or furan [4,5]. In these cases the enthalpy of formation of the aromatic products is sufficient to overcome the unfavorable entropic considerations above.

Other carbon–carbon bond forming reactions on single crystals have made use of sacrificial substituents, particularly halogen atoms, as a route to formation of surface ligands, e.g., surface alkyls, which then couple to form higher carbon number products [6–8]. While this approach does not preserve the "atom economy" of simple assembly reactions, it does offer a useful entrée to the surface chemistry of important ligands not accessible by other means. It is severely limited, however, in the likelihood of evolution into new catalytic processes. First, it takes advantage of and may require weak bonds to the sacrificial substituents, and this seems counter to the likely trend of ever less reactive feedstocks. Second, to reach the stage of practical catalysis the regeneration, disposal, or (best of all) recycling of the sacrificial product must be addressed.

We have recently reported three different classes of carbon–carbon bond forming reactions on single crystal surfaces of TiO_2 under ultrahigh vacuum conditions [9–11]. While all three formally require the sacrifice of a heteroatom-containing substituent, the nature and potential fate of these substituents is quite different than, for example the halogen-containing side products of alkyl halide coupling. These three reactions are (1) carboxylic acid ketonization, (2) aldol condensation (with dehydration) of aldehydes and (3) metathetical coupling of aldehydes and ketones. The first of these "sacrifices" CO_2 and water, the second water only, and the third donates oxygen atoms to the surface, the reduction of which might generate water, CO_2, or even a desired organic oxidation product. The first two of these reactions have precedents for operation as steady-state catalytic reactions [12–14], the third does not.

We consider below results along the path aimed at making the third of these reactions, the metathetical coupling of carbonyl compounds, catalytic. We consider this example important for three reasons. First, it represents an attempt to turn a stoichiometric reaction, "discovered" in UHV studies, into a new catalytic process. Second, it demonstrates that sacrificial substituents in such reactions need not be weakly bound (the C=O bond strength of aldehydes is typically 175 kcal/mol [15]). Third, it is an example of a class of reactions, metathesis, for which the number of molecules is conserved, and which should therefore be a thermodynamically feasible synthetic tool under UHV conditions.

The metathetical coupling of carbonyl compounds, also known as the McMurry reaction [16,17], was originally observed on $TiCl_3$ in liquid slurries in the presence of stoichiometric amounts of strong reducing agents ($LiAlH_4$, $LiBH_4$, etc.). It involves reductive dimerization of two aldehydes or two ketones on reduced sites to form symmetric olefins, leaving two surface oxygen atoms:

$$2RR'CO + nM^{x+} \rightarrow R'RC{=}CRR' + 2[O] + nM^{(x+4/n)+}.$$

The active site for this reaction proposed from liquid phase studies [16,18] was Ti^0, which would undergo a four electron oxidation to Ti^{4+} in the scheme above. Our investigation of the site requirement for this reaction on TiO_2 single crystal surfaces has clearly demonstrated that Ti^0 sites are not required; all titanium cations in oxidation states less than +4 appear to participate in the reaction [11,19]. This observation bodes well for catalysis, as a smaller cycle of oxidation states would be required than in the mechanism proposed by McMurry and others [16–18]. However, the extrapolation of the reactivity of a single crystal at UHV to a powder at atmospheric pressure is not without difficulties. The formation of other products by consecutive or parallel reactions due to readsorption or diffusion (the surface area ratio between our powder and single crystal samples in TPD experiments is $\approx 10^5$) and the effects of pressure on the kinetics and thermodynamics of bimolecular processes may complicate the "scale-up". As a first step toward making the carbonyl metathesis reaction catalytic, we compare below the results from temperature programmed desorption (TPD) experiments on single crystal and powder samples, and demonstrate in the powder experiments each of the steps (carbonyl metathesis, catalyst reduction) required to complete the catalytic cycle.

