

Stabilizing reactive intermediates through site isolation*

Christophe Copéret

*Université de Lyon, Institut de Chimie de Lyon, C2P2 Equipe LCOMS, CNRS,
Université Lyon 1, CPE Lyon 43 Bd du 11 Novembre 1918 69616, Villeurbanne
Cedex, France*

Abstract: This overview describes the reaction of organometallics with oxide surfaces and the formation of highly reactive species. In the case of silica, the surface can be seen as a large siloxy ligand, which helps to stabilize reactive intermediates through site isolations. This is translated into very highly reactive and stable well-defined alkene metathesis catalysts as well as the formation of hydrides species, which display unusual reactivities toward alkanes (e.g., low-temperature hydrogenolysis and metathesis of alkanes). In the case of alumina, it allows the formation of highly reactive, but stable cationic species or masked carbenic species whose structures are unusual by comparison with molecular chemistry.

Keywords: surface; catalysis; organometallic; reactive species; heterogeneous.

INTRODUCTION

Looking for reactivity and stability at the same time seems to be a conundrum, but in fact Nature relies on this concept. For instance, chemical transformation can be performed with unusual high activity and selectivity with enzymes. These systems rely on perfectly designed reaction pockets, which combine molecular recognition properties and site isolation. Thus, for instance, methane is selectively oxidized by molecular oxygen at room temperature into methanol by methane mono-oxygenase (MMO) [1,2]. Similarly, it is possible to make use of metal oxide surfaces to isolate and stabilize reactive sites, and thus in turn generate highly active heterogeneous catalyst. This requires a molecular understanding of surface species via a combined use of advanced spectroscopic and computational studies. Here, we will illustrate this concept with several examples and show that it is possible to understand and tune the surface of oxide materials, silica and alumina, in order to form well-defined systems, to generate highly reactive species and to discover unusual reactivity.

DISCUSSION

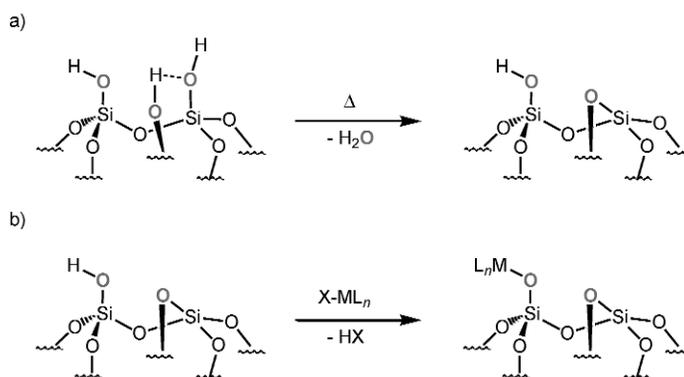
On silica

Generalities

Silica surfaces are mainly composed of silanols and siloxane bridges of various types: silanols can be either isolated, vicinal, or geminal, and siloxane bridges are connected to each other to form cyclic structures of different sizes, typically 8- to 12-membered rings [3–5]. A thermal treatment at elevated

*Paper based on a presentation at the 19th International Conference on Physical Organic Chemistry (ICPOC-19), 13–18 July 2008, Santiago de Compostela, Spain. Other presentations are published in this issue, pp. 571–776.

temperatures leads to the condensation of adjacent silanols yielding water and a siloxane bridge. This process can be used to control the surface OH density, and at 700 °C the silica surface is mainly composed of isolated silanols, which are statistically distributed at an average distance of ca. 1.3 nm. Treatment at higher temperatures further decreases the OH density and leads to the formation of reactive siloxane bridges, and this process is further accompanied by a loss of specific surface area. Using this property, it has been possible to generate well-defined silica-supported systems on silica partially dehydroxylated at 700 °C, $\text{SiO}_{2-(700)}$ by grafting organometallic complexes containing at least one labile ligand $[\text{L}_n\text{M}(\text{X})]$, thus yielding the corresponding monosiloxy complex $[(\equiv\text{SiO})\text{ML}_n]$ along with XH [6]. Overall, this support can be viewed as a large monodentate siloxy ligand (Scheme 1).



Scheme 1 (a) Dehydroxylation process upon thermal treatment. (b) Grafting on isolated silanols.

