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# Diisopropyl ether one-step generation from acetone-rich feedstocks

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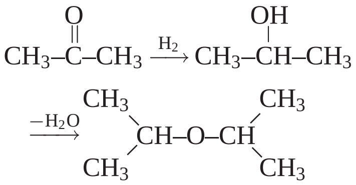
A one-step integrated process for the generation of the high-octane fuel ether, diisopropyl ether (DIPE), from acetone-rich feedstocks has been demonstrated. Three continuous, downflow, reactor configurations have been considered, including a two-bed catalyst design separated by inerts, gradient multicatalyst combinations, and an integrated two-zone layout with differing catalyst compositions. The bifunctional catalysts have both hydrogenation and etherification/dehydration capabilities and may comprise groups IB, VIB, and VIII metals incorporated into acidic, large and medium-pore zeolites, groups III or IV metal oxides, as well as heteropoly acid structures. DIPE syntheses are typically conducted at 100–165 °C, under hydrogen pressure. The gradient reactor design, with careful choice of hydrogenation and etherification catalysts, allows DIPE to be generated in high selectivity and productivity.

**Keywords:** diisopropyl ether, acetone, etherification, hydrogenation

## 1. Introduction

In previous publications in this series, we have demonstrated the synthesis of diisopropyl ether (DIPE) [1] (as well as alternative routes to isopropyl *tert*-butyl ether [2] and methyl *tert*-butyl ether [3]) from acetone-rich feed streams involving initial hydrogenation of the acetone fraction to isopropanol (IPA), followed by dehydration of the intermediate IPA to DIPE:

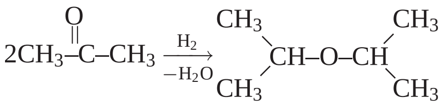


$$CH_3\text{–}\overset{\overset{O}{\|}}{C}\text{–}CH_3 \xrightarrow{H_2} CH_3\text{–}\overset{\overset{OH}{|}}{C}H\text{–}CH_3 \xrightarrow{-H_2O} (CH_3)_2CH\text{–}O\text{–}CH(CH_3)_2 \qquad (1)$$

Such a two-stage DIPE process normally requires the interstage separation of hydrogen in order for the esterification catalyst to remain effective, yet removal of said hydrogen may cause any co-produced propylene to oligomerize in the etherification unit. In a commercial process this could significantly increase the costs associated with DIPE purification, as well as necessitate frequent catalyst regeneration.

Here we describe, for the first time, procedures for the one-step conversion of acetone-rich feed streams to DIPE using novel, dual-functional, catalyst systems that incorporate both ketone hydrogenation capabilities in addition to dehydration activity. DIPE one-step synthesis has been demonstrated in a continuous unit equipment using three types of catalyst bed/reactor configurations.

The excellent octane blending properties of DIPE for reformulated gasoline are now well established [4,5]. Alternative routes to diisopropyl ether synthesis include propene hydration followed by IPA dehydration – pioneered by Mobil Corp. [6]. With low cost, crude acetone feedstocks as the basic building block, we believe that this new, one-step, route to DIPE (equation (2)) enjoys very attractive, long-term, economics [7].



$$2CH_3\text{–}\overset{\overset{O}{\|}}{C}\text{–}CH_3 \xrightarrow[-H_2O]{H_2} (CH_3)_2CH\text{–}O\text{–}CH(CH_3)_2 \qquad (2)$$

## 2. Experimental

### 2.1. Catalyst screening

All catalyst screening studies were performed in continuous microreactor units operated in the downflow configuration. For experiments conducted using a two-bed catalyst design, each bed comprised 4 $cm^3$ of catalyst having the same composition, separated by 4 $cm^3$ of inert material. Internal thermocouples were positioned at the bottom of each catalyst bed. The acetone-rich liquid feed was charged to the unit using a high-pressure pump and hydrogen was metered through a mass flow controller. Liquid products were collected in a chilled receiver at $-15$ °C and 20 bar, and analyzed by gas–liquid chromatography (GC).

The catalyst beds were activated by heating slowly to 315 °C over a period of 6 h, under flowing nitrogen, at 5 bar. The unit pressure was then raised to 35 bar with hydrogen and the catalyst bed held at 315 °C for 10 h under flowing hydrogen. The bed was then allowed to cool to $<90$ °C, and crude (97%) acetone charged to the unit at 1.5 liquid hourly space velocity (LHSV), based upon the total catalyst volume. The hydrogen flow rate was adjusted to give a hydrogen to acetone molar feed ratio of ca. 5 : 1, at a total unit pressure of 35 bar. The typical operating temperature range was 100–165 °C.

