Catalysts for producing methanol and isobutanol mixtures from synthesis gas

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The coproduction of methanol and isobutanol from synthesis gas over new catalysts based on coprecipitated solid solutions of alkaline earth oxides and rare earth oxides promoted by copper has been investigated. It is shown that the catalysts are active and selective to isoalcohol synthesis at temperatures and pressures lower than those required by prior art catalysts.

Keywords: isobutanol synthesis, synthesis gas, Cu / Ce(Y) / Mg catalysts

1. Introduction

Recently, increasing research efforts have been devoted to the selective coproduction of methanol and isobutanol from synthesis gas ($CO/CO_2/H_2$) for use as reactants in subsequent methyl tert-butyl ether (MTBE) synthesis. Isobutanol can be easily dehydrated to isobutene and etherified with methanol over acidic ion-exchange resins to produce MTBE. Modified methanol synthesis catalysts operated both at high reaction temperature ($Mn(Zn)O/Cr_2O_3$/alkali catalysts) [1–3] and low reaction temperature (CuO/ZnO/alkali catalysts) [4–6] show promising catalytic performances for isoalcohol synthesis at pressures near 100 atm. Keim et al. [7] described an alternative catalyst consisting of palladium supported on a coprecipitated manganese, zinc, zirconium, lithium oxide support which is highly selective for a one-step synthesis of isobutanol. However, Keim's catalysts for the production of isoalcohols from synthesis gas require very high reactor temperature (> 400°C) and pressure (> 100 atm). These conditions would require expensive compression steps for synthesis gas produced by conventional methods. Thus, opportunities exist to develop novel catalytic compositions capable of producing methanol and isobutanol mixtures at moderate reactor temperature (e.g. 290–340°C vs. 400°C) and pressure (50 atm vs. 100–250 atm). Recently [8], we have found that catalysts based on coprecipitated mixtures or solid solutions of alkaline earth oxides and rare earth oxides (also including yttrium oxide) can effectively catalyze isobutanol synthesis at lower severity conditions. Examples of these catalysts include magnesium oxide and cerium oxide, Mg_yCeO_x, or magnesium oxide and yttrium oxide Mg_yYO_x solid solutions. In this paper we study the use of these catalytic materials for producing methanol and isobutanol mixtures from $CO + H_2$ feedstocks.

2. Experimental

Catalysts were prepared by coprecipitation of rare earth oxides and alkaline earth oxides at controlled pH. Copper oxide was either coprecipitated or added by impregnation. An acidic nitrate solution containing the catalyst components (solution A) was mixed with a basic solution containing KOH/K_2CO_3 (solution B) to cause precipitation. The two solutions were added to 500 cm^3 of distilled water kept at 60°C contained in a 2 ℓ beaker. Solution A was added by a pump at 15 cm^3/min and the simultaneous addition of solution B was controlled so that the pH of the well stirred mixture was held constant at 9. After solution A was exhausted, the resulting precipitate was filtered, washed with hot water and dried at 90°C overnight. The precursor was then decomposed in air at 400–600°C for 4 h. In the case of supported catalysts, the mixed oxide was impregnated with copper nitrate or potassium carbonate solutions by incipient wetness, dried at 110°C, and calcined at 450°C for 4 h. The supported catalysts are designated by a slash, e.g. $Cu/M_yN_zO_x$, where the amount of copper is given in wt%, and y, z, x represent g-atom quantities. Coprecipitated catalysts are designated without a slash, e.g., $Cu_pM_yN_zO_x$ where p, y, z, and x designate g-atom quantities.

Powder X-ray diffraction patterns (XRD) were collected on a Rigaku diffractometer using monochromatic Cu Kα radiation. The chemical composition of the samples was measured by an inductively coupled plasma (ICP) spectrometer (Jarrel Ash). BET surface areas (S_g) were measured by N_2 adsorption at 77 K in an Omnisorp sorptometer.

