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Dramatic promotion of copper–alumina catalysts by sodium for acetone trimerisation†

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and Nicolas Cadran^a

Na-promoted Cu–Al materials are efficient multifunctional catalysts for the direct conversion of gas phase acetone to diisobutyl ketone (DIBK) with unprecedented yields (up to 31%). The Na content is a major parameter determining the stability and the catalytic performance of these materials.

One-pot processes are interesting with regards to atom and energy efficiency and have been widely investigated in an attempt to develop further sustainable organic synthesis. The aldol condensation of acetone in a single reactor leads to the formation of many products including methyl isobutyl ketone (MIBK) and diisobutyl ketone (DIBK), which are used as solvents in paints.¹

A common global reaction scheme is described in Scheme 1.^{2,3} Self-aldol condensation of acetone on acid–base sites leads to diacetone alcohol (DAA). DAA undergoes dehydration leading to mesityl oxide (MO). Selective hydrogenation of the C=C bond on metallic sites gives MIBK. DIBK is obtained after further aldol condensation of acetone with MIBK followed by dehydration and hydrogenation of different intermediates. Concurrently, the hydrogenation of the carbonyl group of acetone leads to the formation of isopropanol (IPA), which can be dehydrated on the acidic sites of the catalyst, leading to the formation of propene and propane after hydrogenation on metallic sites. Therefore, the selectivity to MIBK and DIBK depends on the relative rates of steps (1) and

(2) described in Scheme 1, which can be varied by modifying the acid–base and hydrogenation properties of the catalyst.^{4–6}

Aldol condensation of gas phase acetone into MIBK has been extensively studied using various zeotypes and metal oxides promoted by transition metals (Pd, Pt, Ni or Cu) such as ZSM-5, X, SAPO, ALPON, MgO, Al₂O₃ or calcined hydrotalcites.^{7–23} In these studies, however, the selectivity towards DIBK was usually low, the largest DIBK yield was reported by Hetterley *et al.* being *ca.* 26% at 70% conversion over a Ni and Al mixed oxide promoted by Pd.²³ De Jesús Martínez-Ortiz *et al.* reported a trimer yield of approximately 8% obtained over different Pd and Cu impregnated mixed oxides of magnesium and aluminium.³ Kozhevnikova *et al.* obtained a maximum yield of 14% using a Zn–Cr mixed oxide promoted by Pd.²²

We report here noble metal-free Cu–Al-based catalysts as promising bifunctional catalysts for the one-pot conversion of gas phase acetone to DIBK. Outstanding results on the impact of sodium on the activity and stability of the Cu–Al based materials are described in this communication.

Cu- and Al-based catalysts were prepared by coprecipitation of Cu and Al nitrate precursors in a 30% NaOH solution (pH 8), using similar Cu/Al molar ratios (*i.e.* 0.53 ± 0.01).²⁴ After filtration and washing, the precipitate was dried at 120 °C for 24 h and calcined at 800 °C for 5 hours. The content of sodium in these samples was varied by varying the intensity of the washing step during the synthesis of the different solids (catalysts A–C, Table 1) or by adding sodium nitrate by incipient wetness impregnation of sample B followed by drying and calcination steps (catalysts D and E, Table 1). All catalysts showed the copper aluminate crystalline phase (CuAl₂O₄) and some also showed a CuO phase after calcination, which led to a Cu metallic phase after reduction at 300 °C. Typical *in situ* X-ray diffraction patterns recorded during temperature-programmed reduction of catalyst C are shown in Fig. 1.

The catalytic activity of the different catalysts for the gas-phase aldol condensation of acetone was assessed at 3 bars

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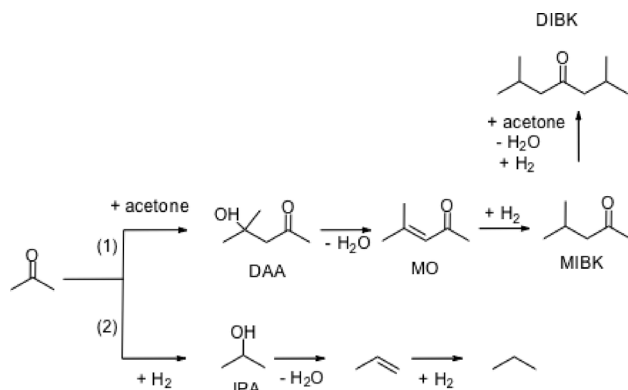
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Scheme 1 Main reaction pathways relating to acetone conversion.

