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One-Step MIBK Synthesis: A New Process from 2-Propanol

J. I. Di Cosimo,[1] G. Torres, and C. R. Apesteguía

Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE), Santiago del Estero 2654, (3000) Santa Fe, Argentina

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The one-step MIBK synthesis from 2-propanol was investigated as an alternative process to current conventional technology that produces MIBK from acetone. The reaction was studied at 473 K and atmospheric pressure using bifunctional Cu-base catalysts. Single M_IO_x, binary $M_IM_{II}O_x$, and Cu-containing $CuM_I(M_{II})O_x$ mixed oxides, where M_I and M_{II} are metal cations such as Mg^{2+}, Al^{3+}, or Ce^{3+}, were obtained by thermal decomposition of precipitated precursors. The density and strength of surface basic sites were obtained by CO_2 chemisorption and by temperature-programmed desorption (TPD) of CO_2, whereas the acid site densities were measured by TPD of NH_3. The MIBK synthesis reaction network involves consecutively the initial 2-propanol dehydrogenation to acetone, the aldol condensation of acetone to mesityl oxide, and the final hydrogenation of this compound to MIBK. Cu/SiO_2 promoted 2-propanol dehydrogenation to acetone but did not form any C_6 condensation products. When copper was supported on protonic HY zeolite, 2-propanol was essentially dehydrated to propylene and the formation of acetone was negligible. Bifunctional Cu-base catalysts were active and selective for MIBK synthesis. The highest MIBK formation rates were obtained on Cu-base solids containing a high density of medium-strength Brønsted base-weak Lewis acid pair sites for promoting the acetone aldol condensation step. $CuMg_{10}Al_7O_x$ was the best catalyst because it contained in intimate contact highly dispersed Cu^0 crystallites with proper Al^{3+} Lewis sites and Mg^{+2}–O^{2-} basic pairs and efficiently combines the active sites required for consecutive reactions leading to MIBK. Catalysts containing strongly basic O^{2-} sites, such as $CuMg_{10}O_x$ and $CuMg_{10}Ce_2O_x$, presented lower condensation rates because isolated O^{2-} hindered stabilization of anionic intermediates for acetone condensation. The effect that the reacting atmosphere (N_2 or H_2) has on catalyst activity and selectivity was investigated on $CuMg_{10}Al_7O_x$. It was found that the catalyst activity is enhanced in N_2, but for a given 2-propanol conversion the selectivity for C_6 aldol condensation products is higher in hydrogen. MIBK yields as high as 25% were achieved in comparison to the 30% typically obtained in current commercial high-pressure processes from acetone. © 2002 Elsevier Science (USA)

Key Words: **MIBK synthesis; bifunctional catalysis; 2-propanol conversion; aldol condensation.**

1. INTRODUCTION

4-Methyl-2-pentanone (methyl isobutyl ketone, MIBK) is a valuable product among the "commodities" with wide applications as a solvent in the manufacture of important chemicals such as inks and lacquers (1). MIBK has been traditionally produced from acetone in a three-step catalytic process: acetone is first converted into diacetone alcohol (DAA) by a liquid-phase base- or acid-catalyzed aldol condensation reaction; DAA is then rapidly dehydrated on an acid catalyst to mesityl oxide (MO), and finally the C=C bond of MO is hydrogenated on a metal, e.g., Ni, to yield MIBK.

Nowadays, MIBK is industrially obtained from acetone (DMK) in one step in trickle-type reactors at low temperatures (393–433 K) and high pressures (1–10 MPa) on multifunctional catalysts such as Pd or Pt supported on sulfonated resins, which contain condensation, dehydration, and hydrogenation functions (1–3). Both the aldol condensation and the dehydration reactions are reversible under these reaction conditions (2) but the catalyst shifts the equilibrium in favor of MO by irreversibly hydrogenating it to MIBK (4). In the one-step synthesis from acetone, acetone conversion is typically 30–40% and the selectivity to MIBK reaches 90% (5); the whole process is more practical and economical than the three-step process. However, MIBK concentration in the reactor effluents before distillation is usually lower than 30 wt%. In addition to the concomitant purification cost, the process requires high pressures to operate efficiently and there is therefore a great interest in developing new one-step gas-phase processes able to operate at atmospheric pressure. Recently, promising catalysts with very different acid–base properties, such as Pd (4) or Ni (6) supported on hydrotalcite-derived Mg–Al oxides, Cu/MgO (7), or Pd(Ni)/AlPON (8, 9) and Pt on HZSM5 (10) or HMFI (11), have been reported for this purpose.

However, in all these processes acetone must be obtained from other sources, such as 2-propanol in a previous step. Acetone from 2-propanol is typically carried out in fixed-bed reactors at 493–573 K on Cu-base catalysts (12). In this process, unreacted 2-propanol is recycled, and hydrogen and acetone are stripped from the product mixture and sent to the MIBK synthesis unit. However acetone must be

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[1] To whom correspondence should be addressed. Fax: 54-342-4531068. E-mail: dicosimo@fiqus.unl.edu.ar.

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previously purified and cooled down, thus increasing the operating cost of the MIBK synthesis.

The main consecutive reactions involved in the reaction network from 2-propanol are the following: (i) dehydrogenation of 2-propanol; (ii) self-condensation of the resulting acetone to mesityl oxide (MO); and (iii) hydrogenation of MO to MIBK.