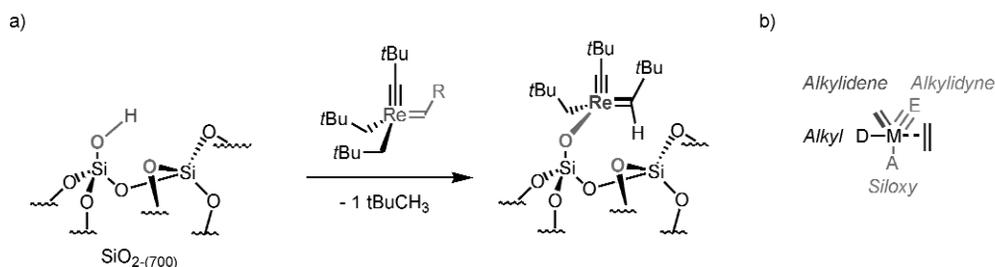
Silica-supported metallocarbene

Alkene metathesis is associated with metallocarbene and metallacyclobutane reaction intermediates for both homogeneous and heterogeneous systems [7–9]. These species have been clearly identified in molecular organometallic chemistry, and the development of better homogeneous catalysts has relied on the preparation of well-defined metallocarbenes as catalyst precursors [10]. In contrast, in the case of classical heterogeneous alkene metathesis catalysts, the catalytic systems are based on group 6 or 7 transition-metal oxide dispersed on oxide supports, and the metallocarbene species have never been directly observed and are probably formed in situ in the presence of the alkene reagent. Additionally, these systems typically have a low number of active sites, which has prevented to obtain a direct evidence for the formation of these intermediates despite extensive studies [11,12]. For instance, for $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$, a highly active system working at room temperature, the number of active sites has been estimated to ca. 2 mol %, the Lewis acidity has been identified to be critical, but the formation of the carbene intermediate is still a matter of debate [13–15]. Thus, one question arises: is it possible to generate a well-defined Re carbene on a surface, active in alkene metathesis?

With this in mind and the accumulated knowledge in the molecular organometallic chemistry of Re [16], the controlled reaction of a Re molecular complex, $[\text{Re}(\equiv\text{C}t\text{Bu})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_2]$ and $\text{SiO}_{2-(700)}$ was attempted, and yielded a well-defined silica-supported Re carbene complex, $[(\equiv\text{SiO})\text{Re}(\equiv\text{C}t\text{Bu})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})]$, (Scheme 2a) as evidenced by mass balance analysis and the use of multiple complementary spectroscopic techniques (IR, solid-state NMR, and extended X-ray absorption fine structure, EXAFS) [17,18]. It is noteworthy that this system turned out to be a highly reactive alkene metathesis heterogeneous catalyst with the following specific properties [17,19,20]:

- well-defined active sites (fast initiation, observation of the stoichiometric amount of cross-metathesis products),
- activities greater than these of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ and comparable to the best homogeneous d^0 catalysts,

- compatibility with functional groups without the need of a co-catalyst in contrast to $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$, and
- unexpected formation of 1-butene as a primary product during the metathesis of propene (98 % selectivity in 2-butenes).



Scheme 2 (a) Grafting of $[\text{Re}(\equiv\text{C}t\text{Bu})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_2]$ on $\text{SiO}_2-(700)$. (b) Proposed model for the greater activity of asymmetric system.

The combined use of experimental and computational studies have shown that the high reactivity of this system was due to the asymmetry at the metal center, that is the presence of both a strong and a weaker σ -donor ligands, the neopentyl and the siloxy groups, respectively (Scheme 2b) [21,22]. Alkene metathesis is best described as a four-step process: coordination, [2+2]-cycloaddition and the corresponding reverse step, cycloreversion, and de-coordination. The asymmetry at the metal center is thus optimal because (1) in the first step (coordination), the activation energy associated to the distortion of the metal fragment from a tetrahedron into a trigonal prism is lowered when the incoming alkene coordinates *trans* to the strong σ -donor ligand while the less σ -donor ligand enters the basal plane containing the alkylidene and the alkylidyne ligands and (2) it forms a less stable metallacyclobutane at the second step ([2+2]-cycloaddition) because the strong σ -donor ligand has to share the basal planes with the two metal-alkyl bonds of the metallacyclobutane.

With the notion that Mo alkylidene complexes are usually more efficient catalysts [9], the development of isoelectronic Mo molecular complex $[\text{Mo}(\equiv\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_2]$ [23] has led to the preparation of corresponding silica-supported system $[(\equiv\text{SiO})\text{Mo}(\equiv\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_2]$, which have been characterized at a molecular level (Scheme 3) [24,25]. It is noteworthy that this sys-

Silica supported		Soluble Model	
$\text{R} = \text{c}-(\text{C}_6\text{H}_9)$			
Spectroscopic data			
^1H NMR $\delta_{\text{Cene-H}}$ (/ppm)	12.05	11.7	
^{13}C NMR $\delta_{\text{Cene-H}}$ (/ppm)	281.2	279	
<i>J</i> -resolved NMR $J_{\text{Cene-H}}$ (/Hz)	110	115	
Metathesis of 1-octene			
Initial rate (min^{-1})	3.6	3.6	
Time to equilibrium (/min)	10	60	