Table 1 Catalyst composition and surface area^a

Catalyst	Cu/Al (mol mol ⁻¹)	Na (ppm)	SBET (m ² g ⁻¹)
A	0.52	<10	73
B	0.54	175	59
C	0.52	1640	73
D	0.54	4110	60
E	0.54	48 000	28

^a Na content was determined by ICP-AES.

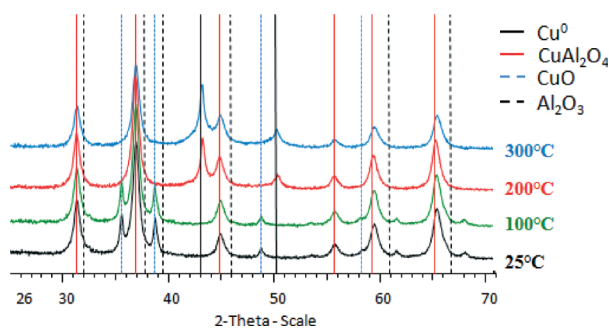


Fig. 1 XRD patterns of catalyst C after reduction for 30 min at different temperatures. Phases: CuO (ICDD PDF No. 04-005-4712); CuAl₂O₄ (ICDD PDF No. 04-015-0578); Cu⁰ (ICDD PDF No. 04-003-1450); Al₂O₃ (ICDD PDF No. 10-0425).

absolute pressure and 200 °C in a fixed bed reactor (stainless steel; 1 g of catalyst; WHSV = 1 h⁻¹; [H₂]/[acetone] = 2.56; [N₂]/[H₂] = 9) by on-line GC analysis. Prior to the reaction, the catalysts were pre-treated with hydrogen at 300 °C for 2 h and then overnight at 200 °C. Conversions are based on carbon weight.

The interest of using CuAl₂O₄ as catalyst consists of the well-known decomposition of these oxides under a reducing atmosphere, which leads to the formation of metallic copper and alumina. The presence of a large concentration of well-dispersed copper metal should suffice to provide a significant hydrogenation activity to the sample and make unnecessary the use of noble metals.²⁵

The conversion of acetone with time on stream for our five catalysts is shown in Fig. 2. Distinct behaviours concerning

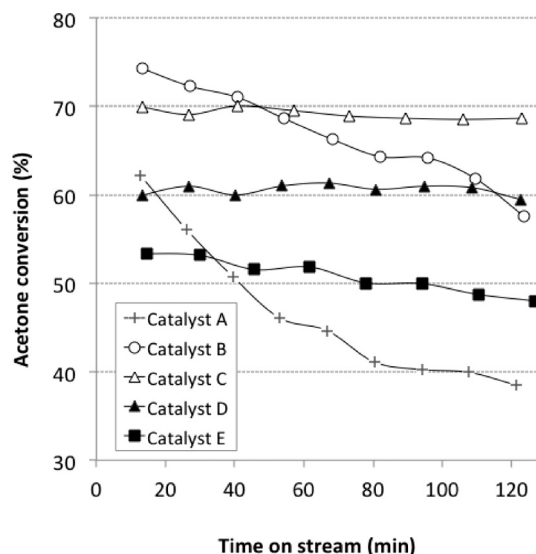


Fig. 2 Acetone conversion as a function of time on stream. Operating conditions: $T = 200$ °C, $P = 3$ bar, WHSV = 1 h⁻¹ (1 g of catalyst, acetone = 1 g h⁻¹), N₂ = 9 L h⁻¹, H₂ = 1 L h⁻¹. Conversion based on carbon weight.

the stability of the catalysts were noted. Samples A, B and E to a lesser extent exhibited significant deactivation with time on stream. In contrast, the conversion measured over samples C and D remained stable at ca. 70% and 60%, respectively. These data clearly indicate that there is an optimal range of Na loading in which the catalytic activity is stable under our experimental conditions.

The yields of the main classes of products obtained over the various samples after 10 and 120 min are shown in Fig. 3. A fuller product distribution is given in the ESI.† Samples A and B, which had the lowest Na content, exhibited the highest yields of light products (C₁–C₄), particularly propene/propane and some cracking products of acetone dimers (such as methane and isobutene). This can be rationalised by the fact that, at low sodium content, the sample acidity is sufficient to catalyze the dehydration of IPA in propene or the cracking of, e.g., DAA in isobutene.²⁶ Catalysts A and B were also those that displayed the fastest decrease in the yield of linear trimers with time on stream (Fig. 3).