The purpose of the present work is to explore the development of a new process for the synthesis of MIBK in one step at mild temperatures and atmospheric pressure using 2-propanol as reactant. This process is intended to be used in solvent manufacturing plants where producing a mixture of acetone, MIBK, and other higher oxygenates would present high commercial interest. In particular, the direct 2-propanol-to-MIBK process would be more suitable when the market demand for MIBK is low and the energy consumption and the intermediate purification cost of the synthesis from acetone make it noncompetitive.

Although there are no antecedents in the literature of direct MIBK synthesis from 2-propanol, this process presents other practical advantages, such as overcoming the unfavorable thermodynamics of the low-temperature MIBK synthesis from acetone, which forms concomitantly significant amounts of 2-propanol (7). Furthermore, 2-propanol is commonly used in fine chemistry hydrogen transfer reactions like the Meerwein–Pondorff–Verley reduction of ketones or aldehydes (13, 14). The known hydrogen-donor capacity of 2-propanol would make it possible to carry out the MIBK synthesis from 2-propanol without supplying gas-phase hydrogen.

In this paper, we study the MIBK synthesis from 2-propanol using bifunctional catalysts that combine in intimate contact a metallic function needed for the hydrogenation–dehydrogenation steps with an acid–base site required by the aldol condensation reaction. Specifically, we have prepared and characterized Cu-base catalysts and we have measured their catalytic properties. We have chosen Cu metal because of its known catalytic properties in the conversion of alcohols to carbonyl compounds such as aldehydes (15) and ketones (16) at low temperatures and by its ability to remove hydrogen atoms from alcohols without breaking the C–O bond (17). Solid bases such as single or mixed oxides containing Mg, Ce, or Al have been chosen for their moderate basic properties.

Results show that our bifunctional Cu-base catalysts are promising material for the novel one-step synthesis of MIBK from 2-propanol at low temperature and atmospheric pressure. The highest activity and selectivity for MIBK formation was obtained on a $CuMg_{10}Al_7O_x$ mixed oxide containing 6.4 wt% Cu. We investigated on this sample the effect of the reaction atmosphere (H_2 or N_2) on the catalyst activity, selectivity, and stability. We also studied the effect the nature of catalyst surface sites (metallic, acid, or base sites) has on the surface properties and catalytic performance. Furthermore, we identified primary and secondary pathways involved in the MIBK synthesis reaction mechanism by varying the contact time in the catalytic tests.

2. EXPERIMENTAL

2.1. *Catalyst Preparation*

Catalyst precursors of single M_IO_x, binary $M_IM_{II}O_x$, or Cu-containing $CuM_I(M_{II})O_x$ mixed oxides, where M_I and M_{II} are metal cations such as Mg^{2+}, Al^{3+}, or Ce^{3+}, were prepared by coprecipitation following similar procedures. For ternary $CuM_IM_{II}O_x$ catalysts, an aqueous solution of the metal nitrates with a total $[Cu^{2+} + M_I + M_{II}]$ cation concentration of 1.5 M was contacted with an aqueous solution of KOH and K_2CO_3 at a constant pH of 10. Both solutions were simultaneously added dropwise to 300 ml of distilled water kept at 338 K in a stirred batch reactor. The resulting precipitates were aged for 2 h at 338 K in their mother liquor and then filtered, washed thoroughly with 900 ml of deionized water at 373 K, and finally dried at 393 K overnight. Dried precipitates were decomposed overnight in air at 723–773 K in order to obtain the corresponding mixed oxides.

In addition, Cu/SiO_2 (SiO_2, Grace 62, 99.7%) and Cu/HY (from NaY, UOP) samples were prepared by incipient wetness impregnation by dropwise addition of an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ with a copper concentration of 0.6 M.

2.2. *Catalyst Characterization*

The crystalline phases in the coprecipitates and in the mixed oxides were determined by X-ray diffraction (XRD) using a Shimadzu XD-D1 diffractometer and Ni-filtered Cu$K\alpha$ radiation. Crystallite sizes were calculated from the CuO(111) diffraction lines using the Scherrer equation.

The total base site densities (n_b) were determined by irreversible CO_2 chemisorption at room temperature. Details are given elsewhere (18). CO_2 adsorption site densities and binding energies were obtained from temperature-programmed desorption (TPD) of CO_2 preadsorbed at room temperature. Samples (150 mg) were pretreated in N_2 at 773 K for 1 h and then exposed to a flow of 100 ml/min of 3% CO_2/N_2 at room temperature for 0.08 h. Weakly adsorbed CO_2 was removed by flowing N_2 and then the temperature was increased to 773 K at 10 K/min. The reactor effluent was fed into a methanator operating at 673 K to convert CO_2 in methane and then analyzed by a flame ionization detector.

Acid site densities were measured by TPD of NH_3 preadsorbed at room temperature. Samples (100 mg) were pretreated in He at 773 K for 1 h and then exposed to pulses of NH_3 until saturation. Weakly adsorbed NH_3 was removed by flowing He and then the temperature was increased to 773 K at 10 K/min. The NH_3 concentration in the effluent was analyzed by a thermal conductivity detector.

BET surface areas (S_g) were measured by N_2 physisorption at its boiling point using a Quantachrome Nova-1000 sorptometer. Potassium and copper contents of the samples were determined by atomic absorption spectroscopy (AAS).