Scheme 3

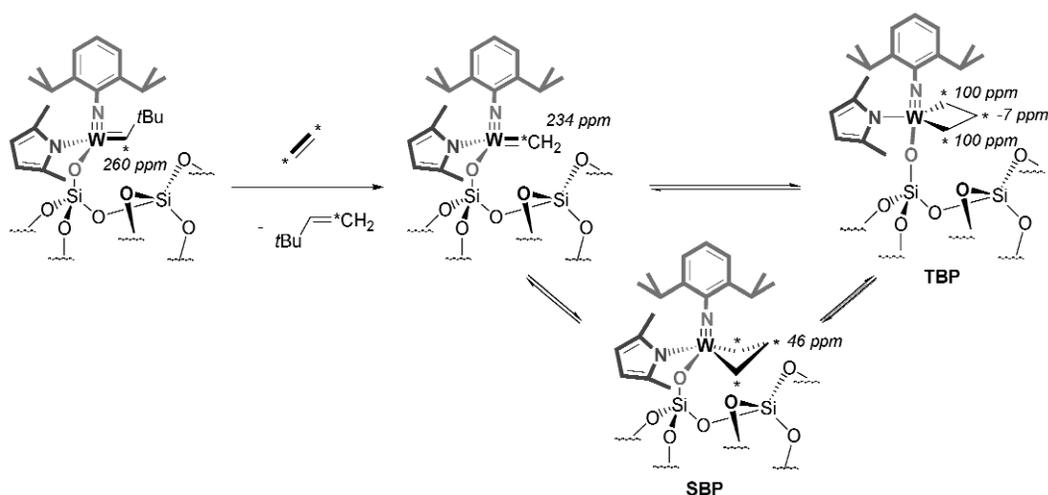
tem displays similar spectroscopic signatures with its molecular equivalent $[(R_3SiO)Mo(=NAr)(=CHtBu)(CH_2tBu)]$, which clearly shows that they are very similar in nature. In fact, they also display similar reactivities as evidenced by similar initial rates in the metathesis of 1-octene. However, the difficulty of achieving full conversion for the molecular complex (longer reaction time) clearly shows that it is not as stable as the silica-supported system, and this shows the stabilization of reactive intermediates on silica surfaces and the advantage of site isolation.

Additionally, it is noteworthy that, on going from Re to Mo, the initial activity is not improved, but that the better selectivity (99.4 %) and stability of the Mo system make it an overall better catalyst (Table 1). In contrast, on going from Mo to W, the selectivity is the same, the stability is greater, but the low rates make the W system not as efficient in terms of overall turnover number (TON) [26]. Further improvement of the catalyst was obtained by replacing the pending neopentyl by amido ligands $[(=SiO)M(=NAr)(=CHtBu)(NR_2)]$, for which initial activities (ca. $\times 3$; with >300 mol/mol/min for Mo), selectivities ($>99.9\%$), and stabilities are greatly improved so that much higher TON can be achieved (138 000) [27,28]. Finally, modifying the imido ligand was also successful in improving the overall performances of the catalytic system, yielding up to 275 000 using a combination of 2,5-dimethylpyrrolyl and adamantylimido ligands.

Table 1 Representative examples of catalyst precursors and their performances (initial activity, overall turnover after 1500 min and selectivity).

Initial rates	120	120	8.4
TON	6000	22 000	6000
Selectivity	96 %	99.4 %	99.4 %
Initial rates	374	320	24
TON	138 000	101 000	25 000
Selectivity	$> 99.9\%$	$> 99.9\%$	$> 99.9\%$
Initial rates	560	780	
TON	135 000	275 000	
Selectivity	$> 99.9\%$	$> 99.9\%$	