All the samples were tested in a fixed-bed flow reactor

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using 1 : 1 CO/H_2. Samples were reduced in situ in 100% hydrogen at 260°C and 1 atm for 4 h. The feed was introduced at 260°C and pressurized to setpoint. The catalyst remained at these conditions for 24–48 h before the temperature was increased. A Hewlett-Packard 5880 gas chromatograph and a 5995 GC-MS were used to analyze all the products. Both on-line and off-line samples were analyzed by GC-MS for CO_2, methanol, ethanol, linear C_3–C_6 primary alcohols, branched C_4–C_6 primary alcohols, secondary alcohols (isopropanol, 2-butanol), methane, ethane, linear C_3–C_{12} aliphatic hydrocarbons, branched C_4–C_6 hydrocarbons, ethylene, linear C_3–C_5 olefinic hydrocarbons, dimethyl ether (DME) and esters (methyl acetate, methyl propanoate, methyl *i*-butanoate).

3. Results and discussion

In table 1 we have summarized typical catalytic results obtained at 320°C and 50 atm using catalysts consisting of copper, ceria, magnesia and potassium. Methanol and isobutanol were the major products of the oxygenate fraction over CeO_2 (column 2). The product distribution of both the alcohol and hydrocarbon fraction did not follow a Schulz–Flory distribution and the branched alcohols/linear alcohols ratio (Bra/Lin) was high (4.2). This is consistent with previous reports on hydrocarbon synthesis [9,10] showing that ceria, and in general rare earth oxides, form selectively branched C_4 hydrocarbons from $CO + H_2$ at severe reaction conditions (temperatures higher than 400°C, pressures greater than 300 atm). Nevertheless, ceria exhibited low activity with significant hydrocarbon formation, giving a total alcohols/total hydrocarbons ratio (Alc/Hyd) of nearly 1.7. The addition of 7 wt% Cu to CeO_2 increased dramatically the productivities to methanol and isobutanol and, as a result, the Alc/Hyd ratio increased to ca. 3.3 (column 3). The formation of linear C_{2+} alcohols became significant and the Bra/Lin ratio decreased from 4.2 (ceria) to nearly 0.9. When copper oxide was coprecipitated with magnesia and ceria, the catalytic activity as well as selectivity and productivity to isobutanol clearly increased, whereas the productivity to methanol did not change significantly ($Cu_{0.5}Mg_5CeO_x$ catalyst, column 4). Compared with the 7% Cu/CeO_2 catalyst, CO conversion increased from 16.4 to 20.8% and isobutanol productivity from 5.1 to 7.1 g/(kg_{cat} h). The gain in isobutanol productivity was accompanied by a simultaneous decrease of the formation rate of linear alcohols and, as a consequence, the Bra/Lin ratio increased from 0.9 (7% Cu/CeO_2) to 3.7. On a methanol-free basis, isobutanol represented about 75% of the alcohol fraction. Finally, the impregnation of $Cu_{0.5}Mg_5CeO_x$ catalyst with 1% potassium produced a less active catalyst; however, the presence of the alkali dopant decreased the formation rate of hydrocarbons and DME. As a consequence, the alcohol selectivity increased and the Alc/Hyd ratio went from 2.8 to 4.1. The K-doped $Cu_{0.5}Mg_5CeO_x$ catalyst had similar isobutanol and methanol productivities as the undoped catalyst.

Table 1 shows a catalyst consisting of metallic copper in a coprecipitated mixture of ceria and magnesia that selectively produces methanol and isobutanol mixtures from syngas at relatively low temperatures and pressures. The selective formation of isobutanol in the C_{2+} alcohol fraction also occurred when ceria was replaced in the catalyst formulation either by other rare earth oxides or by yttria, and magnesium was replaced by other alkaline earth metals. Table 2 illustrates the results obtained at 290°C over three catalysts containing metallic copper, magnesium oxide and a second oxide consisting of yttria, ceria, neodymia, or mixtures thereof. With

Table 1
Alcohol synthesis (productivities, expressed in g/(kg_{cat} h)) over the Cu/Ce/Mg/K catalytic system. $T = 320°C$, GHSV = 1832 cm^3(STP)/(g_{cat} h), $H_2 : CO = 1$, $P = 50$ atm. Data measured after 120 h into the run

Product	CeO_2	7% Cu/CeO_2	$Cu_{0.5}Mg_5CeO_x$	1% $K/Cu_{0.5}Mg_5CeO_x$
methanol	8.41	60.0	64.0	66.8
ethanol	0.18	4.61	0.77	1.45
1-propanol	0.12	3.33	1.02	1.84
1-butanol	0	0.43	0.07	0.17
isobutanol	1.24	5.14	7.07	7.16
1-pentanol	0.03	0.44	0.33	0.31
2-m-1-butanol	0.11	0.92	0.42	0.71
DME	0.11	0.72	2.82	1.04
methane	1.01	6.78	9.98	3.78
X_{CO}(%) [a]	3.5	16.4	20.8	15.5
Alc/Hyd [b] (%C)	1.7	3.3	2.3	4.1
Bra/Lin [c]	4.2	0.9	3.7	2.2

[a] CO conversion.

