In Situ NMR Investigations of Heterogeneous Catalysis with Samples Prepared under Standard Reaction Conditions**

James F. Haw*, Patrick W. Goguen, Teng Xu,
Timothy W. Skloss, Weiguo Song, and Zhike Wang

In situ study of reaction mechanisms is a very high priority in heterogeneous catalysis.[1] One of the most successful methods has been magic angle spinning (MAS) solid-state NMR spectroscopy.[2, 3] Unfortunately, standard in situ NMR experiments use reaction conditions that differ in important aspects from those of actual catalysis. Catalytic reactors operate under flow conditions with addition of reactants and removal of volatile products.[4] Contact times between reactants and catalysts typically range from several tenths of a second to several seconds. In most in situ NMR experiments a sealed sample is used, and acquisition of a single ^{13}C NMR spectrum typically requires several hundred seconds. To partly compensate for the discrepancy in time scales, in situ NMR experiments are commonly performed at temperatures 100–150 K below those used for corresponding studies in flow reactors. Although there have been various attempts to make the reaction conditions used with in situ MAS NMR more like those in flow reactors,[5-9] such experiments have not yet been extended to probe irreversible reactions on time scales of a few seconds or less.

Here we report a novel approach to NMR studies of heterogeneous catalysis that provides information on short time scales and under actual reaction conditions. The inspiration for these experiments is the quenching of reactions in solution, which is extensively applied in spectroscopic studies of enzymatic catalysis.[10] Our pulse–quench catalytic reactor (Figure 1) has all of the characteristics of a standard research microreactor including provision for continuous and/or pulse introduction of reactants and gas chromatography (GC) for analysis of volatile products that exit the reactor. The most significant feature of the pulse–quench reactor is the provision for rapidly switching the gas stream that flows over the catalyst bed to cryogenically cooled nitrogen; the catalyst temperature can therefore be reduced very rapidly. Instrumentally, this is achieved through the use of high-speed, pneumatically actuated valves and computer control. The temperature of the catalyst bed is measured by a fast-response thermocouple that is in contact with zeolite pellets on the downstream end of the catalyst bed. The catalyst is cooled by 150 K in the first 170 ms of a quench, and reaches ambient temperature or lower in less than one second. Our experience indicates that the time resolution of in situ experiments with the pulse–quench reactor is 200 ms or less.

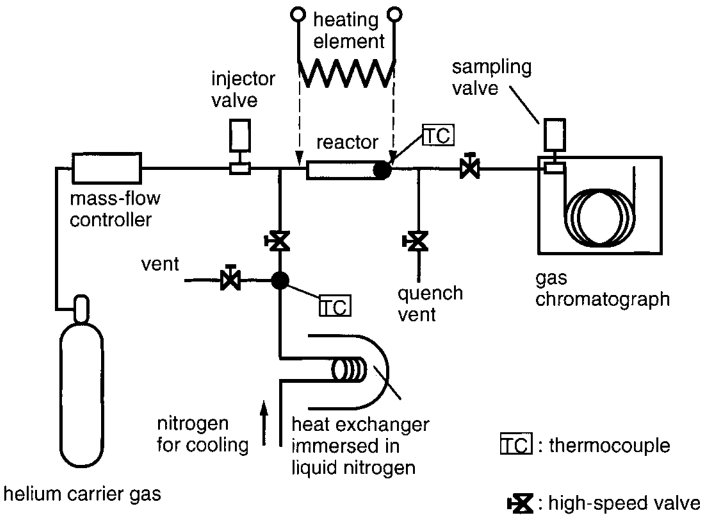


Figure 1. Schematic representation of the pulse–quench reactor used to prepare samples under standard flow-reactor conditions for study by NMR spectroscopy. The gray region indicates the catalyst bed. All valves and the heating element are under computer control.

