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Diisopropyl ether syntheses from crude acetone

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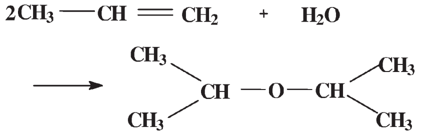
Diisopropyl ether (DIPE) may be generated via a novel, two-step process from crude, by-product, acetone streams through initial acetone hydrogenation over a bulk-metal, nickel-rich catalyst to give isopropanol (IPA), followed by dehydration of said IPA intermediate in the presence of an acidic, large-pore zeolite catalyst. Three classes of acidic zeolite have proven effective for selective DIPE production, including Beta-zeolite, β-zeolites modified with certain transition metals, and dealuminized Y-zeolites.

Keywords: diisopropyl ether, Beta-zeolite, acetone, isopropanol

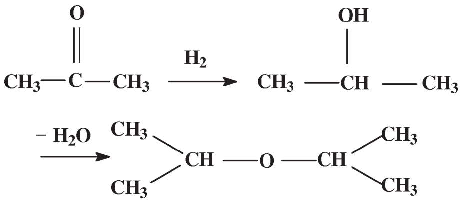
1. Introduction

Diisopropyl ether (DIPE) has been proposed as an alternative oxygenate to methyl *tert*-butyl ether (MTBE) and *tert*-amyl methyl ether (TAME) in gasoline fuel blending, since it has similar physical and blending properties to MTBE and TAME [1–3]. Mobil Corp. have announced a new etherification technology to produce DIPE, based upon propylene (a readily available refinery product) and water (equation (1)), that has the advantage of allowing refiners to produce an oxygenate without relying upon an "external" supply of alcohols [4–6].



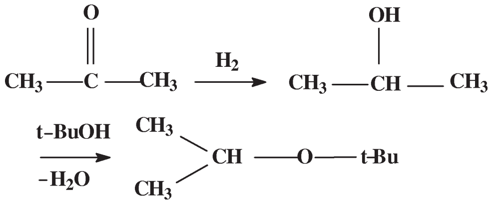
$$2CH_3-CH=CH_2 + H_2O \longrightarrow \overset{CH_3}{\underset{CH_3}{>}}CH-O-CH\overset{CH_3}{\underset{CH_3}{<}} \qquad (1)$$

We have investigated an alternative route to DIPE, starting from low-value, crude acetone streams. These liquid streams are generated in large volume as a result of propylene oxide/MTBE manufacture [7] and typically comprise 20–80% acetone (Ac_2O). In particular, during propylene oxide cogeneration, a large number of C-1 to C-4 oxygenates may be coproduced, including acetone, *tert*-butanol, formic acid, acetic acid, and their ester derivatives [7]. We have now demonstrated that the Ac_2O fraction may be selectively converted to DIPE in a two-step process involving initial hydrogenation to isopropanol (IPA), followed by IPA dehydration to DIPE (equation (2)) [8].



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{H_2} CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3 \xrightarrow{-H_2O} \overset{CH_3}{\underset{CH_3}{>}}CH-O-CH\overset{CH_3}{\underset{CH_3}{<}} \qquad (2)$$

Other alternative approaches to utilizing these low-value, crude acetone streams as fuel blending agents include combining the crude Ac_2O/*tert*-butanol mix with additional methanol and making MTBE [8], along with the DIPE, or adjusting the acetone/*tert*-butanol molar ratio and etherifying to give significant quantities of isopropyl *tert*-butyl ether (IPTBE, equation (3)) [9]. This ether also has excellent octane blending properties [1], as well as a low oxygen content and low vapor pressure.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{H_2} CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3 \xrightarrow[-H_2O]{t\text{-}BuOH} \overset{CH_3}{\underset{CH_3}{>}}CH-O-t\text{-}Bu \qquad (3)$$

In this paper, we focus on the development of processing and catalysts for the selective synthesis of DIPE from crude acetone.