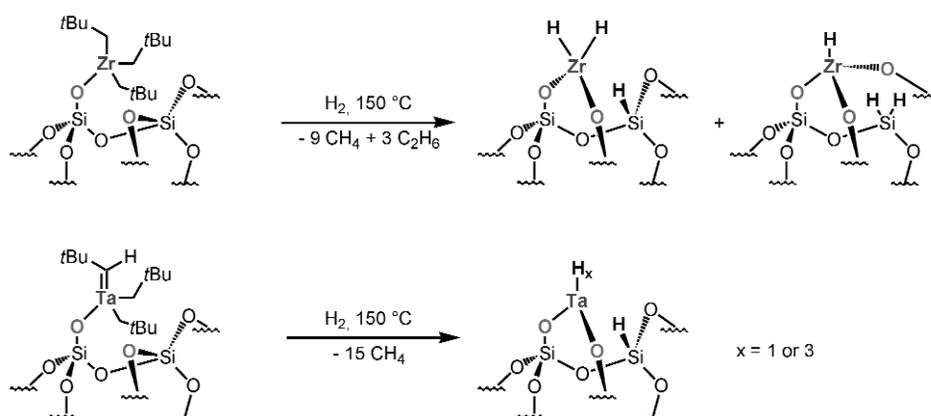
A similar beneficial effect is found upon changing the neopentyl by a 2,5-dimethylpyrrolyl ligand and in the case of the isoelectronic W complexes $[(\equiv\text{SiO})\text{W}(\equiv\text{NAr})(=\text{CH}t\text{Bu})(\text{X})]$ ($\text{X} = \text{CH}_2t\text{Bu}$ vs. NR_2) [26,29] improved initial rate, selectivity, and stability, clearly showing the problem associated with the neopentyl ligand. However, despite a much greater stability than this observed for Mo and Re systems, the rate of metathesis is still slow and the overall performances are lower than those of Mo. This can be associated with the greater stability of the metallacyclobutanes, which can be observed in some cases [30]. In fact, the reaction of $[(\equiv\text{SiO})\text{W}(\equiv\text{NAr})(=\text{CH}t\text{Bu})(\text{NR}_2)]$ with ^{13}C di-labelled ethene gives a mixture of methyldene and metallacyclobutane species (Scheme 4), the latter being present as square-based pyramid and trigonal bipyramid isomers in a roughly one-to-one ratio [29]. It is noteworthy that the catalyst precursor and these intermediates have roughly the same reactivity (rates and stability), which clearly shows, for the first time in heterogeneous catalysis, that the methyldene and the metallacyclobutane species are indeed reaction intermediates of alkene metathesis.



Scheme 4

Silica-supported metal hydrides

Upon treatment of supported perhydrocarbyl complexes under H_2 at high temperatures (ca. 150 °C), these systems evolve into mononuclear metal hydride surface complexes, through successive steps involving (1) the formation of putative hydride siloxy intermediates, $[(\equiv\text{SiO})\text{MH}_x]$, and (2) the reaction of these species with adjacent siloxane bridges leading to the formation of new M–O bonds with the concomitant formation of Si–H surface species (Scheme 5) [31–33]. Because of the heterogeneity of the local environment (silica is amorphous), it typically leads to a mixture of surface species. For instance, $[(\equiv\text{SiO})\text{Zr}(\text{CH}_2t\text{Bu})_3]$ is transformed into a mixture of $[(\equiv\text{SiO})_3\text{Zr}-\text{H}]$ and $[(\equiv\text{SiO})_2\text{Zr}(-\text{H})_2]$, $[\text{Zr}-\text{H}]$ [34], while $[(\equiv\text{SiO})\text{Ta}(\text{CH}_2t\text{Bu})(\text{CH}_2t\text{Bu})_2]$ gives $[(\equiv\text{SiO})_2\text{Ta}-\text{H}_x]$, $[\text{Ta}-\text{H}]$ ($x = 1$ and 3) [35,36].



Scheme 5

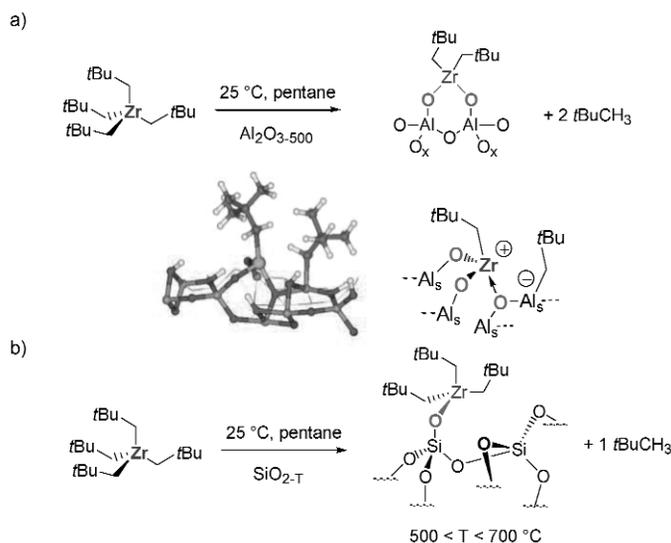
Not surprisingly, the relative unsaturated coordination sphere of these species—formally 8 and 10 electron species—make them highly reactive. In fact, silica-supported Zr and Ta hydrides react catalytically with alkanes at low temperatures as follows (Scheme 6):