2. Experimental

2.1. SINGLE CRYSTAL

TPD experiments were conducted in a Physical Electronics model 548 ultrahigh vacuum chamber described previously [9,20]. The UHV system was equipped with a single pass CMA for AES, LEED optics and quadrupole mass spectrometer. The mass spectrometer was multiplexed with an IBM personal computer used for data acquisition in TPD experiments. TPD and product quantitation procedures were previously described in detail [9,20]. The (001)-oriented TiO_2 single crystal was prepared from a rutile single crystal boule (99.99%, Atomergic Chemetals Corp.). The crystal was aligned to within 0.5° of the (001) plane by the Laue method. The crystal mount and the cleaning procedures were both described elsewhere [9,20]. Acetaldehyde and benzaldehyde (Gold Label, Aldrich) were contained in a glass sample tube attached to a dosing manifold connected to the UHV chamber. Both aldehydes were cleaned by freeze–pump–thaw cycles. The reactant vapors were dosed onto the single crystal through leak valves equipped with stainless steel dosing needles. All TPD results were obtained following saturation exposures of aldehydes ($\approx$ 2–3 L based on uncorrected measurements of the chamber background pressure during direct dosing of the crystal from the dosing needle [21]).

2.2. POWDER

Titania (P25) was purchased from Degussa. CeO_2 was obtained by calcination of Ce nitrate (Aldrich) at 500°C (5 h). A mixed iron(II, III) oxide was purchased from Aldrich. Titanium metal (Aldrich) was mechanically mixed with titania in some experiments in a glove box in order to minimize oxidation of the zerovalent metal. Catalyst samples (100 mg) were placed on a fritted glass disk support within a quartz U-tube reactor. All were reduced prior to use with H_2 at 500°C for 12 h, unless otherwise specified. The flow reactor system was connected to a UTI 100 C mass spectrometer maintained at 10^{-7} Torr by a diffusion pump. The TPD equipment and procedures were described elsewhere [22]. The reduced samples were exposed to aldehydes at their respective vapor pressures at room temperature to saturation. A partial pressure ratio of acetaldehyde to benzaldehyde of ≈ 2 was obtained in cross-coupling experiments by preparing a mixture of benzaldehyde and acetaldehyde, which was transferred into the saturator. After dosing, the oxide sample was purged with He (99.999) for ≈ 1 h before starting the temperature ramp. As many as 50 masses could be sampled every 2–3 s with the multiplexed mass spectrometer.

3. Results

3.1. CARBON–CARBON BOND FORMATION FROM ACETALDEHYDE ON TiO_2(001) SINGLE CRYSTAL SURFACES

Two C–C bond forming reactions were observed during TPD of acetaldehyde on TiO_2(001) single crystals: (1) Aldolization of acetaldehyde to crotonaldehyde

Table 1
Relative yield of products of aldol condensation and carbonyl metathesis on $TiO_2(001)$ single crystal surfaces during TPD

Relative yield	Sputtered	{011}-faceted	{114}-faceted
$[C_4HO+C_4OH]$ [a] ×2 [b]/[acetaldehyde]	0.325	1.10	1.50
[butene]×2/[acetaldehyde]	0.374	0.033	0.051
[stilbene]×2/[benzaldehyde]	5.44	1.8	0.72

[a] C_4HO is $CH_3CH{=}CHCHO$ and C_4OH is $CH_3CH{=}CHCH_2OH$.

[b] Relative yields are ×2 since two molecules of aldehyde were used to form one molecule of product in the cases of both aldolization and carbonyl coupling.

and crotyl alcohol and (2) metathesis to form butene. Aldolization involves the abstraction of a hydrogen atom, in the α position of the aldehyde, by basic surface oxygen atoms on the stoichiometric oxide surface. Both faceted structures of the stoichiometric $TiO_2(001)$ surface (the {001}- and the {114}-faceted structures [23]) were active for this reaction [24]. When these stoichiometric surfaces were reduced by sputtering with argon ions prior to aldehyde adsorption, the aldolization of acetaldehyde dropped dramatically, as shown in table 1. The ratio of the aldolization products ($CH_3CH{=}CHCHO + CH_3CH{=}CHCH_2$-$OH$) to acetaldehyde decreased from 1.5 on the {114}-faceted surface to 0.325 on the sputtered surface. The decrease in aldolization was accompanied by an increase in the formation of butene. Butene can be formed directly by carbonyl metathesis. This reaction, as one might expect, is favored on reduced surfaces. TPD after acetaldehyde adsorption on the sputtered surface demonstrated the formation of high yields of butene with a significant decrease in the crotonaldehyde yields (table 1). The relative yield of butene from acetaldehyde decreased as the prior annealing temperature of the surface was increased. This yield dropped by an order of magnitude from the sputtered surface to the stoichiometric surfaces.