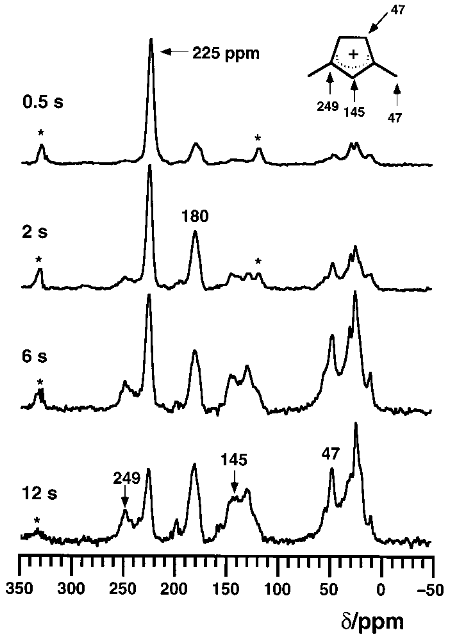


Figure 2. ^{13}C MAS NMR spectra for the reactions of (2-^{13}C)acetone on zeolite HZSM-5 under a flow of He carrier gas. Each spectrum is of a sample prepared by injecting acetone onto a freshly activated catalyst, allowing the reaction to occur for the time indicated at 623 K, and then thermally quenching the catalyst bed to 298 K. The spectra were measured at 77 K. The asterisks denote spinning sidebands.

Figure 2 shows results for the reactions of acetone on the acidic catalyst zeolite HZSM-5 (Figure 2), which we previously studied by conventional in situ NMR techniques in sealed rotors at lower temperatures.[11] We used the pulse–quench reactor to introduce (2-^{13}C)acetone (20.6 μL, two molecules per acid site) onto activated HZSM-5 pellets at 623 K with continuous removal of volatile products in a He flow. Samples were prepared (see Experimental Section) prior to quenching with reaction times ranging from 500 ms to

---

[*] Prof. J. F. Haw, P. W. Goguen, Dr. T. Xu, Dr. T. W. Skloss, W. Song, Z. Wang
The Laboratory for Magnetic Resonance and Molecular Science
Department of Chemistry
Texas A&M University
College Station, TX 77843 (USA)
Fax: (+1) 409-845-7638
E-mail: haw@chemvx.tamu.edu

[**] This work was supported by the National Science Foundation (CHE-9528959).

1433-7851/98/3707-0948 $ 17.50+.50/0

12 s. Acetone ($\delta = 225$, CO) undergoes aldol condensation to 4-hydroxy-4-methylpentan-2-one (observed by gas chromatography (GC) in the product stream), which is dehydrated to 4-methylpent-3-en-2-one on the zeolite. Cracking of acetone dimers produces acetic acid ($\delta = 180$, COOH) and isobutylene (observed by GC). Oligomerization, isomerization, and cracking of hydrocarbons formed from isobutene result in many products that show other signals in the ^{13}C NMR spectra (Figure 2) and the gas chromatogram. Comparison of the spectra in Figure 2 with those from conventional in situ studies of this reaction suggests that there is no loss of acetone or other volatile species during transfer from the reactor to the MAS-NMR rotor.

Figure 2 also shows the development of strong ^{13}C NMR signals at $\delta = 249$, 145 (partially overlapped), and 47 after 2 to 12 s. This unique cluster of chemical shifts is the signature of alkyl-substituted cyclopentenylcarbenium ions; the 1,3-dimethylcylopentenyl cation shown in Figure 2 is a simple example of such a species. This very stable class of carbenium ion was previously observed in an early in situ NMR study of propene oligomerization,[12] but not in conventional in situ studies of acetone chemistry.

We have demonstrated a powerful experimental tool for studying reaction mechanisms of heterogeneous catalysis. The pulse–quench reactor can be used to prepare samples for NMR study under conditions identical to those for microreactor studies. In particular, in situ NMR spectrscopy can now be applied to probe reactions at appreciably higher temperatures and with continuous removal of volatile products from the catalyst. For the first time, NMR studies of irreversible reactions on zeolites have been carried out on time scales shorter than typical catalyst contact times.

Experimental Section

The catalyst was prepared from zeolite powder (Si/Al = 19) mixed with a minimum amount of alumina binder (typically 30 wt %) and extruded into pellets with a diameter of 1 mm. The catalyst (0.25 g, dry weight) was packed into a stainless steel tube (inner diameter 7.5 mm, outer diameter 10 mm) to form a bed that is 8 mm long. The entire length of the tube (5.5 cm) was heated to a controlled temperature with heating tape, and the catalyst was activated in the pulse–quench reactor under a flow of He immediately prior to reaction. The catalyst bed was isolated immediately following the quench and transferred to a MAS rotor, which was sealed in a glovebox at room temperature. The sample was at no time exposed to the atmosphere. Solid-state ^{13}C MAS NMR spectra were measured at 75.4 MHz with cross polarization on a Chemagnetics CMX-300 spectrometer.