2.3. *Catalytic Testing*

Catalytic tests were conducted at 473 K and atmospheric pressure in a fixed-bed reactor. Samples sieved at 0.35–0.42 mm were pretreated in N_2 at 723–773 K for 1 h before reaction in order to remove adsorbed H_2O and CO_2. In addition, Cu-containing catalysts were reduced *in situ* in flowing H_2 at 573 K for 1 h prior to the catalytic test.

The reactant, 2-propanol (Merck, ACS, 99.5% purity), was introduced via a syringe pump and vaporized into flowing N_2 or H_2 to give a 2-propanol partial pressure of 7.7 kPa. A low 2-propanol partial pressure was selected for analytical purposes in order to avoid excessive overcondensation and formation of heavy oxygenates (C_{9+} ketones and alcohols). Reaction products were analyzed by online gas chromatography using an ATI Unicam 610 chromatograph equipped with a flame ionization detector and a 0.2% Carbowax 1500/80-100 Carbopack C column. Data were collected every 1 h for 10 h. Main reaction products were identified as propane (C_3), acetone (DMK), methyl isobutyl ketone (MIBK), and methyl isobutyl carbinol (MIBC). At high conversion levels di-isobutyl ketone (DIBK) and other unidentified heavy condensation products were also obtained. Catalytic results were calculated at initial conditions, i.e., by extrapolation of the reactant and product concentration curves to zero time on stream.

3. RESULTS AND DISCUSSION

3.1. *Catalyst Characterization*

The physicochemical properties of the catalysts prepared in this work are given in Table 1. Most of $CuM_I(M_{II})O_x$ samples contained about 7 wt% Cu. The residual potassium level in all the samples was below 0.1 wt%, showing that K^+ was almost completely removed by washing the coprecipitated precursors.

X-ray diffraction patterns of unreduced $CuM_I(M_{II})O_x$ mixed oxides showed in all cases broad XRD lines corresponding to quasiamorphous structures, probably because the hydrated precursors were decomposed at low temperatures (723–773 K). Copper oxide (CuO, tenorite) was detected as a poorly crystalline phase, thereby suggesting that copper was highly dispersed in $M_I(M_{II})O_x$ mixed oxide matrix. The Mg^{2+} cations formed MgO and in cerium-containing oxides this metal was oxidized to CeO_2. The diffraction pattern for Cu/SiO_2 exhibited a well-defined CuO phase; calculations showed that on this sample the CuO crystallite size was about 250 Å.

TABLE 1

Characterization of $M_I(M_{II})O_x$, $CuM_I(M_{II})O_x$, Cu/SiO_2, and Cu/HY Catalysts: Chemical Composition, BET Surface Areas, and CO_2 Chemisorption Results

Catalyst	Cu loading[a] (wt%)	Surface area (m^2/g)	Base site density[b] ($\mu mol/m^2$)
Al_2O_3	—	230	0.7
$Mg_{10}Al_{20}O_x$	—	296	1.3
CeO_2	—	75	1.9
$Mg_{10}Ce_2O_x$	—	103	2.9
MgO	—	125	3.3
Cu/SiO_2	6.1	233	0.0
Cu/HY	6.7	340	<0.1
$CuAl_{16}O_x$	6.4	211	0.6
$CuMg_{10}Al_{20}O_x$	3.8	244	1.2
$CuMg_{10}Al_7O_x$	6.4	211	1.6
$CuCe_4O_x$	7.4	74	2.4
$CuMg_{10}Ce_2O_x$	6.9	102	3.0
$CuMg_{10}O_x$	10.1	150	3.1

[a] By AAS.

[b] By CO_2 chemisorption.

In previous work (19, 20), we characterized the surface basicity of different Mg-based oxides by using a variety of spectroscopic techniques and identified three different surface Brønsted basic sites. We also determined the following base strength order for these sites: low coordination O^{2-} anions > oxygen in Mg^{2+}–O^{2-} pairs > OH groups. In the present work, we have measured the total catalyst base site density (n_b) by CO_2 chemisorption and the relative base site strength by TPD of CO_2. The TPD traces for $M_I(M_{II})O_x$ and $CuM_I(M_{II})O_x$ samples are presented in Figs. 1a and 1b, respectively.

The n_b values for $CuM_I(M_{II})O_x$ samples and their homologues $M_I(M_{II})O_x$ are between 0.5 and 3.5 $\mu mol/m^2$ (Table 1). As a general trend, both the surface areas and the basic properties of $CuM_I(M_{II})O_x$ mixed oxides are very close to those determined for copper-free $M_I(M_{II})O_x$ samples. In fact, results in Table 1 and in Figs. 1a and 1b indicate that neither the base site density nor the site strength distribution of $M_I(M_{II})O_x$ samples are significantly modified by the addition of copper in the catalyst formulation. Nevertheless, it is observed in Table 1 that the n_b values depend on the acid–base properties of metal cations M_I and M_{II}. Mixed oxides containing Lewis acidic cations such as $CuAl_{16}O_x$ or Al_2O_3 present low base site densities ($n_b < 1$ $\mu mol/m^2$) whereas n_b is higher than 3 $\mu mol/m^2$ for the oxides containing less-electronegative cations, such as $CuMg_{10}O_x$ or MgO. On the other hand, the number of surface basic sites in Cu/SiO_2 and Cu/HY samples is negligible.