3.2. BENZALDEHYDE REACTION ON $TiO_2(001)$ SINGLE CRYSTAL SURFACES

Benzaldehyde does not contain an α-H atom and is thus incapable of aldolization. TPD after benzaldehyde adsorption at room temperature on the sputtered surface indicated the desorption of high yields of stilbene (PhCH=CHPh, $m/e = 180$). Stilbene is the product formed from the coupling of two molecules of benzaldehyde:

$$2PhCHO \rightarrow PhCH{=}CHPh + 2[O].$$

As a result of this reaction oxygen deposition occurred, as evidenced in XPS measurements by the increase in the $Ti(2p_{3/2})$ core levels corresponding to Ti^{4+} at 459.3 eV and the decrease of the $Ti(2p_{3/2})$ core levels corresponding to Ti^{x+} ($0 < x < 4$) [11]. The ratio of stilbene to benzaldehyde desorbed, as shown in table 1, was 5.44 on the sputtered surface. This was ≈ 15 times higher than that of butene from acetaldehyde. This result is in agreement with the carbonyl coupling results from slurry experiments, where it has generally been observed that aromatic carbonyl compounds couple more efficiently than do their aliphatic counterparts [16]. Based on these single crystal results, benzaldehyde coupling would appear to be the preferred probe reaction, on the basis of both activity and selectivity, for the attempt to extrapolate these results to higher surface area materials and higher pressures.

3.3. BENZALDEHYDE TPD ON REDUCED TITANIA POWDER

Unfortunately, stilbene is a minor product of benzaldehyde reduction on reduced TiO_2 powders. The products desorbing during TPD after benzaldehyde adsorption at room temperature on titania powder are presented in fig. 1.

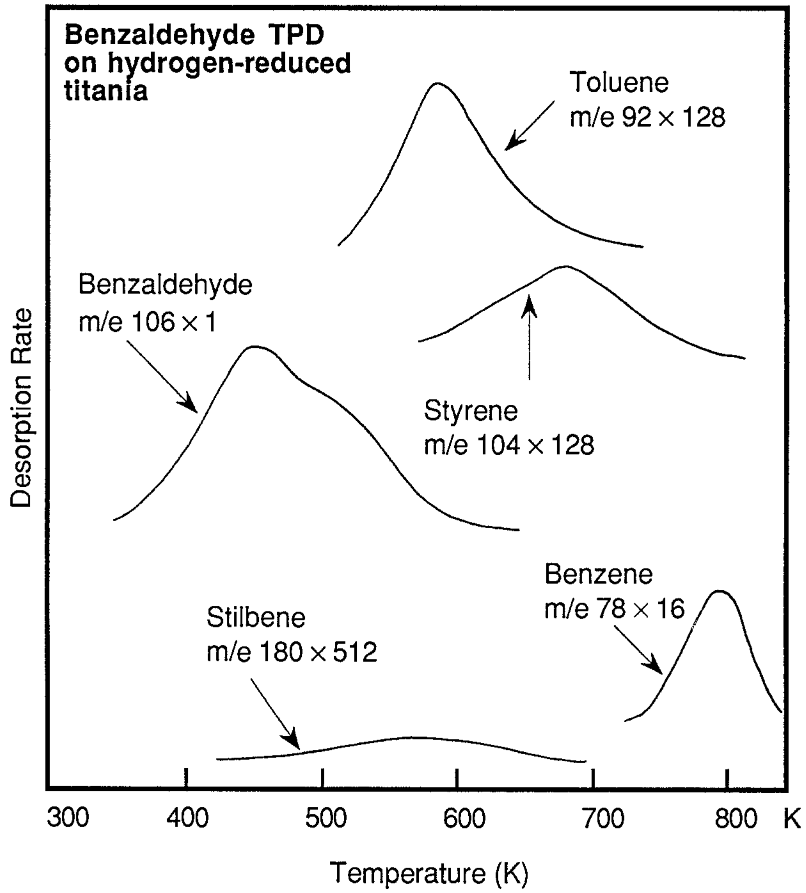

Fig. 1. Temperature programmed desorption (TPD) after benzaldehyde adsorption, at room temperature, on the surface of reduced titania powder.