- Low-temperature H/D exchange reactions of D_2/CH_4 mixtures [37,38]: this probably takes place for both systems, [Zr–H] and [Ta–H], via a σ -bond metathesis mechanism [39].
- Hydrogenolysis of alkanes [40,41]: while [Ta–H] eventually transforms any acyclic alkanes into methane, [Zr–H] does not hydrogenolyse the C–C bond of ethane, which leads to mixtures of ethane and methane. This is due to the different nature of the surface species and the associated reaction mechanisms of C–C cleavage: α - vs. β -alkyl transfer for [Ta–H] and [Zr–H], respectively.
- Alkane metathesis: at 150 °C, [Ta–H] transforms an alkane into its lower and higher homologs, and, for instance, propane is converted into a mixture of mainly ethane and butane [42]. This reaction involves metallacarbene and alkene intermediates and the key C–C bond formation/cleavage step is in fact a π -bond metathesis [43–46]. More recently, it has been shown that [Zr–H] can also catalyze this reaction, but it leads to different products [47]. For instance, propane is converted into mainly methane, ethane, and 2-methylpropane. It has been proposed that this reaction involves a bis-hydride species and a different mechanism (β -alkyl transfer/insertion processes).
- Cross-metathesis of methane and higher alkanes [48]: this reaction has been discovered using [Ta–H] and probably involves the reverse step of alkane metathesis.
- Non-oxidative coupling of methane [49]: this reaction is highly endothermic, leading to low conversions, and involves the C–H activation of methane on Ta carbene or carbyne intermediates.

must be some more dehydrated unit cell as evidenced by the presence of very reactive Lewis acid sites (Scheme 8b), which react with H_2 and CH_4 via heterolytic splitting, yielding the corresponding Al_S-H and Al_S-CH_3 surface species (Scheme 8c) [56]. In fact, CH_4 reacts only with Al_{III} , while H_2 reacts with both Al_{III} and Al_{IV} .

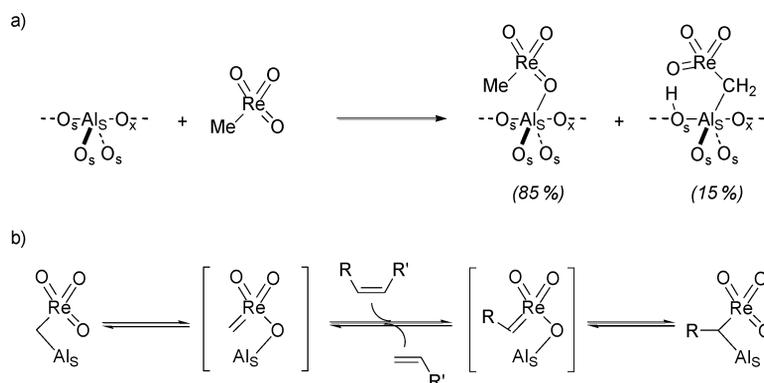
Surface complexes: From cationic species to masked carbenes

The reaction of $[Zr(CH_2tBu)_4]$ with $Al_2O_{3-(500)}$ yields 2 equiv of $tBuCH_3$ per grafted Zr, and the combined use of spectroscopic (IR and solid-state NMR) and computational studies are in agreement with the formation of cationic surface species, which result from, first, a protonolysis of two Zr–C bonds by surface OH groups followed by a transfer of one of the remaining neopentyl ligand onto an adjacent Al_S site (Scheme 9) [57]. This is in contrast to what is observed on $SiO_{2-(700)}$, which yields a neutral species, $[(\equiv SiO)Zr(CH_2tBu)_3]$. These results fully explain the difference of reactivities of alumina vs. silica-supported systems: the former is a highly active polymerization catalyst, while the latter is totally inactive [58–61]. Note, however, that the formation of cationic species on alumina is not general, and, for instance, grafting of $[W(\equiv CtBu)(CH_2tBu)_3]$ on $Al_2O_{3-(500)}$ generates the corresponding monoaluminoxy surface species $[(Al_SO)W(\equiv CtBu)(CH_2tBu)_2]$, which interacts with surrounding OH groups.



Scheme 9 (a) Grafting of $[Zr(CH_2tBu)_4]$ on $Al_2O_{3-(500)}$ and proposed active site for polymerization. (b) Grafting of $[Zr(CH_2tBu)_4]$ on $SiO_{2-(700)}$.