Similarly, the TPD traces of Figs. 1a and 1b show that the relative base site strength depends on the electronegativity of the metal cations. In both $M_I(M_{II})O_x$ and $CuM_I(M_{II})O_x$ samples the Al^{3+} cations give rise to the weakest basic sites

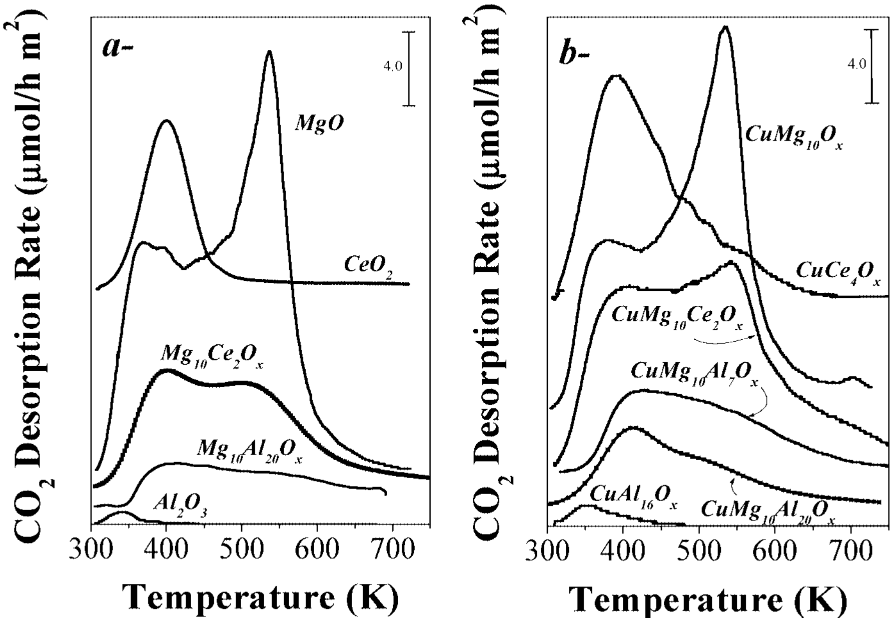


FIG. 1. CO_2 TPD traces. (a) $M_I(M_{II})O_x$ catalysts; (b) $CuM_I(M_{II})O_x$ catalysts.

(CO_2 desorption temperature ≈350 K), whereas Ce^{4+} introduces low- (≈400 K) and medium-strength (≈500 K) basic sites. The Mg^{2+} cations generate not only weak and medium basic sites but also strong basic sites shown as a high-temperature desorption peak (≈550 K).

3.2. The Role of Metallic Copper in MIBK Synthesis

To elucidate the effect of the metallic site on the synthesis of MIBK from 2-propanol, several catalytic experiments were carried out at 473 K with Cu/SiO_2, $CuM_I(M_{II})O_x$, and $M_I(M_{II})O_x$ catalysts feeding the reactor with a reactant mixture H_2/2-propanol = 12 (molar composition). The values of initial 2-propanol conversions (X_0) and initial selectivities obtained in the catalytic tests are shown in Table 2.

All the copper-free $M_I(M_{II})O_x$ oxides, excepting alumina, exhibit poor activity for 2-propanol conversion reactions; high contact times ($W/F^0_{C_3H_7OH} = 120$ g of cat h/mol) were needed to convert 2–12% 2-propanol. Alumina is a well-known dehydration catalyst and readily converts 2-propanol to propylene, which resulted in the main reaction product. MIBK and MIBC were the only C_6 condensation products formed. In no case was the C_6 α,β-unsaturated intermediate (mesityl oxide, MO) detected. The lack of MO among the reaction products may be attributed to the known ability of basic oxides for promoting the hydrogen transfer reduction of α,β-unsaturated ketones to the corresponding saturated ketones and alcohols when 2-propanol is the hydrogen donor (13). Formation of MIBC via a MO hydrogen transfer reduction may also explain the low MIBK/MIBC selectivity ratios obtained on $M_I(M_{II})O_x$ samples.

The Cu/SiO_2 sample efficiently promotes 2-propanol dehydrogenation to DMK but does not form any C_6 condensation product. This is consistent with results given in Table 1 which show that silica does not contain surface basic sites.

Copper-containing $CuM_I(M_{II})O_x$ samples are much more active than the $M_I(M_{II})O_x$ oxides. As shown in Fig. 2, the 2-propanol conversion rate was about three orders of magnitude higher on $CuM_I(M_{II})O_x$ oxides than on the

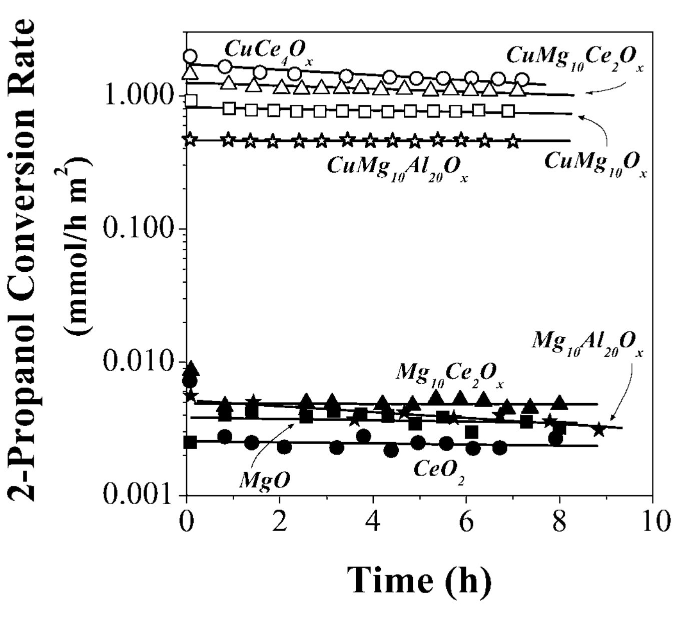


FIG. 2. 2-Propanol conversion rates on $M_I(M_{II})O_x$ and $CuM_I(M_{II})O_x$ catalysts as a function of time on stream (473 K, 101.3 kPa total pressure; H_2/2-propanol = 12).

