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In Situ Observation of Transient Reaction Phenomena Occurring on Zeolite Catalysts with the Aid of Positron Emission Profiling

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Zeolites are widely used in the petroleum refining industry as solid acid catalysts to convert hydrocarbons into gasoline products of high octane number by isomerization or by cracking reactions. Stable operation at mild reaction conditions is made possible by the addition of noble metals to acidic zeolites. For example, after addition of platinum to the zeolite H-mordenite n-hexane isomerizes to its structural isomers at 240 °C rather than at 400 °C. The state of the platinum in the working catalyst and the distribution profiles of the reactive surface intermediates are strongly dependent on pretreatment and reaction conditions. Thus in situ measurement is necessary.

Positron emission tomography (PET) is a noninvasive, in situ, radiochemical imaging technique used in nuclear medicine to monitor biomedical functions. This technique has recently been applied to systems in engineering research by Bridgwater et al. to study mechanical mixing within a powder mixer. In addition we have shown that this technique can be used to provide information on the concentration distributions of reactants and products as a function of time and position along the reactor bed during the CO oxidation under steady-state conditions. This information is essential for the development of kinetic models describing the rates of elementary reaction steps.
We have since developed a new detection system for positron emission profiling (PEP), which is a one-dimensional analogue to PET. This study is the first to measure in situ reaction profiles under transient conditions.

Due to the short half-life of $^{14}$C (20.3 min) the positron-emitting molecules must be produced on-site with a cyclotron in combination with chemical processing. We have developed a unique route for on-line synthesis of $^{14}$CH$_2$CH$_2$H$_{2n-1}$ ($3 \leq n \leq 6$) based on our method for the homologation of olefins by $^{14}$CO.$^{11}$ An optimized vanadium-promoted Ru/SiO$_2$ system is used to adsorb CO and 1-pentene. Secondly, the mixture of hydrocarbons formed by hydrogenative desorption at 110°C is separated by a technique of freezing, flash heating, and gas chromatography. Finally, a pulse that contains approximately $2 \times 10^{-6}$ moles of nonlabeled n-hexane and 1 MBq of n-$^{14}$CH$_2$CH$_2$H$_{11}$ (about $10^{-12}$ mol) can be injected into the feed stream of the zeolite-containing, solid-bed reactor positioned in a newly developed PEP detection system.

The PEP system is based on two banks of nine detection elements. Each element consists of a specially shaped and polished Bi$_2$Ge$_3$O$_{12}$ scintillation crystal and a slit-shaped photomultiplier. The system is optimized for imaging in one dimension; the detector thus has a faster sampling time (0.5 s) and a higher sensitivity than state-of-the-art research PET cameras whilst maintaining a resolution of 2.7 mm.$^{[9]}$ Reactor bed lengths varying between 4 and 50 cm can be handled.

Figure 1a shows the PEP image obtained after a pulse of labeled n-hexane was injected into a feed stream of n-hexane/hydrogen flowing through a bed of Pt/H-mordenite. The catalytic reactor was operating under steady-state conditions at 230°C, quickly (the near horizontal band), and some remain on the catalyst surface. Analysis of the radio-labeled reaction products by trapping and subsequent GC separation with NaI scintillation detection revealed light alkanes between C$_1$ and C$_4$.

When one uses a Pt/H-mordenite catalyst that was first used in the steady-state hydroisomerization of n-hexane at 230°C, very different results were obtained. The reaction was interrupted by stopping the hexane feed, and after 5 minutes the labeled n-hexane was again injected into the hydrogen stream (see Fig. 1c). In contrast to the profile shown in Figure 1b, an image similar to that shown in Figure 1a was obtained. The differences in the observed retention times between (a) and (c) is due to differences in the number of adsorption sites available.$^{[13]}$ Analysis of the trapped products revealed only C$_6$ hydrocarbons.

Apparenty, the undesirable metal cracking reactions that occur on freshly reduced platinum are suppressed by “preconditioning” the surface of the platinum metal by the hydroisomerization reaction. As concluded from Figure 1b this “preconditioning” involves the deposition of a carbonaceous overlayer that prevents cracking of the hexane. As we will see from the experiments reported in Figure 2, the only function of the “preconditioned” platinum surface is to dehydrogenate hexane to hexene or to hydrogenate olefins. This result is consistent with the conclusions of others who work on model transition metal catalysts: hydrogenation and dehydrogenation reactions occur on a surface covered by a carbonaceous overlayer.$^{[14-16]}$ The effect of the carbonaceous overlayer may be to restrict the surface ensemble size available to the cracking reaction; the hydrogenation and dehydrogenation reactions are less structure-sensitive.$^{[17]}$

The hydroisomerization reaction must be carried out in the presence of hydrogen in order to avoid loss of activity through “deactivation”. The following type of experiments illustrate the details of deactivation of the acid sites. Steady-state hydroisomerization of n-hexane over Pt/H-mordenite at 240°C is interrupted by replacing the feed with flowing helium. After 5 minutes labeled n-hexane is injected into the helium stream (Fig. 2a). A rapid reaction near the beginning of the reactor bed forms products that remain strongly adsorbed. Only a small portion of the pulse passes through the bed. Radio-GC analysis of this fraction revealed mainly unchanged C$_6$ hydrocarbons with small amounts of C$_5$ and C$_7$ hydrocarbons. All of the labeled products remaining on the surface could be removed if

which converts 19% of hexane into structural isomers. Since these isomers have similar adsorption/desorption and diffusion properties on H-mordenite to n-hexane, the pulse continues through the reactor in a manner similar to that of n-hexane on the zeolite alone.$^{[13]}$