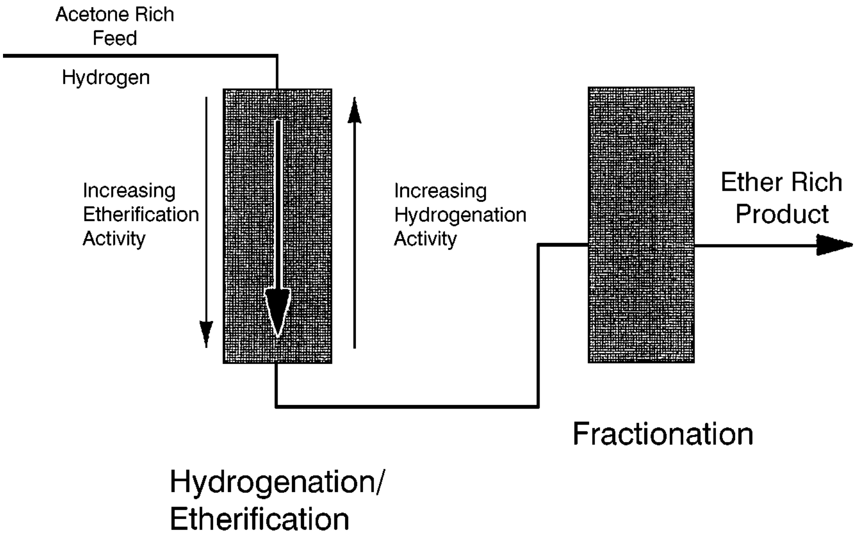


Figure 1. Gradient reactor configuration, three catalysts.

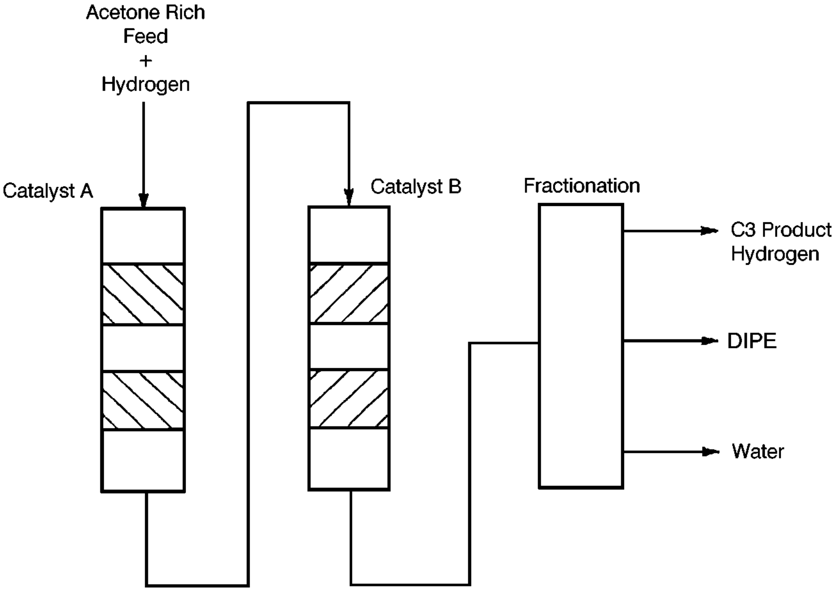


Figure 2. Two-zone reactor configuration, two catalysts.

For the gradient reactor studies the microreactor unit consisted of two reactors in series separated by a quench zone. The top reactor was loaded with 4 $cm^3$ of catalyst with the highest hydrogenation activity and the lowest dehydration/etherification activity. This first reactor was operated adiabatically. The second reactor had two catalyst beds of 4 $cm^3$ each separated by a 4 $cm^3$ bed of inert material. The top bed in the second reactor contained a catalyst having an intermediate hydrogenation and etherification activity. The bottom bed in the second reactor contained the catalyst with the highest dehydration/etherification activity. The total catalyst charge was 12 $cm^3$. A typical gradient reactor configuration is illustrated in figure 1.

For the integrated, two-zone reactor design with differing catalyst compositions, figure 2 illustrates the unit setup. Here the top and bottom catalyst beds (A and B) are of different composition.