In some cases, grafting does not occur on OH groups, but on the Lewis acid sites. For instance, the reaction of $MeReO_3$ with $Al_2O_{3-(500)}$ yields both coordination complexes $[Al_S(O_3ReMe)]$ and $[Al_S(CH_2ReO_3)]$ species in a 85:15 ratio (Scheme 10a); the latter resulting from the C–H activation of the methyl ligand of $MeReO_3$ onto reactive Al_S-O sites (as already discussed for H_2 and CH_4) [62]. While this system is a highly active alkene metathesis catalyst, no carbenic species have been detected. Additionally, while $[Al_S(O_3ReMe)]$ is not reactive, $[Al_S(CH_2ReO_3)]$ can exchange its methylene ligands, and in fact both $[Al_S(CH_2ReO_3)]$ and $[Al_S(CH(CH_3)ReO_3)]$ have been observed in the metathesis of propene. They probably correspond to the resting states of the catalyst, and the actual propagating carbene species is formed in situ in the presence of alkenes (Scheme 10b) [62,63].



Scheme 10 (a) Grafting of MeReO_3 on $\text{Al}_2\text{O}_{3-(500)}$. (b) Proposed resting states and active sites of $\text{MeReO}_3/\text{Al}_2\text{O}_{3-(500)}$.

CONCLUSION

Oxide surfaces can be indeed exploited to generate highly reactive species. In the case of silica, it is possible to control the OH density through a thermal pretreatment and therefore to guarantee the site isolation of well-defined surface organometallic complexes, which can be used as reactive and stable single-site catalyst precursors. Furthermore, under H_2 , it is also possible to generate mononuclear hydride species, with unusual structure, stability, and reactivity, which allows the catalytically transformation of unactivated alkanes at low temperatures. While the formation of these hydride species on oxide surfaces is limited to early transition metals, which have strong M–O bond, it is possible to extend this approach to late transition metals by tuning the surface of silica with silanes and the formation of strong Si–Ru bonds, which are stable at relative high temperatures. Finally, in the case of alumina, the thermal treatment does not only allow the control of the OH density, but also generates the formation of Lewis acid sites and defect sites. These sites are very reactive: (1) they can abstract the adjacent alkyl group of a supported species to form cationic species and (2) they can even react with H–H or C–H bonds, and in the specific case of MeReO_3 generates at room temperature $\text{Al}_s\text{CH}_2\text{ReO}_3$ species, which is the active site of a highly active alkene metathesis catalyst. It is therefore clear through these examples that surfaces can stabilize reactive species, and we are currently further investigating this concept to discover unusual systems and new reactivities.

REFERENCES

1. J. D. Lipscomb, L. Que Jr. *J. Biol. Inorg. Chem.* **3**, 331 (1998).
2. M.-H. Baik, M. Newcomb, R. A. Friesner, S. J. Lippard. *Chem. Rev.* **103**, 2385 (2003).
3. B. A. Morrow. *Stud. Surf. Sci. Catal.* **57**, A161 (1990).
4. B. A. Morrow, I. D. Gay. *Surf. Sci. Ser.* **90**, 9 (2000).
5. T. Tao, G. E. Maciel. *J. Am. Chem. Soc.* **122**, 3118 (2000).
6. C. Copéret, M. Chabanas, R. P. Saint-Arroman, J.-M. Basset. *Angew. Chem., Int. Ed.* **42**, 156 (2003).
7. Y. Chauvin. *Angew. Chem., Int. Ed.* **45**, 3741 (2006).
8. R. H. Grubbs. *Angew. Chem., Int. Ed.* **45**, 3760 (2006).
9. R. R. Schrock. *Angew. Chem., Int. Ed.* **45**, 3748 (2006).
10. R. R. Schrock. *Chem. Rev.* **102**, 145 (2002).
11. J. C. Mol. *Top. Catal.* **27**, 97 (2004).
12. J. C. Mol. *J. Mol. Catal. A* **213**, 39 (2004).