A very different behavior is observed if the platinum metal is freshly reduced. After reduction by H$_2$ at 400°C, the temperature was lowered to 230°C, and a pulse of labeled n-hexane was then injected into a hydrogen stream. The pulse adsorbs strongly near the beginning of the reactor bed and reacts rapidly (Fig. 1b). Some of the radio-labeled species exit the reactor very

![Fig. 1. Positron emission profiling (PEP) images of n-$^{14}$CH$_2$CH$_2$H$_{11}$ pulse experiments on a Pt/H-mordenite catalyst bed (t = residence time). The color scale indicates the concentration of the $^{14}$C label: the brighter the color, the higher the concentration. Labeled samples were injected into the feed streams (1 atm; 150 nL min$^{-1}$ total flow rate). a) The reactor was operating under steady-state conditions at 230°C with a feed mixture of n-hexane/H$_2$ (1/28 mol). b) $^{14}$C-n-hexane pulse in hydrogen over the catalyst with freshly reduced Pt at 230°C. c) $^{14}$C-n-hexane pulse in hydrogen over the catalyst, which was previously used in the hydroisomerization reaction at 230°C.

![Fig. 2. PEP images of separate n-$^{14}$CH$_2$CH$_2$H$_{11}$ pulse experiments on a Pt/H-mordenite catalyst. The hydroisomerization reaction under steady-state conditions was interrupted 5 min prior to injection by switching to a flow of hydrogen. Injection was then made into a stream of helium (75 nL min$^{-1}$) at 240°C. a) The majority of n-hexane is dehydrogenated to hexene on the Pt surface, and the hexene isomers remain strongly adsorbed to acidic sites in the absence of hydrogen. b) Conditions similar to those for (a) but at injection made at 230°C.
The temperature was increased to 400 °C in a stream of hydrogen. Analysis of this fraction revealed mainly C₆ hydrocarbons with small amounts of C₅, C₇, C₈, and C₉ species. This shows that n-hexane is rapidly dehydrogenated by platinum, and the resulting hexene molecules are adsorbed on the acid sites of the zeolite. In the absence of hydrogen they can not be rehydrogenated and therefore remain adsorbed, poisoning the sites for subsequent reaction. Dimerization or further oligomerization reactions do not occur to a great extent, since no large fraction of higher and lower hydrocarbons was found. The PEP image shown in Figure 2b was obtained when the above reaction was repeated at 230 °C. Comparison with Figure 2a reveals that a greater portion of the hexane pulse passes unchanged through the bed; the lower reaction rate is due to the lower reaction temperature.

These experiments under transient conditions provide the first direct demonstration of the so-called bifunctional reaction mechanism[18, 19] proposed for alkane hydroisomerisation. The platinum promoter acts as an alkane dehydrogenation and an alkene hydrogenation catalyst. The zeolitic protons protonate the alkanes, which then, as predicted by theory,[20, 21] remain strongly adsorbed (enthalpy of protonation ≈ 180 ± 20 kJ mol⁻¹).

The protonated alkenes isomerize. From steady-state experiments we deduced an activation energy of isomerization to isohexane of approximately 135 ± 20 kJ mol⁻¹[22]. The protonated, isomerized intermediate remains strongly adsorbed. Further reaction only proceeds in the presence of gaseous hydrogen. Desorbing alkenes then will be hydrogenated by platinum to form the product alkanes. This is consistent with previous studies, which showed that the reaction has a positive order in hydrogen partial pressure in the absence of platinum.[23]

In summary a technique has been developed that enables the analysis of reactant concentration profiles as a function of time. Radiochemical PEP measurements with a great variety of alkanes extensively used in practice are now possible under a wide range of practical reaction conditions. Here we have demonstrated the use of the technique to probe the elementary reaction steps in the hydroisomerization of hexane.

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The Titanium(IV)-Catalyzed Epoxidation of Alkenes by tert-Alkyl Hydroperoxides**


Ever since it was reported that titaniumsilicates, such as TS-1 synthesized by the company Enichem,[24] could catalytically and selectively oxidize certain organic compounds in the presence of H₂O₂ (for example, phenol to hydroquinone[25] and propene to propene oxide[26]), there has been considerable interest in other low-temperature selective oxidations with various kinds of TiIV-containing siliceous microporous catalysts.[27] Corma et al. have demonstrated the catalyst merit of using larger pore microporous materials,[28] such as TiIV-containing β-zeolite, and the commercially available tert-buty1 hydroperoxide (TBHP) as a sacrificial oxidant.

Interest in TiIV-catalyzed epoxidations of alkenes has recently intensified, because TiIV-containing mesoporous MCM41 silicas with their larger pore apertures (typically 30 Å) are capable of oxidizing relatively bulky reactants.[6, 7] Two distinct kinds of TiIV-modified MCM41 epoxidation catalysts have been described. The first (TiCMCM41) accommodates the titanium ions (identified along with distances between Ti and the 0 atoms attached to silicon by X-ray absorption spectroscopy[6]) within the walls of the mesoporous silica. The second (TiO-MCM41) has the tetra-coordinated TiIV ions grafted onto the inner surfaces of the mesoporous host and is formed from a titanocene dichloride precursor as recently described by Maschmeyer et al.[12, 19] TiO-MCM41 reported here (Si:Ti ratio of 1:0.058) was synthesized from Ti(OPr)₄, which was incorporated into the MCM41 synthesis gel, according to the procedure of Rey et al.[110] The Ti/MCM41 used in this study had a Si:Ti ratio of 1:0.041.

Sheldon and co-workers have concluded that alkyl hydroperoxide catalyzed epoxidation of olefins occurs by a heterolytic mechanism in the presence of TiO₂-SiO₂ mixed-oxide cata-

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