Received: October 28, 1997 [Z11090IE]
German version: *Angew. Chem.* **1998**, *110*, 993–995

Keywords: carbocations · heterogeneous catalysis · microreactors · NMR spectroscopy · zeolites

---

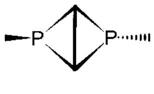
[1] National Research Council, *Catalysis Looks to the Future*, National Academy Press, Washington, DC, **1992**.
[2] J. F. Haw in *NMR Techniques in Catalysis* (Eds.: A. Bell, A. Pines), Marcel Dekker, New York, **1994**.
[3] J. F. Haw, J. B. Nicholas, T. Xu, L. W. Beck, D. B. Ferguson, *Acc. Chem. Res.* **1996**, *29*, 259–267.
[4] B. C. Gates, *Catalytic Chemistry*, Wiley, New York, **1992**.
[5] P. W. Goguen, J. F. Haw, *J. Catal.* **1996**, *161*, 870–872.
[6] M. Hunger, T. Horvath, *J. Chem. Soc. Chem. Commun.* **1995**, 1423–1424.
[7] H. Ernst, T. Freude, T. Mildner, *Chem. Phys. Lett.* **1994**, *229*, 291–296.
[8] D. B. Ferguson, J. F. Haw, *Anal. Chem.* **1995**, *67*, 3342–3348.
[9] T. Mildner, H. Ernst, D. Freude, W. F. Holderich, *J. Am. Chem. Soc.* **1997**, *119*, 4258–4262.
[10] R. C. Bray, *Biochem. J.* **1961**, *81*, 189–193.
[11] T. Xu, E. J. Munson, J. F. Haw, *J. Am. Chem. Soc.* **1994**, *116*, 1962–1972.
[12] J. F. Haw, B. R. Richardson, I. S. Oshiro, N. L. Lazo, J. A. Speed, *J. Am. Chem. Soc.* **1989**, *111*, 2052–2058.

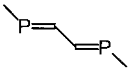
Valence Isomerization in the Solid State: From 1,3-Diphosphacyclobutane-2,4-diyl to 1,2-Dihydro-1,2-diphosphete**

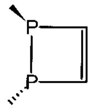
Olaf Schmidt, André Fuchs, Dietrich Gudat, Martin Nieger, Wilfried Hoffbauer, Edgar Niecke,* and Wolfgang W. Schoeller*

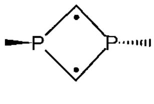
Dedicated to Professor Achim Müller
on the occasion of his 60th birthday

Four-membered heterocycles of the type $P_2C_2R_4$ have attracted a great deal of interest as building blocks in organophosphorus and organometallic chemistry.[1] Within the series 2,4-diphosphabicyclobutane (**I**), 1,4-diphosphabutadiene (**II**), and 1,2-dihydro-1,2-diphosphete (**III**), the bicyclic system is the least and the 1,2-diphosphete the most stable valence isomer.[2] Hence, it appears logical that the most important synthetic route to **III** involves the valence isomerization of 1,4-diphosphabutadienes.[3]


I


II


III


IV

Recently we proved the existence of another valence isomer of **I**–**III**, the biradicaloid 1,3-diphosphacyclobutane-2,4-diyl (**IV**).[4] Although compounds of type **IV** are even less stable than those of type **I**, isolable derivatives do exist owing to the fact that isomerization to **I** by formation of a transannular C–C bond is forbidden according to the Woodward–Hoffmann rules. To gain more insight into the chemistry of

---

[*] Prof. Dr. E. Niecke, Dipl.-Chem. O. Schmidt, Dr. A. Fuchs,
Priv.-Doz. Dr. D. Gudat, Dr. M. Nieger, Dr. W. Hoffbauer
Institut für Anorganische Chemie der Universität
D-53121 Bonn (Germany)
Fax: (+49)228-735-327

Prof. Dr. W. W. Schoeller
Fakultät für Chemie der Universität
D-33501 Bielefeld (Germany)

[**] We thank the Deutsche Forschungsgemeinschaft (SFB 334) and the Fonds der Chemischen Industrie for financal support, and Dr. W. Hoffbauer for recording the solid-state NMR spectra.