2. Experimental

Catalysts used in this work were purchased or prepared as follows. The nickel, copper, chromium bulk-metal catalyst used for acetone hydrogenation was obtained as $1/8''$ tablets from Engelhard Corp. Designated Ni-2715 by the supplier, it contained about 72 wt% nickel. The Beta-zeolites (80% Beta, 20% alumina binder and 50% Beta, 50% alumina) in $1/16''$ diameter forms were purchased from PQ Corp. Typically, said β-zeolite powders have a SiO_2/Al_2O_3 ratio of 23–26 and a surface area of 650–750 m^2/g.

A typical preparation of a transition-metal-modified β-zeolite is as follows. To 102 g of β-zeolite (80% Beta, 20% alumina binder), $1/16''$ extrudates, was added a solution of ferric chloride hydrate (1.04 g), chromium(II) nitrate, hydrate (1.64 g), and manganese(II) nitrate, hydrate

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(1.10 g) in 92 ml of distilled water. Impregnation of the β-zeolite was allowed to occur over 1–3 h, the solids were then filtered off, dried at 120 °C overnight, calcined at 315 °C for 2 h, followed by 540 °C for another 2 h, then reduced in a stream of hydrogen at 350 °C. The recovered green solid extrudates comprised: 0.27% Fe, 0.19% Cr, 0.08% Mn. The titratable acidity was 0.35 meq/g.

A similar preparation of a platium-modified β-zeolite is as follows. To a sample of β-zeolite (50% Beta, 50% alumina, $1/16''$ diameter extruded form, 176 g) was added a solution of tetramine platinum(II) nitrate (1.75 g) in 120 ml of distilled water, with stirring. After mixing for up to 1 h, the solids were recovered by filtration, dried at 120 °C for 2 h, calcined at 540 °C for 3 h, and reduced in a stream of hydrogen at 400 °C for 4 h.

Dealuminized Y-zeolite (LZY-84) was purchased from UOP Corp.; it has a unit cell size of 24.52 Å and a silica/alumina molar ratio of 8.4. It was used here in $1/16''$ diameter extruded form containing ca. 20% binder.

Acetone hydrogenation was typically conducted as follows. To a 50 cm^3 capacity, continuous reactor system equipped with the appropriate temperature/pressure controls was charged a sample of Ni-2715, bulk-metal catalyst in $1/8''$ tableted form. A crude acetone mix also containing significant quantities of methanol and *tert*-butanol was passed, upflow, through the unit at a LHSV of 0.5 in the presence of excess hydrogen (90 l/h). Hydrogenation of the acetone fraction was achieved at ca. 160 °C under these conditions. Isopropanol was the principal product fraction, as determined by GLC analyses.

Diisopropyl ether syntheses were conducted as follows. To a 316 stainless steel tubular reactor ($1/2''$ i.d., $12''$ long) provided with the necessary temperature, pressure controls, was charged 50 cm^3 of β-zeolite (80% Beta, 20% alumina binder) in $1/16''$ diameter extruded form. A sample of crude hydrogenated acetone feedstock, prepared as described *supra*, was fed, upflow, through the bed of β-zeolite catalyst at a series of dehydration temperatures (typically 120–180 °C). Total unit pressure was maintained at ca. 50 bar. Samples of crude product effluent were collected on stream, in 316 ss bombs, and analyzed by GLC and GC-MS techniques.

3. Results and discussion

Diisopropyl ether, an excellent gasoline blending oxygenate, may be efficiently generated from low-value, crude acetone streams in a two-step procedure involving hydrogenation and dehydration (equation (2)). Typical acetone by-product streams from propylene oxide/MTBE plants may also contain significant quantities of methanol (MeOH), *tert*-butanol (tBA), and allyl *tert*-butyl peroxide (ATBP), as well as detectable amounts of formic acid, acetic acid, and their ester derivatives, such as *tert*-butyl formate (tBF) [7,10]. Typically, said crude acetone streams may comprise 20–80% Ac_2O. In this work, we selected a large volume stream comprising 61.7% acetone, 13.9% *tert*-butanol, and 3.3% allyl *tert*-butyl peroxide, together with 0.1% each of isopropanol and *tert*-butyl formate.