TABLE 2

Catalytic Results for 2-Propanol Conversion on $M_I(M_{II})O_x$, $CuM_I(M_{II})O_x$, Cu/SiO_2, and Cu/HY Catalysts[a]

Catalyst	$W/F^0_{C_3H_7OH}$ (gh/mol)	Initial 2-propanol conversion (%)	Initial selectivity (carbon atom %)						
			C_3	DMK	MIBK	MIBC	Others[b]	MIBK/MIBC	Total C_6
Al_2O_3	120	58.9	48.1	17.3	0.3	0.4	14.3	0.7	0.7
$Mg_{10}Al_{20}O_x$	120	11.9	3.4	46.0	6.6	22.2	21.8	0.3	28.8
CeO_2	120	2.4	3.0	77.8	1.2	9.1	8.9	0.1	10.3
$Mg_{10}Ce_2O_x$	120	6.1	0.6	81.8	1.6	8.7	7.3	0.2	10.3
MgO	120	7.2	0.2	80.7	1.8	10.6	6.7	0.2	12.4
Cu/SiO_2	10	41.7	0.4	99.6	0.0	0.0	0.0	—	0.0
Cu/HY	0.2	43.3	71.0	0.1	0.0	0.0	—	—	0.0
$CuAl_{16}O_x$	3.6	41.0	1.9	92.8	1.8	1.1	2.4	1.6	2.9
$CuMg_{10}Al_{20}O_x$	3.6	40.0	0.2	87.0	6.7	4.6	1.5	1.5	11.3
$CuMg_{10}Al_7O_x$	1.2	41.2	<0.1	73.9	11.3	8.1	6.6	1.4	19.4
$CuCe_4O_x$	3.6	45.6	0.0	68.9	10.4	8.2	12.5	1.3	18.6
$CuMg_{10}Ce_2O_x$	3.6	43.4	<0.1	85.9	7.6	5.1	1.3	1.5	12.7
$CuMg_{10}O_x$	3.6	42.2	0.1	88.3	6.1	4.0	1.5	1.5	10.1

[a] $T = 473$ K, $P = 101.3$ kPa, H_2/2-propanol = 12.

[b] DIBK, di-isopropyl ether and C_{9+} oxygenates.

homologues $M_I(M_{II})O_x$ catalysts. This activity difference cannot be explained by modifications in catalyst basicity because the base site density and strength of $M_I(M_{II})O_x$ samples are not changed by addition of copper in the catalyst formulation (Fig. 1). The higher activity measured for bifunctional $CuM_I(M_{II})O_x$ catalysts is due, in fact, to the ability of Cu^0 atoms finely dispersed in the oxide matrix to promote the α-proton abstraction rate from 2-propanol, leading to a remarkable enhancement of the DMK formation rate.

In Table 2 we also present the product distribution obtained on $CuM_I(M_{II})O_x$ samples at isoconversion ($X_0 =$ 40%). Catalytic tests were performed at $W/F^0_{C_3H_7OH} =$ 3.6 g of cat h/mol except for the $CuMg_{10}Al_7O_x$ sample, which showed a higher activity and reached 40% 2-propanol conversion at $W/F^0_{C_3H_7OH} = 1.2$ g of cat h/mol. On $CuM_I(M_{II})O_x$ samples the selectivity toward MIBK was higher than that to MIBC, thereby indicating that MIBK formation is favored in the presence of metallic copper. Furthermore, the MIBK/MIBC ratio did not depend on the catalyst basic properties and was about 1.5 for all the samples.

3.3. *The Role of Catalyst Acid or Base Properties in MIBK Synthesis*

In previous work we studied the reaction pathways followed by primary (20, 21) and secondary (19) alcohols on strongly basic copper-free Mg-based catalysts such as Mg–Al mixed oxides or alkali-promoted MgO. We found that on these materials the active site for dehydrogenation and aldol condensation reactions is a Brønsted base–Lewis acid surface pair site of moderate basic properties. In the present work, we have tested bifunctional $CuM_I(M_{II})O_x$ catalysts in the synthesis of MIBK from 2-propanol to investigate the effect of both Brønsted basic sites (oxygen anions) and moderately acidic Lewis sites (metals cations M_I and M_{II}) on the product selectivity. Table 2 shows the product distribution obtained at about 40% 2-propanol initial conversion.

The $CuAl_{16}O_x$ catalyst produces essentially DMK because it is not basic enough to catalyze the consecutive C–C bond formation reaction required to yield C_6 condensation products. The dehydrating activity to C_3 of this sample is attributed to the acidic Al^{3+} cations. Incorporation of 16.2 wt% of a less electronegative cation such as Mg^{2+} in the catalyst formulation (sample $CuMg_{10}Al_{20}O_x$) decreases the dehydrating activity compared to $CuAl_{16}O_x$ and gives rise to a moderate formation of condensation products (11.3% selectivity toward C_6 compounds). This is consistent with the fact that the $CuMg_{10}Al_{20}O_x$ sample contains more (Table 1) and stronger (Fig. 1b) surface basic sites compared to $CuAl_{16}O_x$.