Stilbene desorption was quite small (approximately 1% of the total carbon-containing species desorbed). Higher yields of toluene, styrene and benzene, in addition to benzaldehyde, were observed. Each product was identified by the ion corresponding to the mass of its parent molecule, as well as its fragmentation pattern, and yields were calculated from the peak area of each product corrected for the mass spectrometer sensitivity. The negligible amounts of stilbene observed represent a major difference between the powder TPD results and those obtained on the reduced $TiO_2(001)$ single crystal surface. This difference may be due to secondary reactions in the powder studies. It has been reported that in the presence of heterogeneous catalytic systems based on tungsten, molybdenum or rhenium oxides, the formation of styrene from stilbene and ethylene is favored [25]. Under the conditions of our powder experiments stilbene formed by carbonyl metathesis may readsorb and decompose to styrene and benzene. Regardless of the mechanism, styrene production requires carbon–carbon bond formation; toluene, in contrast is likely formed by simple reduction.

In order to confirm that the small yield of stilbene was not related to the absence of Ti^0, a mechanical mixture of 20 wt% Ti metal with titania was prepared in glove box, transferred to the reactor, and then reduced under hydrogen at 500°C for 12 h. Stilbene was completely absent from TPD spectra of benzaldehyde on this mixture. An increase in the fractional yields of styrene and benzene was observed, however the toluene yield increased by ≈ 17 times relative to that on the reduced TiO_2 powder. These observations suggest that unimolecular reduction competes with bimolecular reductive coupling, and that very low oxidation states in fact favor the former.

3.4. CROSS COUPLING OF ALDEHYDES ON TiO_2 POWDERS

While stilbene formed from the coupling of two molecules of benzaldehyde was apparently unstable and decomposed to styrene and benzene, the formation of 1-phenylpropene from the cross-coupling of acetaldehyde and benzaldehyde was successfully carried out on reduced TiO_2 powders:

$$\mathrm{PhCHO} + \mathrm{CH_3CHO} \rightarrow \mathrm{PhCH{=}CHCH_3} + 2[\mathrm{O}] .$$

Fig. 2 presents the $m/e = 118$ desorption spectrum corresponding to the parent mass of phenylpropene after adsorption of a mixture of CH_2CHO + PhCHO at room temperature. While the oxidized surface, i.e. the surface heated in oxygen at 773 K then evacuated in He while cooling, did not show formation of phenylpropene (fig. 2a), the surface reduced in hydrogen for 4 h clearly produced cross coupling (fig. 2b). Moreover, the amount of phenylpropene increased considerably when the surface was reduced in hydrogen for longer periods of time at higher temperatures (fig. 2c).

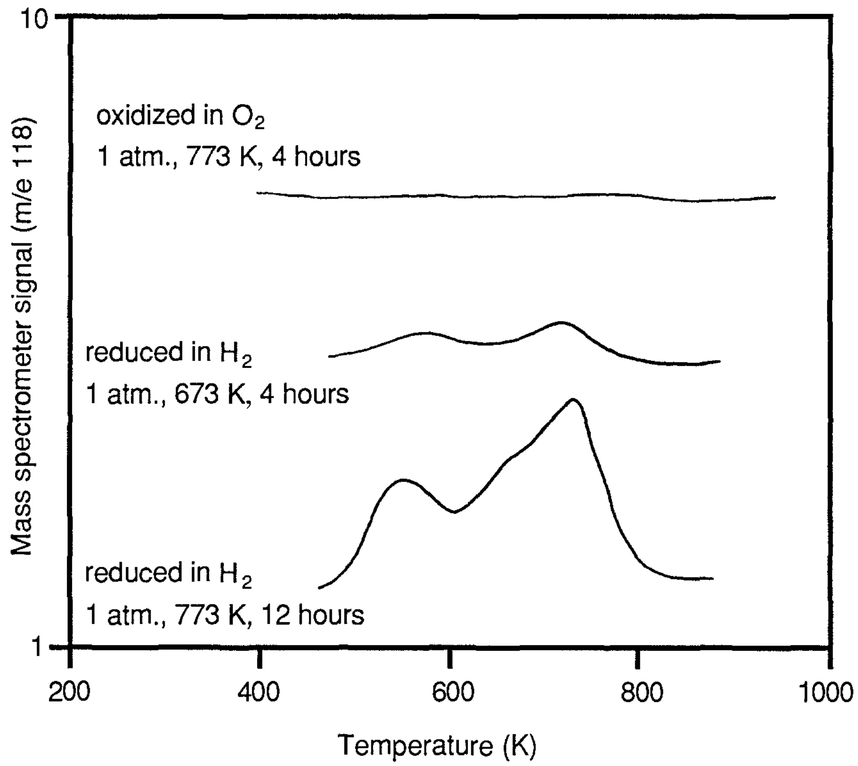

Fig. 2. Phenylpropene desorption during TPD after adsorption of (benzaldehyde + acetaldehyde) at room temperature on the surfaces of oxidized and hydrogen-reduced titania powders.