Selective hydrogenation of said acetone stream in a continuous, upflow reactor system packed with nickel, copper, chromium bulk-metal catalyst comprising ca. 72% Ni, at 160 °C, provided near quantitative (99%) acetone conversion levels at LHSV of 0.5, with isopropanol (IPA) as the major product fraction. Typical experimental data are summarized in table 1, preparative details may be found in section 2. Selectivity to IPA was typically in the range 76–80 mol%. Catalyst activity may be sustained for extended periods without loss of performance – particularly in terms of acetone conversion levels and IPA selectivities. An added, critical, feature of using this type nickel-rich, bulk-metal catalyst is that any allyl *tert*-butyl peroxide or *tert*-butyl hydroperoxide fractions present in this crude acetone feed are quantitatively converted to more innocuous alcohols, e.g., *tert*-butanol, under the hydrogenation conditions of table 1 – without causing catalyst deactivation.

Dehydration of the IPA intermediate to diisopropyl ether (DIPE) has also been demonstrated in contiuous, upflow reactor systems using three classes of acidic, large-pore zeolites [8]:

- zeolite Beta,
- transition-metal-modified β-zeolites,
- dealuminized Y-zeolite.

Typically, DIPE is generated in up to ca. 14% concentration in the crude liquid product under moderate dehydration conditions. Table 2 illustrates DIPE syntheses from the crude IPA stream of table 1 using an acidic β-zeolite catalyst (80% Beta, 20% alumina binder in $1/16''$ diameter extruded form) over a reaction temperature range of 120–180 °C. At 180 °C, the estimated isopropanol conversion level is 67% and the crude liquid effluent comprises 13.9 wt% diisopropyl ether (see sample #4). Total ether production in this case is 31.4 wt%, with methyl isopropyl ether (MIPE) and dimethyl ether (DME) as significant components – together with C-4 olefin/dimer. Clearly these particular ethers, plus alkenes, could be avoided if one started with a purer acetone feed stream, or if the IPA intermediate was fractionated prior to dehydration. At lower operating temperatures (e.g., 120 °C) with the same crude IPA feed stream, MTBE is the major product fraction – from methanol/*tert*-butanol etherification [11], but at 180 °C, methyl *tert*-butyl ether is no longer equilibrium favored [12]. Diisopropyl ether preparative conditions and practices are detailed in section 2. It is particularly noteworthy that the Beta-zeolite catalyst maintains dehydration activity and good DIPE selectivity with this crude hydrogenated Ac_2O feedstock over extended periods [8].

Somewhat similar product distributions are realized when using a 0.3% palladium-impregnated 50% Beta-

Table 1
Crude acetone hydrogenation to isopropanol.

Catalyst	Temp. (°C)	LHSV	Sample	Composition[a] (%)					
				Ac_2O	IPA	MeOH	tBA	tBF	ATBP
			Feed	61.7	0.1	13.9	16.7	0.1	3.3
Ni-2715	160	0.5	Product	0.8	48.3	15.8	30.8	<0.1	<0.1

[a] Ac_2O = acetone; IPA = isopropanol; MeOH = methanol; tBA = *tert*-butanol; tBF = *tert*-butyl formate; ATBP = allyl *tert*-butyl peroxide.

Table 2
Isopropanol dehydration to diisopropyl ether – Beta-zeolite.

Catalyst	Temp. (°C)	Sample	Composition[a] (%)										
			Ether					Ac_2O	IPA	MeOH	tBA	H_2O	C_4H_8/C_8H_{16}
			DIPE	MIPE	MTBE	IPTBE	DME						
		Feed						0.8	48.3	15.8	30.8	5.7	
Beta-zeolite	120	#1	0.9	0.6	8.1	1.3	0.2	1.3	46.4	12.4	9.3	10.5	7.8
	140	#2	3	1.8	4.6	0.9	1.5	1.8	42	12.9	5.1	12.1	10.2
	160	#3	9.1	6.6	1.2	0.2	2.8	2.3	29.3	10.9	1.8	16.5	10.1
	180	#4	13.9	12.8	0.3	0.4	4	2.2	15.8	4.4	0.8	8	10.9

[a] DIPE = diisopropyl ether; MIPE = methyl isopropyl ether; MTBE = methyl *tert*-butyl ether; IPTBE = isopropyl *tert*-butyl ether; DME = dimethyl ether; other designations as defined in table 1.