13. X. Chen, X. Zhang, P. Chen. *Angew. Chem., Int. Ed.* **42**, 3798 (2003).
14. S. Narancic, P. Chen. *Organometallics* **24**, 10 (2005).
15. A. Salameh, C. Copéret, J.-M. Basset, V. P. W. Bohm, M. Roper. *Adv. Synth. Catal.* **349**, 238 (2007).
16. R. Toreki, G. A. Vaughan, R. R. Schrock, W. M. Davis. *J. Am. Chem. Soc.* **115**, 127 (1993).
17. M. Chabanas, A. Baudouin, C. Copéret, J. M. Basset. *J. Am. Chem. Soc.* **123**, 2062 (2001).
18. M. Chabanas, A. Baudouin, C. Copéret, J.-M. Basset, W. Lukens, A. Lesage, S. Hediger, L. Emsley. *J. Am. Chem. Soc.* **125**, 492 (2003).
19. M. Chabanas, C. Copéret, J.-M. Basset. *Eur. J. Chem.* **9**, 971 (2003).
20. A.-M. Leduc, A. Salameh, D. Soulivong, M. Chabanas, J.-M. Basset, C. Copéret, X. Solans-Monfort, E. Clot, O. Eisenstein, V. P. W. Boehm, M. Roeper. *J. Am. Chem. Soc.* **130**, 6288 (2008).
21. X. Solans-Monfort, E. Clot, C. Copéret, O. Eisenstein. *Organometallics* **24**, 1586 (2005).
22. X. Solans-Monfort, E. Clot, C. Copéret, O. Eisenstein. *J. Am. Chem. Soc.* **127**, 14015 (2005).
23. A. Sinha, R. R. Schrock. *Organometallics* **23**, 1643 (2004).
24. F. Blanc, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, A. Lesage, L. Emsley, A. Sinha, R. R. Schrock. *Angew. Chem., Int. Ed.* **45**, 1216 (2006).
25. F. Blanc, A. Salameh, J. Thivolle-Cazat, J.-M. Basset, C. Copéret, A. Sinha, R. R. Schrock. *C. R. Chim.* **11**, 137 (2008).
26. B. Rhers, A. Salameh, A. Baudouin, E. A. Quadrelli, M. Taoufik, C. Copéret, F. Lefebvre, J.-M. Basset, X. Solans-Monfort, O. Eisenstein, W. W. Lukens, L. P. H. Lopez, A. Sinha, R. R. Schrock. *Organometallics* **25**, 3554 (2006).
27. F. Blanc, R. Berthoud, A. Salameh, J.-M. Basset, C. Copéret, R. Singh, R. R. Schrock. *J. Am. Chem. Soc.* **129**, 8434 (2007).
28. F. Blanc, J. Thivolle-Cazat, J.-M. Basset, C. Copéret, A. S. Hock, Z. J. Tonzetich, R. R. Schrock. *J. Am. Chem. Soc.* **129**, 1044 (2007).
29. F. Blanc, R. Berthoud, C. Copéret, A. Lesage, L. Emsley, R. Singh, T. Kreickmann, R. R. Schrock. *Proc. Natl. Acad. Sci. USA* **105**, 12123 (2008).
30. A. Poater, X. Solans-Monfort, E. Clot, C. Copéret, O. Eisenstein. *Dalton Trans.* 3077 (2006).
31. V. A. Zakharov, V. K. Dudchenko, E. Paukstis, L. G. Karakchiev, Y. I. Yermakov. *J. Mol. Catal.* **2**, 421 (1977).
32. Y. I. Yermakov, Y. A. Ryndin, O. S. Alekseev, D. I. Kochubei, V. A. Shmachkov, N. I. Gergert. *J. Mol. Catal.* **49**, 121 (1989).
33. J. Corker, F. Lefebvre, C. Lecuyer, V. Dufaud, F. Quignard, A. Choplin, J. Evans, J.-M. Basset. *Science* **271**, 966 (1996).
34. F. Rataboul, A. Baudouin, C. Thieuleux, L. Veyre, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, A. Lesage, L. Emsley. *J. Am. Chem. Soc.* **126**, 12541 (2004).
35. V. Vidal, A. Theolier, J. Thivolle-Cazat, J.-M. Basset, J. Corker. *J. Am. Chem. Soc.* **118**, 4595 (1996).
36. S. Soignier, M. Taoufik, E. Le Roux, G. Saggio, C. Dablemont, A. Baudouin, F. Lefebvre, A. De Mallmann, J. Thivolle-Cazat, J.-M. Basset, G. Sunley, B. M. Maunders. *Organometallics* **25**, 1569 (2006).
37. G. L. Casty, M. G. Matturro, G. R. Myers, R. P. Reynolds, R. B. Hall. *Organometallics* **20**, 2246 (2001).
38. L. Lefort, C. Copéret, M. Taoufik, J. Thivolle-Cazat, J.-M. Basset. *Chem. Commun.* 663 (2000).
39. C. Copéret, A. Grouiller, M. Basset, H. Chermette. *ChemPhysChem* **4**, 608 (2003).
40. C. Lécuyer, F. Quignard, A. Choplin, D. Olivier, J. M. Basset. *Angew. Chem., Int. Ed.* **30**, 1660 (1991).
41. M. Chabanas, V. Vidal, C. Copéret, J. Thivolle-Cazat, J.-M. Basset. *Angew. Chem., Int. Ed.* **39**, 1962 (2000).
42. V. Vidal, A. Theolier, J. Thivolle-Cazat, J.-M. Basset. *Science* **276**, 99 (1997).