[b] Total alcohols/total hydrocarbons ratio.

[c] Branched C_4–C_6 alcohols/linear C_2–C_6 alcohols.

Table 2
Methanol and isobutanol synthesis (selectivities expressed in %C, CO_2-free basis) over ternary Cu–Mg–Y and quaternary Cu–Mg–Y(Nd)–Ce catalysts. $T = 290°C$, $GHSV = 1832\,cm^3(STP)/(g_{cat}\,h)$, $H_2 : CO = 1$, $P = 50$ atm. Data measured after 80 h into the run

Product	7% Cu/Mg_5YO_x	$Cu_{0.5}MgYCeO_x$	$Cu_{0.5}MgNdCeO_x$
methanol	82.5	83.2	82.6
isobutanol	5.4	5.9	8.2
total alcohols	90.6	92.3	93.0
X_{CO}(%) [a]	18.0	17.1	20.6
Alc/Hyd [b] (%C)	13.2	14.6	14.6

[a] CO conversion.

[b] Total alcohols/total hydrocarbons ratio.

all these catalysts, high methanol and isobutanol selectivities were obtained.

Thus, the proposed catalyst formulation appears to combine the hydrogenation function required to form methanol with the basic/aldol condensation function needed to promote branching. The different catalyst functions exist in close contact allowing interaction between the active components. Both the homogeneity and the crystalline phase composition of the present catalysts depended on the rare earth oxide/alkaline earth oxide ratio. Fig. 1 shows the XRD characterization of samples of Cu–Mg–(Ce, Y). When the magnesium content in the catalyst is relatively low (Mg/Ce or Mg/(Ce + Y) = 0.5), a solid solution exists that contains the individual oxide phases of CuO and MgO substituted into a crystalline CeO_2 structure ($Cu_{0.5}MgCe_2O_x$ and $Cu_{0.5}MgYCeO_x$ catalysts). For high magnesium loading (Mg/Ce(Y) = 5), the XRD characterization revealed the presence of a mixture of magnesium oxide and cerium (yttrium) oxide ($Cu_{0.5}Mg_5CeO_x$ and $Cu_{0.5}Mg_5YO_x$ catalysts). In addition to changes in catalyst composition, the synthesis technique also influences the precursor homogeneity and physicochemical properties of the resulting mixed oxides. The coprecipitation technique used here produced homogeneous precipitates which after thermal decomposition in air formed mixed metal oxides with high surface area (fig. 1).