Table 3
Isopropanol dehydration to diisopropyl ether – palladium-on-Beta-zeolite.

Catalyst	Temp. (°C)	Sample	Composition[a] (%)										
			Ether					Ac_2O	IPA	MeOH	tBA	H_2O	C_4H_8/C_8H_{16}
			DIPE	MIPE	MTBE	IPTBE	DME						
		Feed						0.8	48.3	15.8	30.8	5.7	
Pd/Beta-zeolite	120	#1	1.6	0.3	9.7	2.2	0.2	0.8	46.3	12	10.1	10.5	10.5
	140	#2	3.1	1.9	5	1	0.6	1.1	42	12.7	5.7	12	11.9
	160	#3	8.7	6.7	<0.1	0.3	1.1	1.4	31	10.9	1.5	15.9	11
	180	#4	12.7	13.2	<0.1	0.2	1.8	1.6	18.4	5.5	0.6	8.4	11.3

[a] Designations as per tables 1 and 2.

zeolite catalyst (table 3), as well as 0.3% platinum-impregnated 50% β-zeolite catalyst and a 1% nickel-, 1% copper-impregnated 80% β-zeolite [8]. The relationship between DIPE production and the temperature of dehydration is illustrated in figure 1 for both the Ni,Cu-β-zeolite and for a Fe,Cr,Mn-β-zeolite (whose preparation is detailed in section 2). The influence of catalyst structure and dehydration temperature upon IPA conversion levels is detailed in figure 2. These transition-metal-modified β-zeolites were selected for study based on our earlier discoveries that they provide superior etherification performance in related service, e.g., MTBE production from *tert*-BuOH/MeOH mixtures [12,13], as well as ETBE syntheses from *tert*-BuOH/EtOH combinations [15].

Over the same temperature range, the dealuminized Y-zeolite (LZY-84) proved to be substantially less active than the β-zeolite samples, both in terms of DIPE productivity (see figure 1) and IPA conversion levels (figure 2). This poorer etherification performance of the Y-zeolite could be related to the more prevalent cogeneration of isobutylene (from *tert*-BuOH dehydration) and its oligomers with this zeolite, particularly at the higher operating temperatures [8]. Pentasil zeolites, including ZSM-5, have also been screened by us for DIPE synthesis in related studies [15]. A number of schemes have been proposed for the separation and purification of the DIPE product [2,3].

We conclude then that both the large-pore Beta-zeolite (having a constraint index no greater than 2 [3]), as well as transition-metal-modified β-zeolites, are very effective catalysts for sustainable DIPE production using crude isopropanol feedstocks. While the presence of alkyl peroxides, such as ATBP and HTBP, in the original crude acetone is not deliterious to the performance of these solid acid catalysts [8], the concentration of water in the feed should be closely controlled. As noted by others [5], an aqueous content in the crude IPA feed of $>10\%$ can significantly impact the level of DIPE productivity. On the other hand, the use of crude IPA containing both MeOH and *tert*-butanol may provide a dialkyl ether-rich mix of products – including DIPE, MIPE, MTBE, IPTBE and DME [8] – in high total yield and effluent concentration (e.g., 31.4% concentration, see table 2, sample #4).

