Novel and effective copper-aluminum propane dehydrogenation catalysts

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DOI
10.1002/chem.201102580

Publication date
2011

Document Version
Final published version

Published in
Chemistry - A European Journal

Citation for published version (APA):

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The importance of solid catalysts for converting petro-
and bulk chemicals is reflected in the sheer magnitude of
their market size: catalysts’ sales topped nine billion dollars
in 2009.[1] This large value mirrors also the increasing aca-
demic interest in heterogeneous catalysis research.[2] As far
as bulk chemicals (such as ethene, propene, and their deriva-
tives) are concerned, there is a strong demand for clean and
inexpensive catalysts and synthesis processes.[3] There are
two types of commonly used dehydrogenation catalysts: sup-
ported Cr oxides[4] and Pt-based[5] systems. The problem is
that these catalysts are typically either rare and costly, or haz-
ardous. Moreover, they perform well only at high temperatures[6] (typi-
cally at 500–600°C) due to ther-
modynamic limitations.[7] Optimi-
ization studies have led to the in-
clusion of several promoters of
which tin, especially in the com-
bination with platinum as Pt–Sn/
Al2O3 is one of the most popular.
We report here the discovery
of a new alternative catalyst for
propane dehydrogenation which
does not contain noble or haz-
ardous metals. It is an oxidized
porous Cu–Al alloy with a struc-
ture that is similar to Raney-type
metals.[8] The Raney process, pa-
tented by Murray Raney in 1925
and commercialized by W.R.
Grace & Co.,[9] is one of the
most successful routes for making porous metals. The prob-
lem is that this process requires extreme conditions that
often restrict the final outcome at the nanometric scale. Here we opted for a different approach, applying a modified
version of the ultrasound pore formation method that we
have recently reported: high-power ultrasound.[10]

In a typical synthesis, Cu and Al beads are melted by
using an electric arc. The resulting cake is then pulverized
and sonicated in water. This gives a highly porous material
containing pores predominantly at the micro-scale (see Fig-
ure 1a and 1b for a representative example; catalyst D).[11]

Figure 1c and 1d shows transmission and scanning electron micrographs of such a catalyst. We hypothesize that the
sonication creates pores in the Al component followed by
surface oxidation (compare the XRD profiles (a) and (b) in
Figure 2), whereas Cu supplies the active centers for the cat-
alysis (vide infra). The thickness of the ultra thin oxide layer
was estimated by using 3D field ion microscopy as less than
2.0 nm.[10b]

We prepared a series of catalysts with different Cu con-
tent (Table 1, entries 1–4), and found that using 25 wt% Cu
(catalyst D) gave the most promising results. This catalyst
was then activated under different conditions in an effort to
optimize the preparation recipe (see entries 4–6). We see a
reduction of conversion in the first minutes, probably reflect-
ing some initial sintering and coke deposition (see Figure 3).

After this short deactivation period, the catalyst main-
tains its steady-state activity (all values hereafter refer to the steady-state period). Our catalyst gave reason-
able propane consumption rates already at 550\(^\circ\)C (see Table 1). Note that all the reactions gave very good repro-
cibility (±7% for different samples from the same catalyst batch). However, if we look at the theoretical phase dia-
gram of Al–Cu, we see that it shows an eutectic point at

\[548\,^\circ\text{C}.\]

True, our catalyst is not a pure Al–Cu alloy (since at least its surface is passivated with an oxide layer; see Figure 2). Nevertheless, we hypothesized that a partial melting occurs during the pre-treatment at 600\(^\circ\)C (and possibly even during the reaction at 550\(^\circ\)C). Even if only part of the catalyst were melting, it would be perforce the active part. This is because the first sites that would melt would be the high-energy kinks and breaks where catalysis usually happens. Indeed, when we compared samples A and B that had less Cu but a larger particle size (typically >150 \(\mu\)m), we saw that these were more active than those with more copper but smaller sizes. To check this hypothesis, we pre-
pared another batch of the same catalyst D, but this time acti-
vated at 400\(^\circ\)C (all other conditions identical). We then ran the dehydrogenation again, this time 200 degrees lower (i.e. at 350\(^\circ\)C). Excitingly, as Figure 3 shows, this catalyst
gave greater conversions, reaching a stable 4% on stream. This is equivalent to a constant rate of 0.83 mol h\(^{-1}\) g\(^{-1}\). This result is all the more remarkable considering the tempera-
ture difference: a 200\(^\circ\)C offset would be expected to slow
down the reaction by approximately an order of magnitude (all other known catalysts are inactive under these condi-
tions). For comparison purposes, we tested a standard Pt–Sn/Al\(_2\)O\(_3\) catalyst under similar conditions. This catalyst has
been shown in the available literature as the best in terms of activity/selectivity/stability for propane dehydrogenation.

Under the same reaction conditions, Pt–Sn/Al\(_2\)O\(_3\) was practi-
cally inactive at 350\(^\circ\)C and gave less than 1% conversion (<0.2 mol h\(^{-1}\) g\(^{-1}\)) at 550\(^\circ\)C. Searching the literature, we did
not find any reports on propane dehydrogenation over Cu/
Al\(_2\)O\(_3\). But, we note the increase in rate quoted by Sokolova
et al. when adding Cu to Pt/Al\(_2\)O\(_3\).

In conclusion, we show here that high-power ultrasound is
a green chemistry tool for the synthesis of porous copper–

Figure 2. X-ray diffraction patterns of the porous Al-Cu catalyst D before (a) and after (b) ultrasound treatment (the JCPDS-ICDD stand-
ards are also included for ease of comparison).