$CuMg_{10}O_x$ and $CuMg_{10}Ce_2O_x$ oxides contain a high concentration of Mg^{2+} ions that generate strongly basic O^{2-} sites (Fig. 1b). On these catalysts, the dehydrating activity is completely suppressed but no notorious enhancement on the C_6 product formation is observed because the isolated low-coordination O^{2-} sites are almost inactive for C–C bond formation (21).

$CuCe_4O_x$ and $CuMg_{10}Al_7O_x$ are solids of intermediate basicity on which neither the weakest nor the strongest basic sites dominate on the surface. These catalysts exhibited the highest selectivity to condensation compounds, producing about 20% C_6 products at $X_0 = 40\%$. They also yielded significant amounts of DIBK, a valuable C_9 product formed by consecutive aldol condensation of DMK and MIBK. These results confirm previous reports (21) showing that an adequate balance between the basic sites (O^{2-} surface anions) and the neighboring Lewis acidic sites (Mg^{2+}, Ce^{4+}, or Al^{3+} metal cations) is required to efficiently catalyze the aldol condensation step. The role of the Lewis acid sites is to stabilize the anionic intermediates in the C–C bond formation reaction.

Since the presence of Lewis acid sites is necessary for promoting aldol condensation reactions, we investigated whether Brønsted acidic sites could similarly catalyze C–C bond-forming reactions leading to MIBK from 2-propanol. Previous reports have shown that Brønsted solid acids promote the aldol condensation of acetone to MO and hydrocarbons (22, 23) and that bifunctional metal–Brønsted acid catalysts convert acetone to MIBK (11, 24). We prepared a Cu/HY catalyst (Table 1) to explore the Brønsted acid-catalyzed pathways for 2-propanol conversion reactions. The base site density of the Cu/HY sample measured by TPD of CO_2 was 0.03 μmol/m^2 whereas the density of Brønsted acidic sites measured by NH_3 TPD was 3.7 μmol/m^2. The TPD characterization reveals, as expected, the typical strong surface acidity of HY zeolites. Catalytic results show (Table 2) that Cu/HY converts essentially 2-propanol to C_3. Brønsted acid sites dehydrate 2-propanol to propylene ($C_3{=}$) which in the presence of Cu^0 atoms and gaseous H_2 is readily converted to C_3. It is noteworthy that although C_3 is the main reaction product, with a selectivity of about 70%, the total product selectivity does not add 100% because the $C_3{=}$ intermediates yield coke-forming polymeric hydrocarbons that remain adsorbed on the catalyst surface. In summary, formation of DMK on Cu/HY is negligible and the synthesis of C_6 condensation products from 2-propanol via Brønsted acid-catalyzed pathways is therefore unlikely.

3.4. Effect of the Contact Time and the Reaction Atmosphere

In the overall reaction from 2-propanol to MIBC, i.e., $2\ C_3H_7OH \rightarrow C_6H_{13}OH + H_2O$, the hydrogen amount generated by initial dehydrogenation of 2-propanol to DMK is stoichiometrical enough to totally hydrogenate the MO molecule in consecutive steps, leading to MIBK and MIBC. Thus, the supply of hydrogen in the feed might not be necessary for MIBK or MIBC synthesis. We investigated the effect of the reaction atmosphere on the activity and product distribution for 2-propanol conversion reactions. The catalytic tests were performed on $CuMg_{10}Al_7O_x$, the most active and selective of the catalysts used in this work. Experiments were carried out by vaporizing 2-propanol in pure N_2 or H_2 and varying $W/F^0_{C_3H_7OH}$ between 0.4 and 8 g of cat h/mol.

In Fig. 3a, the initial molar yields, η_i^0 (η_i, mol of product i/mol of 2-propanol in the feed) and the corresponding initial 2-propanol conversions obtained on $CuMg_{10}Al_7O_x$ in H_2 are plotted as a function of contact time. The local slope of the curves in Fig. 3a is the formation rate of each product at a given alcohol conversion and contact time. The nonzero initial slope of the DMK curve is consistent with direct formation from 2-propanol and the maximum reflects the conversion of acetone in higher oxygenates by consecutive aldol condensation pathways at increasing contact times. The initial zero slopes for MIBK and MIBC formation reveal, in fact, that these products are produced via consecutive reactions from primary DMK. The C_9 product, DIBK, clearly forms from MIBK. The highest 2-propanol conversion measured in H_2 was about 70%, with a MIBK concentration of 14 wt%.

Catalytic tests carried out in N_2 (Fig. 3b), show that the DMK, MIBK, and MIBC formation pathways are similar to

