Synthesis of 2-Methylpropan-1-ol–Methanol Mixtures from H_2–CO Synthesis Gas over Double-bed Cs/Cu/ZnO/Cr_2O_3 and Cs/ZnO/Cr_2O_3 Catalysts

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A novel double-bed reactor configuration utilizing two sequential catalysts that operate in different optimum temperature regimes increases both the space–time yield and the selectivity of 2-methylpropan-1-ol from H_2–CO synthesis gas.

The coupling of methanol and 2-methyl branched alcohols, produced directly from CO and H_2 synthesis-gas mixtures,[1–3] has been proposed in the literature for the synthesis of ethers such as $MeOBu^t$ and $Et(Me)_2COMe$.[4] Such an application of Higher Alcohol Synthesis (HAS) calls for high productivities and selectivities to 2-methylpropan-1-ol (isobutyl alcohol) and the higher 2-methyl alcohols, the target being an ideal 1 : 1 mole ratio with respect to methanol. Though promising, the catalytic performances of the traditional HAS catalysts operating both at low reaction temperature (Cu-based catalysts)[5,6] and at high reaction temperature (zinc chromite catalysts)[7,8] still do not match the desired requirements. The development of alternative catalytic systems and the reaction engineering of HAS processes are currently fields of exploration.

In this communication, a novel approach to the production of alcohol mixtures with high selectivity to methanol and isobutyl alcohol is reported. This is based on the coupling of known Cu-based and Cu-free catalysts that exploits the advantages of each of the two systems. A double-bed configuration with a Cs-promoted Cu/ZnO/Cr_2O_3 catalyst as the top low-temperature bed and a Cs-promoted ZnO/Cr_2O_3 catalyst as the bottom high-temperature bed has been employed. This design improves by approximately 100% the productivity of isobutyl alcohol and branched oxygenates that can be obtained over either of the two individual catalysts.

The preparation by coprecipitation and the Cs doping (3.0 mol%) of the ternary Cu/ZnO/Cr_2O_3 catalyst (Cu : Zn : Cr = 30 : 45 : 25 mol ratio) used in the present experiments, as well as the apparatus used for the activity tests, have been described elsewhere.[5] In each case, the catalyst was sieved to 0.85–2.0 mm and diluted with 3 mm Pyrex beads (1 : 3 *v*/*v* basis) to minimize thermal and mass transfer effects. The analytical procedures have been also previously reported.[9]

The activity of the ternary Cu-based catalyst in HAS has been extensively investigated over a wide field of operating conditions. A complete kinetic study will be presented in a forthcoming paper. In Table 1 are shown the results obtained at 598 K and 7.6 MPa, with H_2–CO (0.75 : 1) synthesis gas (an optimum for higher alcohol synthesis at high temperature)[9] and a gas hourly space velocity (GHSV) of 18 375 l(STP) (kg cat h)$^{-1}$. Even though not optimal with respect to isobutyl alcohol yield, these conditions favour the overall productivity to methanol and C_{2+} species. The latter include primary alcohols, aldehydes, secondary alcohols, ketones, methyl esters, and hydrocarbons. The current understanding of the complex reaction mechanism leading to the formation of such a variety of products, together with the kinetic and thermodynamic factors controlling their distribution, has been previously summarized.[10–12] It is in particular known that the C_2 and C_3 oxygenates are key intermediates in the carbon chain-growth

Table 1 Higher alcohol synthesis [productivities expressed in g (kg cat h)$^{-1}$] over the 3 mol% Cs/Cu/ZnO/Cr_2O_3 catalyst, the 4 mol% Cs/ZnO/Cr_2O_3 catalyst, and the double-bed combination of the two catalysts. The productivities of aldehydes and ketones have been summed to those of the corresponding primary and secondary alcohols, respectively

Product	Cs/Cu/ZnO/Cr_2O_3[a]	Cs/ZnO/Cr_2O_3[b]	Cs/Cu/ZnO/Cr_2O_3 + Cs/ZnO/Cr_2O_3[c]
methanol	1200.0	173.4	178.8
ethanol	68.7	2.7	7.1
propan-1-ol	83.2	11.5	23.5
butan-1-ol	15.2	0.9	4.2
pentan-1-ol	9.6	0.6	3.1
hexan-1-ol	10.0	0.3	2.4
2-methylpropan-1-ol	65.6	74.1	138.8
2-methylbutan-1-ol	21.0	8.3	32.9
2-methylpentan-1-ol	14.4	5.3	21.7
2-methylhexan-1-ol	13.5	0.9	24.0
butan-2-ol	9.6	2.5	5.2
3-methylbutan-2-ol	10.1	0.9	7.2
pentan-3-ol	10.2	1.2	7.7
2-methylpentan-3-ol	16.0	5.5	23.1
methyl formate	20.4	1.1	11.3
methyl acetate	11.7	0.8	1.7
dimethyl ether	5.3	4.7	4.8
C_{7+} oxygenates	53.9	78.0	81.5
methane	10.4	4.1	12.1
C_2–C_4 hydrocarbons	8.1	15.6	27.9
% CO conv. (CO_2 free)	11.7	4.5	6.6