This reductive cross coupling is not specific to reduced titania. Fig. 3 presents phenylpropene desorption from the reduced (Fe(II, III)) iron oxides (fig. 3b) and reduced ceria (fig. 3c) for the same condition as used for reduced titania. The observation of the metathesis reaction on all three partially reduced oxides clearly indicates that this reaction can occur by gas–solid contact at atmospheric pressure and does not require the presence of zerovalent metals.

4. Discussion

In order for reductive coupling of carbonyl compounds to be carried out as a steady state catalytic process, two reactions must occur: reductive coupling of a pair of aldehydes or ketones (which oxidizes the catalyst), and re-reduction of the catalyst. This hypothetical catalytic cycle is illustrated in fig. 4. The realization of this catalytic process has not yet occurred, but we believe that the work to date has met a number of milestones.

These include:

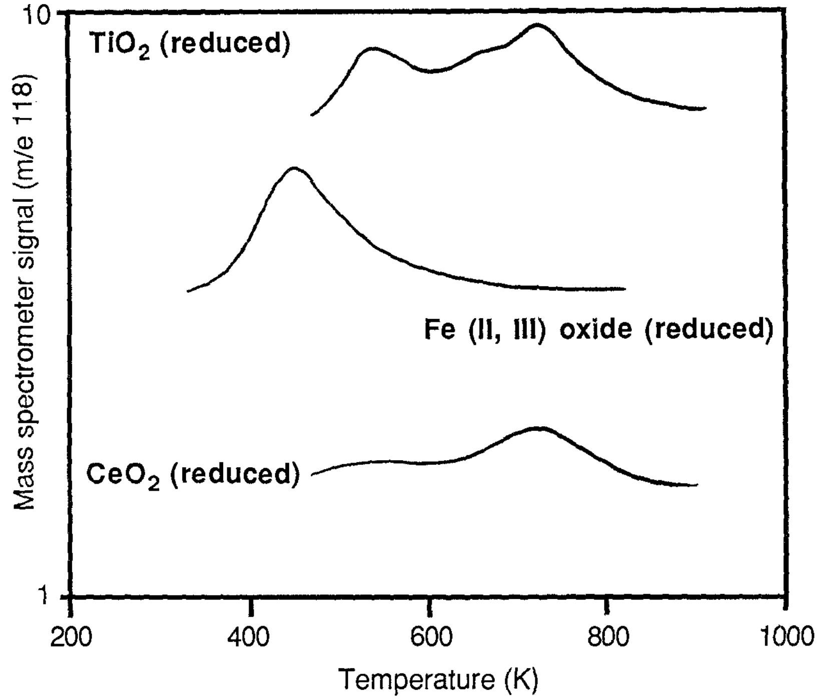

Fig. 3. Phenylpropene desorption during TPD after adsorption of (benzaldehyde + acetaldehyde) at room temperature on the surfaces of reduced titania, iron oxide, and cerium oxide powders.

(1) Demonstration that carbonyl metathesis can be carried out as a gas–solid reaction, and that it does not require a four electron transfer from a single reduced metal center.

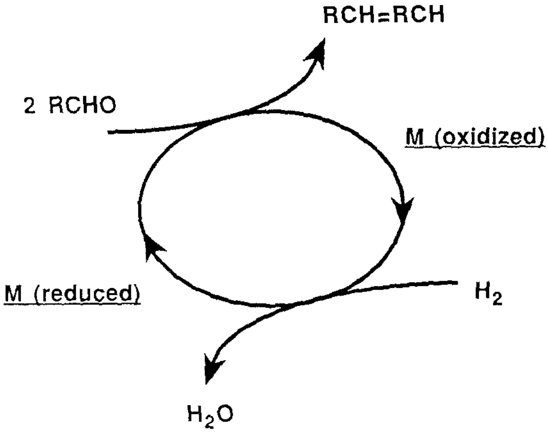

Fig. 4. Hypothetical catalytic cycle for reductive coupling of aldehydes to olefins on the surface of reduced oxides.