43. E. Le Roux, M. Chabanas, A. Baudouin, A. de Mallmann, C. Copéret, E. A. Quadrelli, J. Thivolle-Cazat, J.-M. Basset, W. Lukens, A. Lesage, L. Emsley, G. J. Sunley. *J. Am. Chem. Soc.* **126**, 13391 (2004).
44. J. Basset, C. Copéret, L. Lefort, B. Maunders, O. Maury, E. Le Roux, G. Saggio, S. Soignier, D. Soulivong, G. Sunley, M. Taoufik, J. Thivolle-Cazat. *J. Am. Chem. Soc.* **127**, 8604 (2005).
45. F. Blanc, C. Copéret, J. Thivolle-Cazat, J.-M. Basset. *Angew. Chem., Int. Ed.* **45**, 6201 (2006).
46. J.-M. Basset, C. Copéret, D. Soulivong, M. Taoufik, J. Thivolle-Cazat. *Angew. Chem., Int. Ed.* **45**, 6082 (2006).
47. C. Thieuleux, A. Maraval, L. Veyre, C. Copéret, D. Soulivong, J.-M. Basset, G. J. Sunley. *Angew. Chem., Int. Ed.* **46**, 2288 (2007).
48. D. Soulivong, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, B. M. Maunders, R. B. A. Pardy, G. J. Sunley. *Angew. Chem., Int. Ed.* **43**, 5366 (2004).
49. D. Soulivong, S. Norsic, M. Taoufik, C. Copéret, J. Thivolle-Cazat, S. Chakka, J.-M. Basset. *J. Am. Chem. Soc.* **130**, 5044 (2008).
50. E. Le Roux, M. Taoufik, C. Copéret, A. de Mallmann, J. Thivolle-Cazat, J.-M. Basset, B. M. Maunders, G. J. Sunley. *Angew. Chem., Int. Ed.* **44**, 6755 (2005).
51. E. Le Roux, M. Taoufik, A. Baudouin, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, B. M. Maunders, G. J. Sunley. *Adv. Synth. Catal.* **349**, 231 (2007).
52. Y. I. Yermakov, B. N. Kuznetsov, V. A. Zakharov. *Stud. Surf. Sci. Catal.* **8**, 1 (1981).
53. (a) R. Berthoud, A. Baudouin, B. Fenet, W. Lukens, K. Pelzer, J.-M. Basset, J.-P. Candy, C. Copéret. *Chem.—Eur. J.* **14**, 3523 (2008); (b) R. Berthoud, P. Delichere, D. Gajan, W. Lukens, P. Pelzer, J.-M. Basset, J. P. Candy, C. Coperet. *J. Catal.* **260**, 387 (2008).
54. P. Raybaud, M. Digne, R. Iftimie, W. Wellens, P. Euzen, H. Toulhoat. *J. Catal.* **201**, 236 (2001).
55. M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat. *J. Catal.* **211**, 1 (2002).
56. J. Joubert, A. Salameh, V. Krakoviack, F. Delbecq, P. Sautet, C. Copéret, J. M. Basset. *J. Phys. Chem. B* **110**, 23944 (2006).
57. J. Joubert, F. Delbecq, P. Sautet, E. Le Roux, M. Taoufik, C. Thieuleux, F. Blanc, C. Copéret, J. Thivolle-Cazat, J.-M. Basset. *J. Am. Chem. Soc.* **128**, 9157 (2006).
58. D. G. H. Ballard. *J. Polym. Sci., Polym. Chem. Ed.* **13**, 2191 (1975).
59. R. L. Burwell Jr. *J. Catal.* **86**, 301 (1984).
60. C. W. Tullock, F. N. Tebbe, R. Mulhaupt, D. W. Ovenall, R. A. Setterquist, S. D. Ittel. *J. Polym. Sci., A* **27**, 3063 (1989).
61. T. J. Marks. *Acc. Chem. Res.* **25**, 57 (1992).
62. A. Salameh, J. Joubert, A. Baudouin, W. Lukens, F. Delbecq, P. Sautet, J. M. Basset, C. Copéret. *Angew. Chem., Int. Ed.* **46**, 3870 (2007).
63. A. Salameh, A. Baudouin, D. Soulivong, V. Boehm, M. Roeper, J.-M. Basset, C. Copéret. *J. Catal.* **253**, 180 (2008).