## *2.2. Catalyst preparations*

### *2.2.1. Nickel/copper on 10% Beta zeolite*

To 50 g of 10% $\beta$-zeolite/90% alumina support was added a 40 $cm^3$ aqueous solution containing 51 g of nickel nitrate hexahydrate, 5.4 g of copper nitrate hemipentahydrate, and the minimum amount of distilled water necessary to dissolve said salts. The impregnated support was dried at 120 °C for 2 h and then calcined at 315 °C for 4 h. The calcined support was impregnated again with a 37 $cm^3$ aqueous solution containing 51 g of nickel nitrate hexahydrate, 5.4 g of copper nitrate hemipentahydrate, and the minimum of water necessary to dissolve said salts. The impregnated support was dried at 120 °C for 2 h and then calcined at 480 °C for 8 h. The finished catalyst comprised 32% NiCu.

*2.2.2. Nickel/copper on 50% Beta zeolite*

This catalyst was prepared following the same procedures as described above, except that the support was a mix of 50% $\beta$-zeolite and 50% alumina.

*2.2.3. Nickel/copper/chromium on 80% ZSM-5 zeolite*

This catalyst was prepared using as support an 80% ZSM-5 zeolite, having a silica/alumina mole ratio of 223, and 20% alumina. The dried support (50 g) was impregnated with 35 $cm^3$ solution containing 11.4 g of copper nitrate, 22 g of nickel nitrate, and 4.4 g of chromium nitrate. The impregnated support was dried at 120 °C for 2 h and calcined, first at 315 °C for 2 h and then at 425 °C for 4 h. The resulting catalyst comprised 7 wt% CuO, 2 wt% $CrO_3$, and 1 wt% NiO.

*2.2.4. Nickel/copper on alumina*

This catalyst was prepared by impregnating 46 g of an alumina support with 37 $cm^3$ of a solution of 47 g of nickel nitrate and 5 g of copper nitrate in distilled water. The impregnated alumina was dried at 120 °C for 16 h and then further impregnated with a second, 30 $cm^3$ solution of 47 g of nickel nitrate and 5 g of copper nitrate in distilled water. The final catalyst was dried at 120 °C for 16 h then calcined, first at 315 °C for 4 h, and then at 480 °C for 8 h.

## 3. Results and discussion

The one-step conversion of acetone-rich feed streams to diisopropyl ether (equation (2)) has been demonstrated in this work using dual-functional catalyst systems that incorporate both ketone hydrogenation and dehydration/etherification activities. These catalyst combinations have been tested in three types of reactor configurations, namely:

- a two-bed reactor design separated by inerts, using the same catalyst composition in both beds [8,9];
- a gradient catalyst bed comprising three different catalyst compositions [10];
- an integrated, two-zone layout with different catalyst compositions [11].

All catalyst screening for DIPE synthesis was conducted in continuous microreactor units, operated in the downflow mode as described in section 2. The bifunctional catalysts comprised groups IB, VIB, and VII metals incorporated into acidic, large and medium-pore zeolites, groups III and VI oxides, as well as supported heteropoly acid structures. Typical catalyst preparations are illustrated in section 2. After loading into the microreactors, each catalyst bed was pretreated in a stream of hydrogen, at elevated temperatures, then fed a mix of acetone (97%, also containing methanol plus water) and hydrogen (the $H_2$-to-$(CH_3)_2CO$ molar feed ratio being ca. 5 : 1) over a range of operating temperatures. The typical operating temperature range was 100–160 °C. Experimental details may be found in section 2.

Product composition data for DIPE production using the first reactor configuration – the two catalyst beds with the same composition – are illustrated in table 1. Five catalyst compositions were initially tested, three 32% nickel/copper on 10, 50, and 60% Beta samples, a nickel/copper on 80% ZSM-5, and a 12-tungstophosphoric acid on silica–alumina [3]. It is intended that for each catalyst formulation, the metals component provides the ketone hydrogenation activity, and that the acidic zeolite ensures subsequent IPA etherification. The first four examples each gave quantitative acetone conversions over a range of operating temperatures. In the case of example 3, at 124 °C and an acetone feed rate of 1.5 LHSV, DIPE selectivities of 25 wt% were realized, where the combined DIPE plus IPA yields were ca. 90 wt%. Liquid recovery in this case was quantitative. All other product sample recoveries in experiments 1–4 were >99 wt%. Comparing the data of examples 1–3, it appears that for this particular reactor design, DIPE productivity increases with increase in catalyst $\beta$-zeolite content.