(2) Demonstration that this reaction can be "scaled-up" from single crystals in UHV to high surface area materials at ambient pressure. As noted above, this process is not without pitfalls, related primarily to the maintenance of selectivity.

(3) Demonstration that each of the required steps of the hypothetical catalytic cycle can be carried out as individual stoichiometric reactions. TiO_2 can be reduced with dihydrogen in the absence of aldehydes, aldehydes are reductively coupled on the reduced titania in the absence of dihydrogen.

Successful catalysis will require the attainment of three additional milestones:

(4) Better matching of the temperature and other conditions for the carbonyl coupling and catalyst reduction steps.

(5) Demonstration that reductive coupling can be carried out as a catalytic reaction at steady state under conditions where the carbonyl compounds and the reducing agent are co-fed to the catalyst.

(6) Minimization of side reactions, especially unimolecular reduction, which may be enhanced in the presence of dihydrogen.

We are actively pursuing these goals in order to demonstrate that UHV surface science can drive the development of new catalytic processes.

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References

[1] B.M. Trost, Science 254 (1991) 1471.

[2] T.M. Gentle and E.L. Muetteries, J. Phys. Chem. 87 (1983) 2469.

[3] W.T. Tysoe, G.C. Nyberg and R.M. Lambert, J. Chem. Soc. Chem. Commun. (1983) 623.

[4] R.M. Ormerod and R.M. Lambert, Catal. Lett. 6 (1990) 121.

[5] A.J. Gellman, Langmuir 7 (1991) 827.

[6] X.L. Zhou and J.M. White, Catal. Lett. 2 (1989) 375.

[7] B. Roop, Y. Zhou, Z.-M. Lin, C.J. Jenks, M.A. Henderson, K.G. Lloyd, A. Campion and J.M. White, J. Vac. Sci. Tech. A7 (1989) 2121.

[8] C.J. Jenks, J.-L. Lin, C.-M. Chiang, L. Kang, P.S. Leang, T.H. Wentzlaff and B.E. Bent, in: *Structure-Activity and Selectivity Relationships in Heterogeneous Catalysis*, eds. R.K. Grasselli and A.W. Sleight (Elsevier, Amsterdam, 1991) p. 301.

[9] K.S. Kim and M.A. Barteau, J. Catal. 125 (1990) 353.

[10] H. Idriss, K.S. Kim and M.A. Barteau, in: *Structure-Activity and Selectivity Relationships in Heterogeneous Catalysis*, eds. R.K. Grasselli and A.W. Sleight (Elsevier, Amsterdam, 1991) p. 327.

[11] H. Idriss, K. Pierce and M.A. Barteau, J. Am. Chem. Soc. 113 (1991) 715.

[12] R. Swaminathan and J.C. Kuriacose, J. Catal. 16 (1970) 357.

[13] F. Gonzalez, G. Munuera and J.A. Prieto, J. Chem. Soc. Faraday Trans. I 74 (1978) 1517.
[14] US Patent 4,316,990 (1982).
[15] J. McMurry, *Organic Chemistry* (Brooks/Cole, Monterey, 1984) p. 673.
[16] J.E. McMurry, Chem. Rev. 89 (1989) 1513.
[17] B.E. Kahn and R.D. Rieke, Chem. Rev. 88 (1988) 733.
[18] R. Dams, M. Malinowski, I. Westdorp and H. Geise, J. Org. Chem. 47 (1982) 248.
[19] H. Idriss, K. Pierce and M.A. Barteau, to be published.
[20] K.S. Kim and M.A. Barteau, Surf. Sci. 223 (1989) 13.
[21] K.S. Kim and M.A. Barteau, Langmuir 6 (1990) 1485.
[22] K.S. Kim, M.A. Barteau and W.E. Farneth, Langmuir 4 (1988) 533.
[23] L.E. Firment, Surf. Sci. 116 (1982) 205.
[24] H. Idriss, K.S. Kim and M.A. Barteau, J. Catal., submitted.
[25] US Patent 3,965,206 (1976).