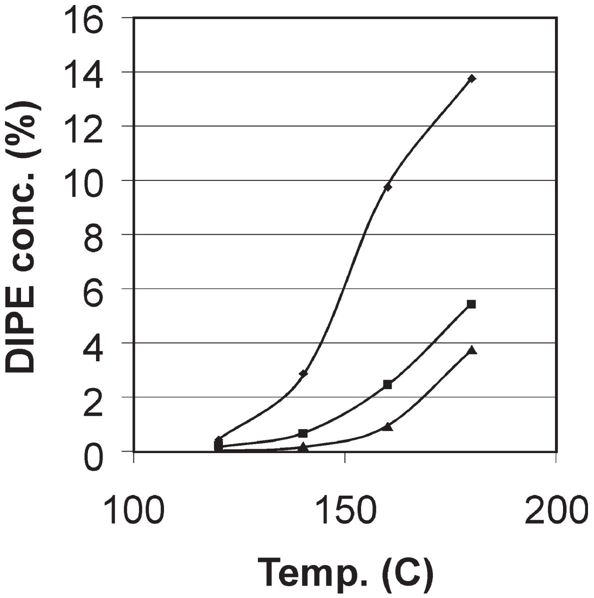

Figure 1. DIPE generation as a function of IPA dehydration temperature for three acidic zeolite catalysts. (♦) Ni,Cu/β-zeolite; (■) Fe,Cr,Mn/β-zeolite; (▲) dealuminized Y-zeolite.

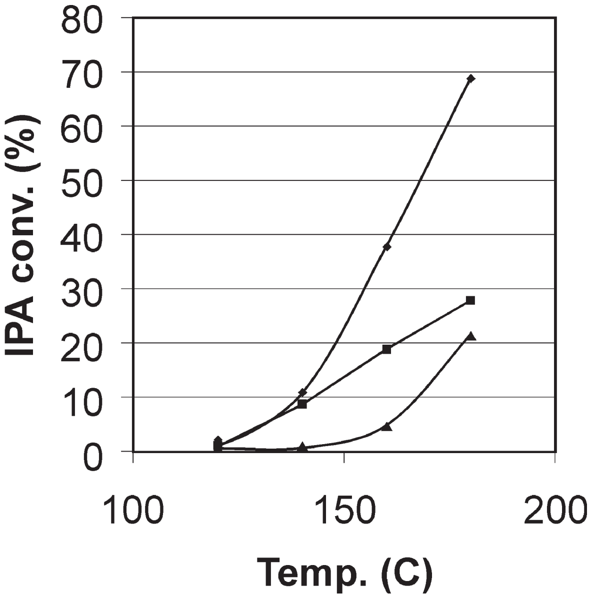

Figure 2. IPA conversion levels as a function of operating temperature. (♦) Ni,Cu/β-zeolite; (■) Fe,Cr,Mn/β-zeolite; (▲) dealuminized Y-zeolite.

Table 4
Dialkyl ether syntheses – thermodynamic data.

Dialkyl ether synthesis		Temp. (K)	ΔH (kcal/mol)	ΔS (kcal/mol)
2IPA $\rightarrow$ DIPE + H_2O	(4)	400	−3.4	0.2
		500	−3.4	1.1
IPA + MeOH $\rightarrow$ MIPE + H_2O	(5)	400	−4.6	−2.7
		500	−4.4	−2.2
tBA + MeOH $\rightarrow$ MTBE + H_2O	(6)	400	−1.6	0.4
		500	−1.5	0.9
tBA + IPA $\rightarrow$ IPTBE + H_2O	(7)	400	−0.2	2.4
		500	−0.1	3.0
2MeOH $\rightarrow$ DME + H_2O	(8)	400	−5.3	−3.4
		500	−5.1	−3.0

Here the DIPE : MIPE : MTBE : IPTBE : DME product molar ratios at 180 °C are typically ca. 1 : 1.3 : 0.02 : 0.02 : 0.6. Lower etherification temperatures lead to higher proportions of MTBE and IPTBE (see samples #1 and 2, tables 2 and 3, generated at 120 and 140 °C, respectively). These changes in dialkyl ether product distribution with increase, or decrease, in etherification temperature (tables 2 and 3) do not appear to follow the thermodynamic data for these five ether syntheses (see, in particular, the $-\Delta H$ values, table 4, equations (4)–(8) [16]). More likely, the increases in DIPE, MIPE, and DME concentrations over the temperature range 120–180 °C are associated with kinetic factors and the competition for surface active etherification sites.

Optionally, these types of DIPE, MIPE, MTBE, IPTBE, and DME ether mixtures could themselves be employed as valuable blends of oxygenates for octane enhancement and gasoline blending [1].

Acknowledgement

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