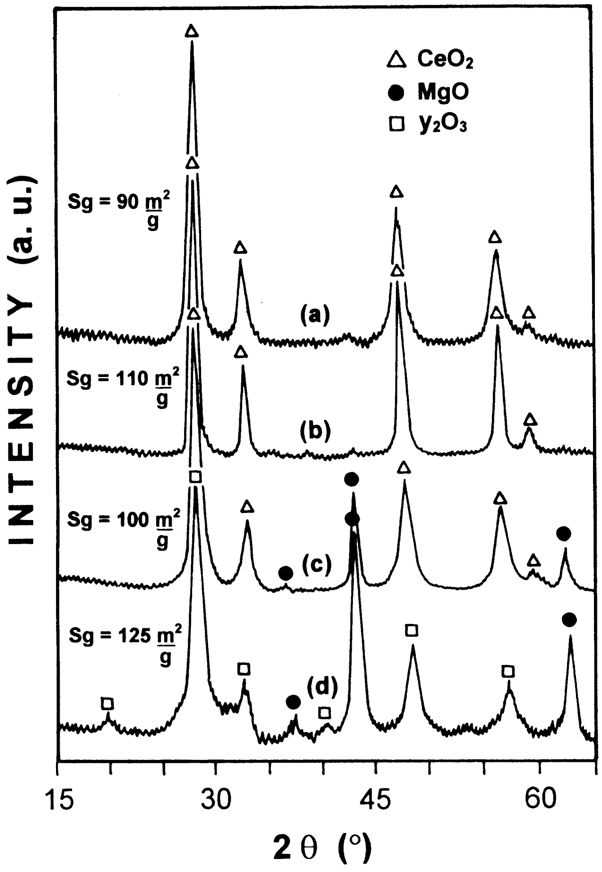

Fig. 1. XRD patterns of ternary Cu–Mg–Ce(Y) and quaternary Cu–Mg–Y–Ce mixed oxides. (a) $Cu_{0.5}MgYCeO_x$, (b) $Cu_{0.5}MgCe_2O_x$, (c) $Cu_{0.5}Mg_5CeO_x$; (d) $Cu_{0.5}Mg_5YO_x$.

In fig. 2, selectivities of the most abundant oxygenated products are reported as a function of temperature, which was increased from 260 to 330°C over a period of about 180 h after an initial 48 h stabilization period. While the methanol selectivity diminishes with increasing temperature, that of isobutanol increases. The C_{2+} linear alcohol selectivity passes through a maximum, whereas selectivity to branched C_5–C_6 alcohols increases with increasing reaction temperature. As a consequence, the oxygenate fraction became depleted in intermediates (ethanol, propanol) and enriched in branched alcohols. These results imply that at reaction conditions the exothermic methanol synthesis reaction is close to equilibrium, and thereby the conversion to methanol decreases by increasing the temperature. On the other hand, the increase of the isobutanol formation rate with temperature indicates that this reaction is kinetically controlled. Previous studies on higher alcohol synthesis [5,11,12] have proposed that the formation of branched alcohols occurs through a sequential mechanism involving three main steps: (i) synthesis of methanol and formation of a C_1 intermediate species, (ii) formation of the primary carbon–carbon bond, probably via the coupling of two C_1 intermediates, followed by a chain-building process dominated by C_1 addition to a C_n alcohol to produce a C_{n+1} alcohol, (iii) addition of the C_1 intermediate to the β carbon of a linear C_n alcohol to produce the branched C_{n+1} alcohol. Our results in fig. 2

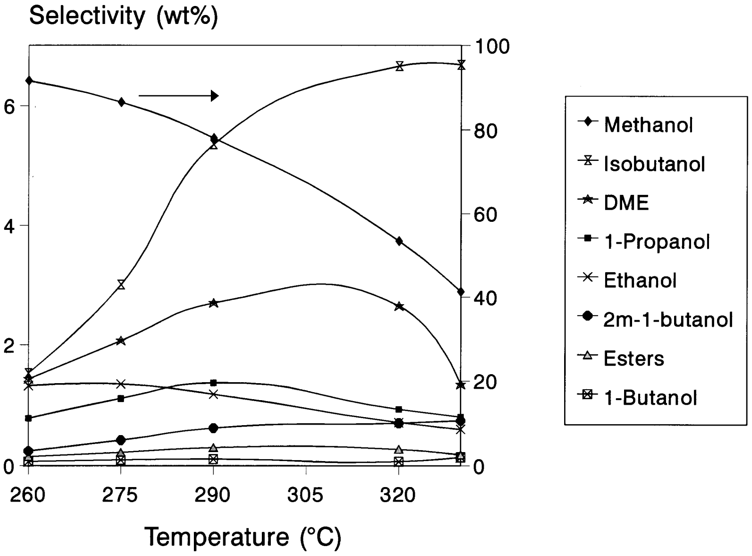

Fig. 2. Effect of temperature on oxygenate selectivities (selectivities expressed on a CO_2-free basis). Catalyst: $Cu_{0.5}Mg_5CeO_x$, GHSV = 1832 cm^3(STP)/(g_{cat} h), $H_2 : CO = 1, P = 50$ atm.

agree with this mechanism where ethanol and propanol are key intermediates in the chain growth process whereas isobutanol is a terminal product due to its low intrinsic reactivity.