In contrast, catalysts C and D exhibited lower yields of light products and essentially stable yields of dimers and trimers between 10 and 120 min. Dimers and trimers were by far the main reaction products over samples C and D. The yields of linear trimers obtained over catalyst C, ca. 33%, were actually the highest ever reported, to the best of our knowledge, including over noble metal-based catalysts.

Finally, catalyst E, with the largest Na content, showed a moderate initial activity and some deactivation despite low dehydration and cracking activities, indicating that larger Na contents have a detrimental impact on the catalyst performance.

It is likely that the presence of Na influences in many different ways the structure of the catalyst, which in turn

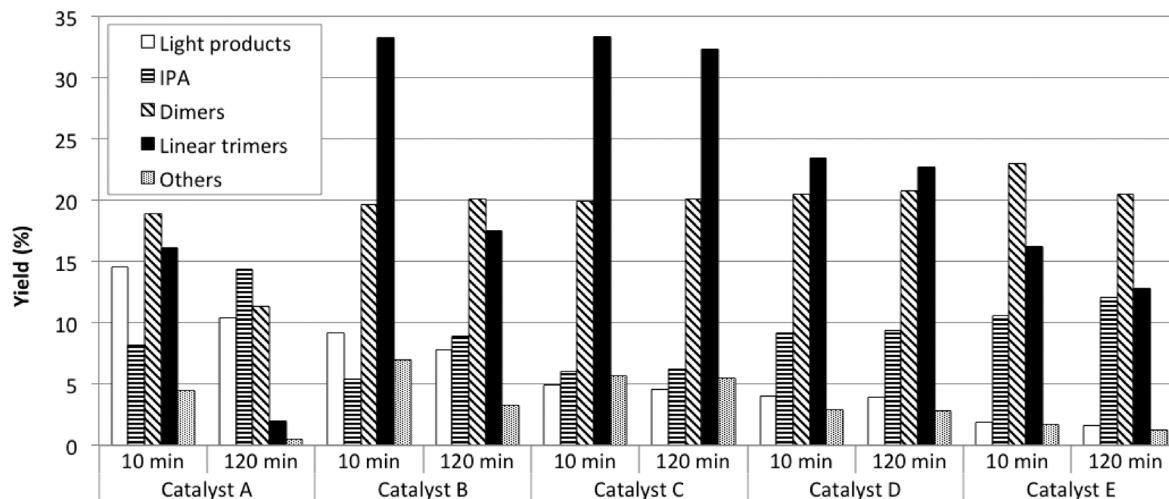


Fig. 3 Yields of the main reaction products of acetone conversion after 10 and 120 min under time on stream for the various catalysts. Light products = propene, propane, cracking products; IPA = isopropanol; dimers = MIBK, MIBA (4-methylpentan-2-ol), 2-MP (2-methylpentane); linear trimers = DIBK, DIBA (2,6-dimethylheptan-4-ol); others = TMB (1,3,5-trimethylbenzene), C_{12} , unknown products. Operating conditions: $T = 200\text{ }^{\circ}\text{C}$, $P = 3\text{ bar}$, $\text{WHSV} = 1\text{ h}^{-1}$ (1 g of catalyst, acetone = 1 g h^{-1}), $N_2 = 9\text{ L h}^{-1}$, $H_2 = 1\text{ L h}^{-1}$. Conversion based on carbon weight. Yields are based on carbon weight%.

determines the catalytic activity and stability. A few hypotheses, supported by the present catalytic tests, can be considered to explain the stabilization of the acetone conversion. In particular, addition of sodium decreases surface acidity and IPA dehydration/cracking reactions, as indicated by the decrease of light gas yields (C_1 – C_4), hence limiting coke precursors such as propylene.

Another effect of Na could be the modification of the structure of the Cu metallic particles. More work would be needed to assess the structural effects induced by the promotion with Na and then attempt to relate those to the improved catalytic properties. This surely will be a difficult task, since the reaction network is highly complex, involving many intermediates and catalytic steps (Scheme 1).

In conclusion, noble metal-free Na–Cu–Al-based formulations are outstanding catalysts for the production of DIBK from the direct aldol condensation of acetone in the presence of hydrogen. The presence of sodium dramatically modifies the catalytic properties of Cu–Al-based catalysts for this reaction. Intermediate doping of sodium (corresponding to a level of *ca.* $1\text{ }\mu\text{mol m}^{-2}$) leads to highly selective and stable catalysts for acetone conversion to linear dimers and trimers.

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