Table 1
Diisopropyl ether syntheses from acetone – two-bed reactor configuration, single catalyst.

| Exp. | Catalyst | Temp. | Product composition (wt%) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | (°C) | $C_3$ | Acetone | IPA | DIPE | $C_6/C_9$ | Water |
| 1 | NiCu/10% Beta | 101 | 0.9 | 0 | 97.4 | 0.5 | 0.5 | 0.9 |
| | | 113 | 1.8 | 0 | 94.6 | 1.9 | 0.5 | 1.1 |
| | | 130 | 0.5 | 0.1 | 89.6 | 6.6 | 0.9 | 2.4 |
| | | 143 | 6.8 | 0.1 | 71.4 | 14.6 | 1.8 | 5.1 |
| | | 163 | 22.1 | 0.2 | 49.2 | 17.1 | 2.6 | 8.6 |
| 2 | NiCu/50% Beta | 99 | 2.9 | 0 | 91 | 4 | 0.4 | 1.6 |
| | | 104 | 2.8 | 0 | 84.3 | 8.2 | 0.5 | 4.1 |
| | | 111 | 1.8 | 0 | 86 | 9.3 | 0.5 | 2.4 |
| | | 119 | 2.9 | 0.1 | 81.7 | 11.5 | 0.6 | 3.1 |
| | | 129 | 14.1 | 0.1 | 61.1 | 19 | 0.4 | 5 |
| 3 | NiCu/60% Beta | 124 | 0.3 | 0 | 65 | 24.8 | 1.8 | 7.9 |
| 4 | NiCuCr/ZSM-5 | 104 | 1.8 | 0 | 82.7 | 9.8 | 1.3 | 4.5 |
| 5 | PW12/$SiO_2$–$Al_2O_3$ | 141 | 1.6 | 4.6 | 82.5 | 10.9 | 0.5 | 3.8 |

DIPE production as a function of operating temperature is illustrated in figure 3 for the nickel–copper/50% Beta catalyst of example 2.

A significant improvement in DIPE productivity has been realized by running the acetone hydrogenation/dehydration sequence using a gradient reactor configuration. Such a unit has a series of fixed-bed catalyst zones loaded along the reactor axis so that there is a hydrogenation activity gradient along the reactor in one direction and an etherification activity gradient in the opposite direction. A typical layout is illustrated in figure 1. In the DIPE synthesis examples illustrated here, there are three distinct catalyst beds of differing compositions, and the metal loadings in each of the beds range from 40–25% to 20–10 and 10–0% metals, while the zeolite content increases from 0–5% to 40–60 and 70–90%. Table 2 includes GC product analyses data for two such experiments. In both runs 6 and 7, the catalyst charge has been loaded so that the initial zone (first seen by the fresh acetone feed) contains a high hydrogenation function and a low etherification function, while successive zones display decreasing hydrogenation catalyst activity and more etherification activity. In the first (top) catalyst bed, the catalyst composition is selected to provide high conversion of the acetone to IPA, without significant condensation to undesirable $C_6$ and $C_9$ products, or the dehydration of IPA intermediate to $C_3$ gas plus water. As the acetone/IPA stream passes further down the unit, the remaining acetone is reduced and the alcohol fraction is etherified in those subsequent catalyst zones that display increasing quantities of acid functionality. In the case of example 6, the precise catalyst compositions are:

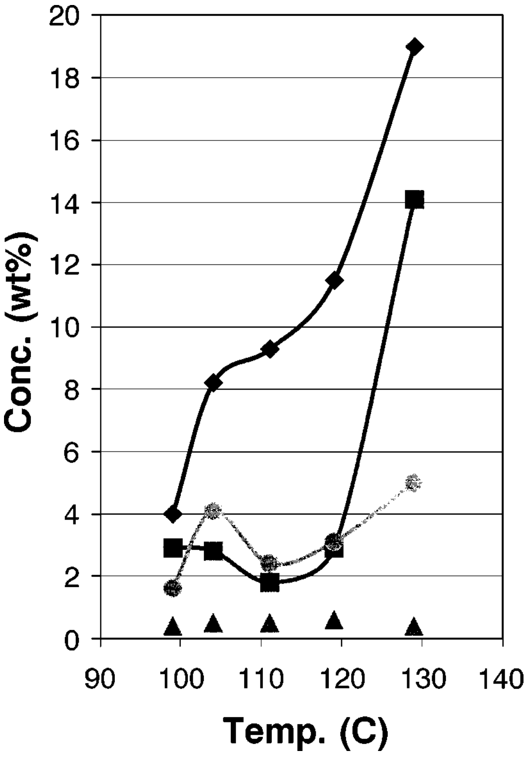


Figure 3. DIPE generation from acetone as a function of catalyst bed temperature, single catalyst. (◆) DIPE, (■) $C_3$, (▲) $C_6/C_9$ and (●) water.

- top bed: 32% Ni plus Cu on alumina;
- middle bed: 16% Ni plus Cu on 50% Beta/50% alumina;
- bottom bed: 80% Beta/20% alumina.

Again the acetone conversions are essentially quantitative over the full temperature range considered (see column three, table 2, for the typical temperatures in each of the three catalyst zones). However in this case, it is noteworthy that the IPA + DIPE molar selectivities exceed 98% and we are able to minimize the coproduction of $C_3$ gas, as well as $C_6/C_9$ condensation products (DIPE to $C_3/C_6/C_9$ wt ratio $>30$). Consequently, DIPE effluent concentrations reach ca. 38% when the catalyst temperature sequence is 104–159–146 °C. Liquid recoveries in this experimental series were again essentially quantitative.

Somewhat similar data are realized in experiment 7 where the catalyst configuration is:

- top bed: 32% Ni plus Cu on 10% Beta/90% alumina;
- middle bed: 16% Ni plus Cu on 50% Beta/50% alumina;
- bottom bed: 8% Ni plus Cu on 80% Beta/20% alumina.

Table 3 data illustrate the production of DIPE using the third reactor configuration – a two-zone reactor design, outlined in figure 2. Here the acetone feed is hydrogenated to an isopropanol-rich effluent by multi-metal catalyst A, and

Table 2
Diisopropyl ether syntheses from acetone – gradient reactor configuration, three catalysts.

| Exp. | Catalyst | Temp. (°C) | Product composition (wt%) $C_3$ | Acetone | IPA | DIPE | $C_6/C_9$ | Water |
|---|---|---|---|---|---|---|---|---|
| 6 | $NiCu/Al_2O_3$ + NiCu/50% Beta + 80% Beta | 101–131–133 | 0.2 | 0 | 81.6 | 13.6 | 0 | 3.5 |
| | | 99–134–128 | 0.3 | 0 | 74.9 | 20 | 0 | 4.9 |
| | | 102–138–142 | 0.5 | 0.5 | 64.5 | 26.3 | 0 | 6.6 |
| | | 100–143–139 | 0.7 | 0 | 58.4 | 32.7 | 0 | 8.1 |
| | | 102–150–143 | 0.7 | 0 | 51.1 | 37.4 | 0 | 10.3 |
| | | 104–159–146 | 1.1 | 1 | 42.5 | 37.5 | 0 | 11.9 |
| 7 | NiCu/10% Beta + NiCu/50% Beta + NiCu/80% Beta | 106–129–129 | 0 | 0 | 86.5 | 9.9 | 0.3 | 3.3 |
| | | 105–142–136 | 0.7 | 0 | 64.9 | 26 | 0.3 | 7.7 |
| | | 105–141–132 | 0.5 | 0 | 71.6 | 21.9 | 0 | 6 |
| | | 107–146–139 | 0.6 | 0 | 65.3 | 24.4 | 0 | 6 |

Table 3
Diisopropyl ether syntheses from acetone – two-zone reactor configuration, two catalysts.