Table 1. Composition, surface area and initial dehydrogenation rate for Al–Cu catalysts A–D.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Cu [wt%]</th>
<th>BET ([\text{m}^2\text{g}^{-1}])</th>
<th>Initial rate ([\text{mol h}^{-1}\text{g}^{-1}])</th>
<th>Activation atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>1([a])</td>
<td>A</td>
<td>5</td>
<td>48</td>
<td>1.35</td>
<td>O(_2)</td>
</tr>
<tr>
<td>2([b])</td>
<td>B</td>
<td>10</td>
<td>45</td>
<td>1.73</td>
<td>O(_2)</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>15</td>
<td>42</td>
<td>0.20</td>
<td>O(_2)</td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>25</td>
<td>34</td>
<td>0.79</td>
<td>O(_2)</td>
</tr>
<tr>
<td>5</td>
<td>D</td>
<td>25</td>
<td>34</td>
<td>0.54</td>
<td>H(_2)</td>
</tr>
<tr>
<td>6</td>
<td>D</td>
<td>25</td>
<td>34</td>
<td>0.01</td>
<td>Ar</td>
</tr>
<tr>
<td>7([c])</td>
<td>D</td>
<td>25</td>
<td>34</td>
<td>0.27</td>
<td>O(_2)</td>
</tr>
<tr>
<td>8([c])</td>
<td>D</td>
<td>25</td>
<td>34</td>
<td>3.39</td>
<td>O(_2)</td>
</tr>
</tbody>
</table>

[a] Particle size > 150 \(\mu\)m. [b] Reaction run without steam. [c] Catalyst ac-
tivation at 400\(^\circ\)C, reaction at 350\(^\circ\)C.

Figure 3. Temporal propane conversion for catalyst D at 350\(^\circ\)C (○) and 550\(^\circ\)C (●). Inset: relationship between the catalyst space time (i.e.
amount of catalyst per propane molar flow pass) and initial propane con-
version. Note: the benchmark Pt–Sn/Al\(_2\)O\(_3\) catalyst (not shown) gives <1% conversion at 550\(^\circ\)C.
aluminum frameworks stabilized by metal oxide. Furthermore, this material is inexpensive (production expenses are approximately 3 € per liter) and the method can be easily scaled-up by using different sonotrodes (or a series of them), as these may vary widely in size and shape. These new porous materials (or “metal sponges”) allow an alloy bulk and an oxidized surface, and can catalyze propane dehydrogenation at low temperatures. Thanks to their high activity and because they contain no noble metals, they open exciting opportunities in low-temperature dehydrogenation catalysis for making bulk chemicals.

Experimental Section

A detailed description of the materials and instrumentation used in this study, as well as the procedure for preparing the reference Pt–Sn/Al2O3 catalyst, are given in the Supporting Information.

Procedure for preparing the Al–Cu alloy: Commercial Al and Cu beads were alloyed by an arc melting device (Bühler) with a melt stream of 300 A. After reaching a vacuum of 10–5 mbar, 500 mbar Ar were transferred to the reactor. For homogenization, the melt of Cu and Al was turned around three times. Five different alloy samples (30 g each) were prepared. The Cu content in these samples was 25 wt% (118 mmol), 20 wt% (94 mmol), 15 wt% (71 mmol), 10 wt% (47 mmol), and 5 wt% (24 mmol), respectively. The resulting solid was cut in pieces and then ground by using a rotary mill (PULVERISSETTE 14, Fritsch GmbH) with a sieve ring of 1.5 mm. After milling, the powder was sieved with a mesh of 14.

Procedure for catalyst preparation: Five grams of the Al–Cu alloy powder were dispersed in ultrapure water (50 mL) and sonicated for 60 min with an ultrasound tip (Hirschel VIP1000 bid instrument; operated at 20 kHz with a maximum output power of 1000 W and a head area of 3.8 cm2, equipped with a booster B2–1.2). The maximum intensity was calculated to be 57 W cm–2, at a mechanical amplitude of 81 μm. During the treatment the sample was cooled in an ice bath. After the treatment, the sample was dried at 120 °C for 24 h.

General procedure for propane dehydrogenation: The catalyst was activated in situ before reaction in a flow of 77 mL min–1 Ar and 3 mL min–1 O2 at 600 °C. The reagents were carried out at 1 atm and 550 °C in a continuous-flow fixed-bed vertical quartz reactor (4 mm i.d.), which was controlled with a fully automated system built in house.[14,15] The partial pressures of CH4 and Ar were fixed at 0.5 atm where 2 g h–1 of steam were supplied by means of Bronkhorst mass flow controllers (total flow = 80 cm3 min–1); the ratio of catalyst mass (W) to initial C3H8 molar flow (C0) was better than 7%. The fractional conversion of C3H8 is defined in this study as Xc=(F−F0)/F, where F0 represents the molar flow of C3H8 at Ar. Repeated reactions with different samples from the same batch of catalyst delivered raw data that were reproducible to within ±7%.

Acknowledgements

We thank B. Putz and S. Koch (Universität Bayreuth) for help with the PXRD analysis and the miling, Dr. M.C. Mittelmeijer-Hazeleger (University of Amsterdam) for technical assistance. J. S. and D. A. thank SFB840 for financial support.

Keywords: heterogeneous catalysis ⋅ nanostructures ⋅ olefins ⋅ propylene ⋅ sonochemistry