The effect of contact time on isobutanol/methanol ratio at three temperatures is presented in fig. 3 for 1% $K/Cu_{0.5}Mg_5CeO_x$ catalyst. It is observed that the isobutanol/methanol ratio increases with increasing contact time at each temperature. In general, long contact times favor isobutanol and branched alcohol formation while decreasing methanol slightly; linear alcohols (ethanol, propanol and butanol) do not change appreciably. These results are easily explained by considering the above stepwise chain growth and branching mechanism where methanol is a primary product, linear alcohols are intermediate compounds and branched alcohols are terminal products.

Figs. 2 and 3 therefore show that increasing temperature and longer contact times increase the isobutanol to methanol ratio. However, the production of CO_2, methane and higher hydrocarbons also increase at higher temperatures. In fig. 4 we have presented the selectivities to carbon dioxide, total alcohols, and total hydrocarbons obtained using the $Cu_{0.5}MgNdCeO_x$ catalyst at 260, 290, and 320°C. It is observed that selectivities to CO_2 and hydrocarbons, 1.4 and 6%, respectively, at 260°C, increase to 16 and 32% at 320°C. Carbon dioxide is produced via the water–gas-shift reaction

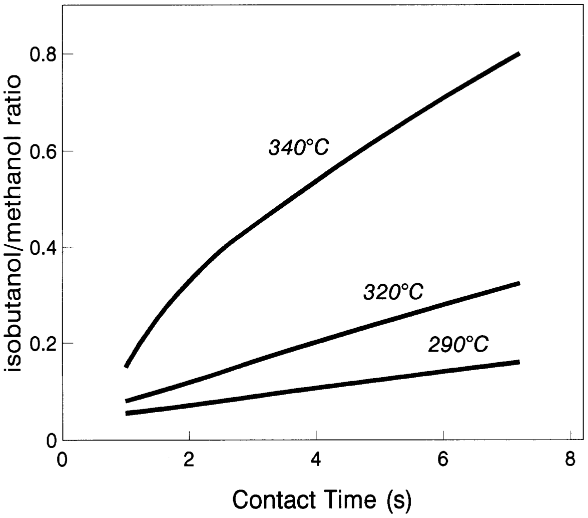

Fig. 3. Effect of contact time and temperature on isobutanol/methanol ratio. Catalyst: 1% $K/Cu_{0.5}Mg_5CeO_x$, $H_2 : CO = 1, P = 50$ atm.

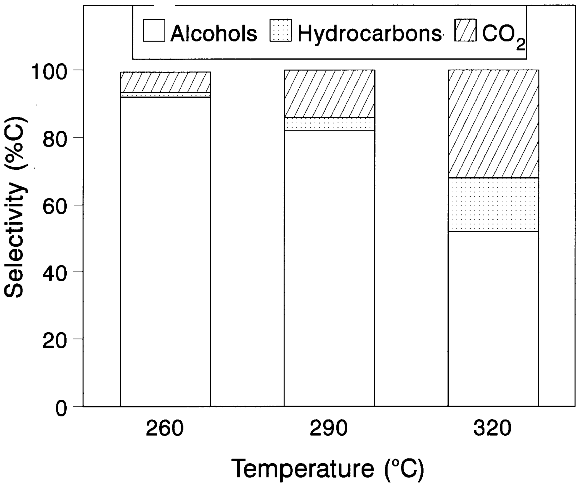

Fig. 4. Effect of temperature on global product distribution. Catalyst: $Cu_{0.5}MgNdCeO_x$, GHSV = 1832 cm^3 (STP)/(g_{cat} h), $H_2 : CO = 1$, $P = 50$ atm.

($CO + H_2O \rightleftharpoons CO_2 + H_2$). This reaction is catalyzed by copper and is favored by low $H_2 : CO$ ratios, high copper dispersion and water formation [13]. Finally, it is noted that long-term runs performed over the $Cu_{0.5}Mg_5CeO_x$ catalyst up to 500 h and from 290 to 350°C showed slow catalyst deactivation when temperatures higher than 340°C were employed, probably due to copper sintering.

In summary, the multicomponent catalysts presented in this paper are promising formulations for selectively producing methanol and isobutanol from $CO + H_2$ using mild reaction conditions. The multicomponent catalyst design provides the compositional and synthesis flexibility required for improving isobutanol formation from synthesis gas. Optimal compositions contain well mixed oxide components that catalyze the pathway methanol → ethanol → propanol → isobutanol efficiently so that short-chain linear alcohols are produced in very small amounts.

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