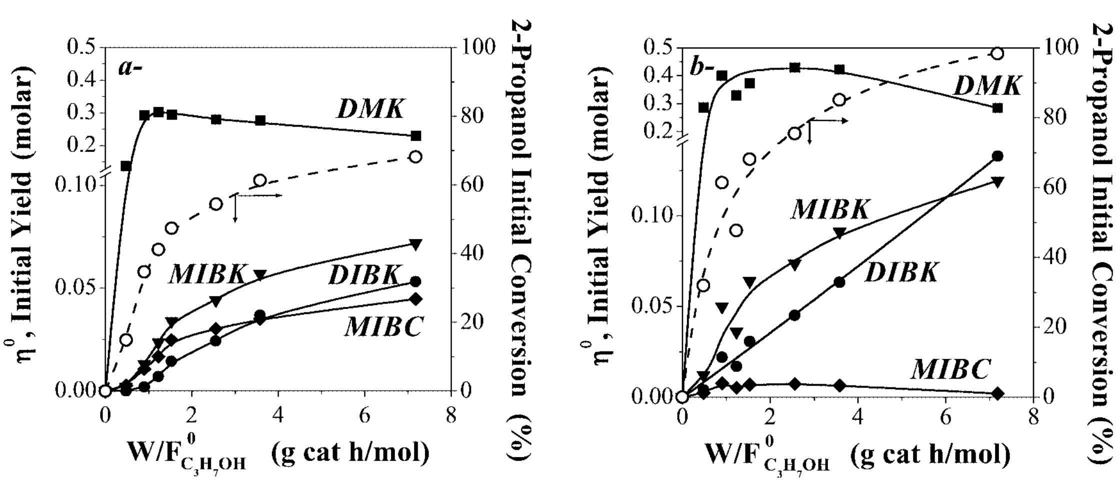


FIG. 3. Effect of the reaction atmosphere on activity and product distribution. 2-Propanol initial conversion and initial product yields as a function of contact time ($CuMg_{10}Al_7O_x$ catalyst, 473 K, 101.3 kPa total pressure). (a) H_2/2-propanol = 12; (b) N_2/2-propanol = 12.

those in H_2 but the yields to MIBK and DIBK improved at the expense of MIBC. This result indicates that when only surface-generated hydrogen is present in 2-propanol conversion reactions, the MIBK aldol condensation to DIBK is favored as compared to MIBK hydrogenation to MIBC. For instance, at total 2-propanol conversion, the DIBK concentration in reactor effluents was 37 wt% whereas that of MIBC was only 0.4 wt%.

On the other hand, it must be noted that MIBK concentrations as high as 25 wt% can be reached in N_2.

In Fig. 4 we have plotted the MIBK/MIBC selectivity ratio as a function of 2-propanol conversion. It is observed that in H_2 the MIBK/MIBC ratio is about 1 and increases slightly, with 2-propanol conversion reaching a value of 1.6 at $X_0 \cong 70\%$. When the reaction is conducted in N_2, the MIBK/MIBC ratio is notoriously improved compared to the reaction in H_2, increasing from a value of 5 at low conversions to 60 at total 2-propanol conversion. These results strongly suggest that in N_2 the MIBK hydrogenation rate to MIBC is not significant because of insufficient surface-generated H_2 pressure.

Inspection of Fig. 3 shows that the activity of $CuMg_{10}Al_7O_x$ for 2-propanol conversion is much higher in N_2 than in H_2. Total conversion of 2-propanol on $CuMg_{10}Al_7O_x$ is reached in N_2 at $W/F^0_{C_3H_7OH}$ values close to 7 g of cat h/mol. Thermodynamically, the dehydrogenation of alcohols may be limited by the presence of hydrogen. However, calculations of the equilibrium conversion for 2-propanol dehydrogenation at 473 K and high H_2 partial pressure (H_2/2-propanol = 12) allow us to rule out a thermodynamic hindrance. Thus, the lower 2-propanol conversion rates measured on $CuMg_{10}Al_7O_x$ when replacing N_2 with H_2 as reaction atmosphere probably reflect a negative order with respect to H_2 in the reaction kinetics.

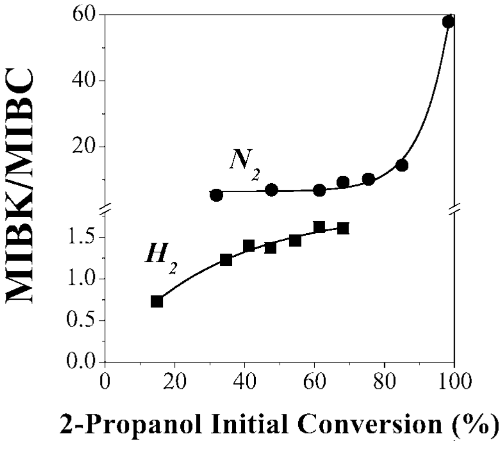


FIG. 4. Effect of the reaction atmosphere on C_6 compound selectivity ratio. MIBK/MIBC ratio as a function of 2-propanol conversion ($CuMg_{10}Al_7O_x$ catalyst, 473 K, 101.3 kPa total pressure; $H_2(N_2)$/2-propanol = 12).

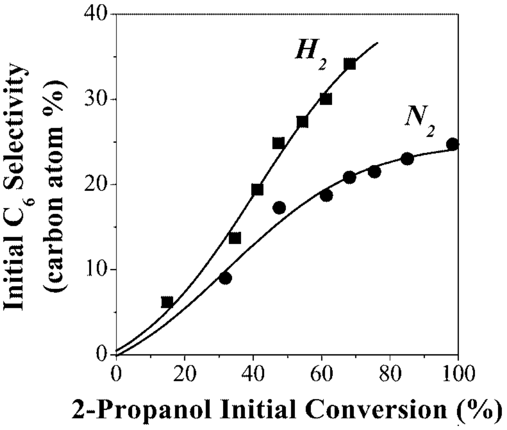


FIG. 5. Effect of the reaction atmosphere on aldol condensation product selectivity. Initial selectivity to C_6 compounds as a function of 2-propanol conversion ($CuMg_{10}Al_7O_x$ catalyst, 473 K, 101.3 kPa total pressure; $H_2(N_2)$/2-propanol = 12).