| Exp. | Catalyst | Temp. (°C) | LHSV | Time-on-stream (h) | Product composition (wt%) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $C_3$ | Acetone | IPA | DIPE | Water |
| 8 | $NiCu/Al_2O_3 + NiCu/80\%$ Beta | 115–126 | 1 | 9 | 0.2 | 0.6 | 83.9 | 8.7 | 4.8 |
| | | 118–137 | 1 | 20 | 0.5 | 0.5 | 54.3 | 30 | 10 |
| 9 | $NiCu/Al_2O_3 + NiCu/30\%$ Beta | 115–127 | 1 | 9 | 0 | 0 | 82.9 | 12.2 | 4.9 |
| | | 115–135 | 1 | 14 | 0.3 | 0.5 | 64.1 | 25.2 | 4.6 |
| | | 151–126 | 2 | 22 | 0 | 0 | 90.4 | 4.7 | 4.9 |
| | | 152–134 | 2 | 30 | 0.3 | 0.5 | 74.3 | 16.2 | 4.7 |
| 10 | $NiCu/Al_2O_3 + NiCu/60\%$ Beta | 116–117 | 1 | 5 | 0 | 0 | 90.5 | 4.6 | 4.9 |
| | | 117–135 | 1 | 9 | 0.3 | 0 | 66.1 | 24.7 | 4.7 |
| | | 118–146 | 1 | 17 | 0.3 | 0 | 50.3 | 35.8 | 4.5 |
| | | 119–147 | 1 | 19 | 0.8 | 0 | 43.1 | 33.2 | 4 |

then said IPA is passed directly to the second reactor, without separation of liquid and gas, where, in the presence of a strongly acidic zeolite-based catalyst, B, it is etherified to DIPE. Example 8 uses a 32% nickel–copper on alumina catalyst in combination with a 32% nickel–copper on 80% Beta/20% alumina support (both prepared as described in section 2). Again near complete acetone conversions were achieved under these test conditions, with IPA and DIPE co-generated as desired products. Small quantities of propene (from IPA dehydration) provided the major co-products. DIPE yields increased substantially with increasing temperature of the bottom reactor. Raising the acetone feed space velocity, and then adjusting the catalyst bed temperatures, is demonstrated in example 9.

DIPE yields of up to ca. 36% were achieved in example 10 using a 32% nickel–copper on 60% $\beta$-zeolite/ 40% alumina as the bottom catalyst bed, at 146 °C. Unfortunately, in this case, there is also a 9.2% coproduction of light ($C_1$ and $C_2$) gases, and if the etherification temperatures are raised still further ($>150$ °C), there is a deleterious effect on the combined IPA + DIPE yields (to $<80\%$) through the formation of additional undesired lights coproduct.

Further extensions of this chemistry (equation (2)) include the addition of alkanols – particularly *tert*-butanol or methanol – to the acetone feed streams, thereby generating, in one step, a mix of DIPE with IPTBE, MTBE, etc. [10]. Again, these one-step, multi-ether syntheses can be conducted in the gradient reactor system without the co-production of large quantities of undesirable $C_3$ and $C_4$ gaseous co-products. Typical alkanol feed concentrations may be in the 10–70% range [10].

## 4. Conclusions

Of the three configurations considered in this program, the gradient reactor design has the triple advantages of:

- the highest exit concentrations of desired DIPE (see table 2, experiment 6);
- very little co-product $C_3/C_6/C_9$ formation;
- quantitative acetone conversion over a broad range of operating temperatures.

Additional improvements in DIPE productivity may be anticipated through further optimization of the hydrogenation/dehydration activities of the three catalyst compositions, as well as the temperature profiles selected for DIPE generation.

## References

[1] J.F. Knifton and P.E. Dai, Catal. Lett. 57 (1999) 193.
[2] J.F. Knifton, P.E. Dai and J.M. Walsh, J. Chem. Soc. Chem. Commun. (1999) 1521.
[3] J.F. Knifton and J.C. Edwards, Appl. Catal. 183 (1999) 1.
[4] W.J. Piel, Fuel Reform. (November/December 1992) 34.
[5] W.J. Piel, Fuel Reform. (March/April 1994) 28.
[6] A. Wood, Chem. Week (15 April 1992) 7.
[7] J.F. Knifton and P.E. Dai, in: *18th Conf. Catal. Organic Reactions*, Charleston, SC, April 2000.
[8] P.E. Dai, R.J. Taylor, J.F. Knifton and B.R. Martin, US Patent 5 476 972 (1995), to Texaco Chemical Inc.
[9] R.J. Taylor, P.E. Dai, J.F. Knifton and B.R. Martin, US Patent 5 637 778 (1997), to Texaco Chemical Inc.
[10] R.J. Taylor, P.E. Dai and J.F. Knifton, US Patent 5 550 300 (1996), to Texaco Chemical Inc.
[11] R.J. Taylor, P.E. Dai and J.F. Knifton, US Patent 5 583 266 (1996), to Texaco Chemical Inc.