[a] *Single Bed* 3 mol% Cs/Cu/ZnO/Cr_2O_3 (2 g): T = 598 K, P = 7.6 MPa, H_2–CO (0.75 : 1) GHSV = 18 375 l(STP) (kg cat h)$^{-1}$. [b] *Single Bed* 3 mol% Cs/ZnO/Cr_2O_3 (2 g): T = 678 K, P = 7.6 MPa, H_2–CO (0.75 : 1) GHSV = 18 375 l(STP) (kg cat h)$^{-1}$. [c] *Double-Bed* catalysts consisting of the top bed = 3 mol% Cs/Cu/ZnO/Cr_2O_3 (1 g) at 598 K and the bottom-bed = 4 mol% Cs/ZnO/Cr_2O_3 (1 g) at 678 K with H_2–CO (0.75 : 1) synthesis gas at P = 7.6 MPa and GHSV = 18 375 l(STP) (kg cat h)$^{-1}$.

process. In contrast, isobutyl alcohol and other branched species behave as terminal products due to their low intrinsic reactivity. An interesting feature of the product distribution obtained over the ternary Cu-based catalyst is the large amount of light alcohols, which can be seen as a remarkable potential carbon source for the production of isobutyl alcohol.

A 4.0 mol% $Cs/ZnO/Cr_2O_3$ catalyst has been prepared by caesium formate doping of a commercial zinc chromite catalyst (Harshaw, Zn-0311 T 1/4, Lot 118). The activity testing was carried out under the same synthesis gas composition, pressure, and flow rate as those used for the $Cs/Cu/ZnO/Cr_2O_3$ catalyst. A reference reaction temperature of 678 K was adopted, consistent with the literature data.[12] The results are reported in the second column of Table 1 and indicate a selective formation of isobutyl alcohol with respect to the short-chain alcohols. Methanol (the production of which decreases with increasing reaction temperature due to thermodynamic constraints)[13] and isobutyl alcohol are in fact the only major products observed, while yields of ethanol and propanol are reduced to very small amounts. This suggests that the high-temperature catalyst has a significant function in the conversion of linear intermediates to terminal branched products. Indeed, the pathway ethanol → propanol → isobutyl alcohol is kinetically so efficient that only low selectivities to the products of competitive routes (*e.g.* $C_2 + C_n$, $C_3 + C_n$)[14] are observed.

A double-bed catalyst configuration has been designed in order to combine the complementary features of the low- and high-temperature catalysts. Equal amounts of the $Cs/Cu/ZnO/Cr_2O_3$ and $Cs/ZnO/Cr_2O_3$ catalyst have been loaded into the top and bottom portions of the reactor, respectively. Separated by inert Pyrex beads, the Cu-containing and the Cu-free beds have been maintained at 598 and 678 K respectively. The activity data are reported in the third column of Table 1. They show an overall productivity to 2-methyl oxygenates of >200 g (kg cat h)$^{-1}$. This represents an improvement of 90% with respect to the performance of the single $Cs/Cu/ZnO/Cr_2O_3$ catalyst, and of 145% with respect to the single $Cs/ZnO/Cr_2O_3$ catalyst. Indeed, the double-bed configuration allows a synergic utilization of the two catalysts, wherein the top low-temperature bed supplies a large quantity of intermediates that feed the subsequent high-temperature bed. The final product distribution (in analogy with the features of the zinc chromite catalyst, but in contrast to the features of the ternary Cu-based catalyst) is depleted in ethanol and propanol, which have been efficiently converted to higher oxygenates, particularly to isobutyl alcohol. Due to the outlet reactor temperature, the rate of production of methanol over the double-bed system is comparable to that obtained over the single zinc chromite catalyst. In effect, a large amount of methanol formed over the first bed is decomposed to CO and H_2 over the second bed. The net result is a total productivity of 480 g C_1–C_6 alcohols (kg cat h)$^{-1}$ and a desirable methanol : 2-methyl branched oxygenates mole ratio of 2 : 1.

In conclusion, it has been shown that the productivity and the selectivity to isobutyl alcohol are significantly enhanced by the present approach to HAS that is based on the subdivision of the overall process into two consecutive steps: a first low-temperature (598 K) step where the chain-growth is initiated by the synthesis of methanol and short-chain alcohols and a second high-temperature (678 K) step where the chain growth is terminated by the synthesis of branched higher alcohols. This configuration allows exploitation of the significant activity of 3% $Cs/Cu/ZnO/Cr_2O_3$ catalyst in the $C_1 \rightarrow C_2$ step (known to be the rate-determining step of the HAS process) and of the enhanced rates of the $C_2 \rightarrow C_3$ and $C_3 \rightarrow$ *iso*-C_4 growth steps over the 4 mol% $Cs/ZnO/Cr_2O_3$ catalyst.

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Footnotes

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