In contrast, the total selectivity toward C_6 aldol condensation products at a given 2-propanol conversion is higher in H_2 than in N_2 (Fig. 5). Results of Fig. 5 may be interpreted by considering that in the presence of gas-phase H_2, the aldol condensation products are more easily formed and released to the gas phase. Hydrogen pressures higher than those provided by the 2-propanol dehydrogenation reaction would be required, then, in the last reaction step (MO hydrogenation) to increase C_6 product selectivity.

Finally, we point out that the catalyst activity decay on-stream was not significantly affected by the nature of the reaction atmosphere. Results of Fig. 6a and 6b obtained in H_2 and N_2, respectively, at similar 2-propanol initial conversions ($X_0 \cong 60\%$) show that the catalyst deactivation rate was similar in both atmospheres.

3.5. Reaction Pathways for the Synthesis of MIBK on Bifunctional Cu^0-Base Catalysts

Based on catalytic results obtained on $M_I(M_{II})O_x$ and $CuM_I(M_{II})O_x$ samples we postulate in Scheme 1 the probable reaction pathways involved in the synthesis of MIBK from 2-propanol.

In the first reaction step, 2-propanol is either dehydrogenated to DMK or dehydrated to propylene. Because DMK is the intermediate required to yield MIBK, a potential catalytic material for MIBK synthesis must be active and selective for 2-propanol dehydrogenation.

On copper-free basic catalysts, 2-propanol is dissociatively adsorbed on Brønsted base–Lewis acid pair sites which break the O–H bond and form a surface alkoxide intermediate. The subsequent abstraction of H^α or H^β from the 2-propoxide anion intermediate leads to DMK or C_3=, respectively. Predominant formation of either ketone or olefin will depend therefore on the relative acidity

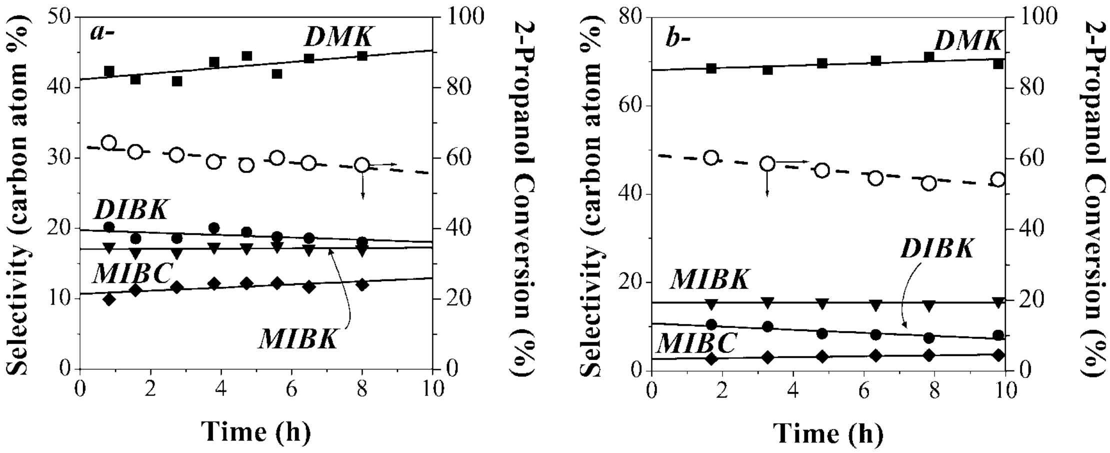
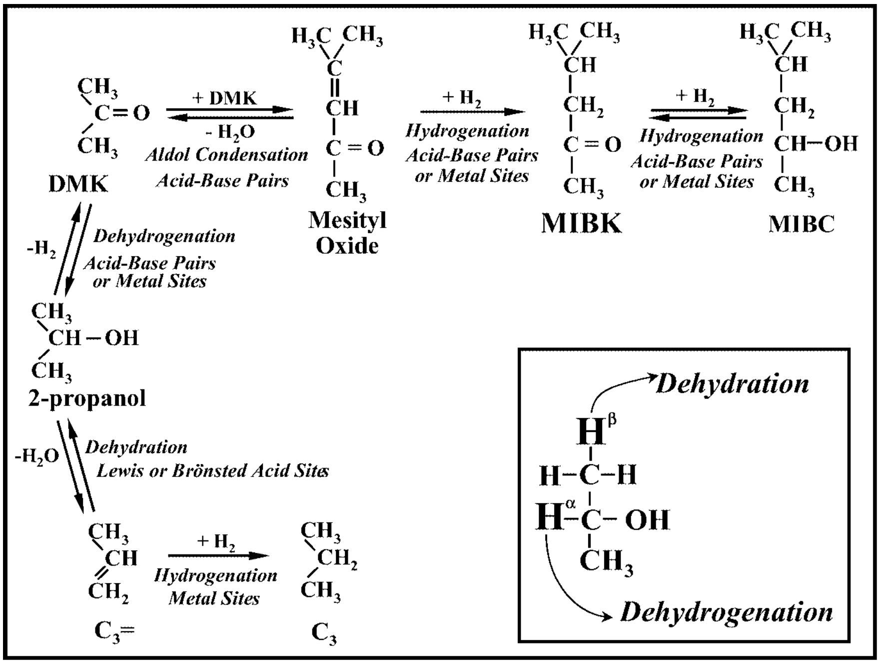


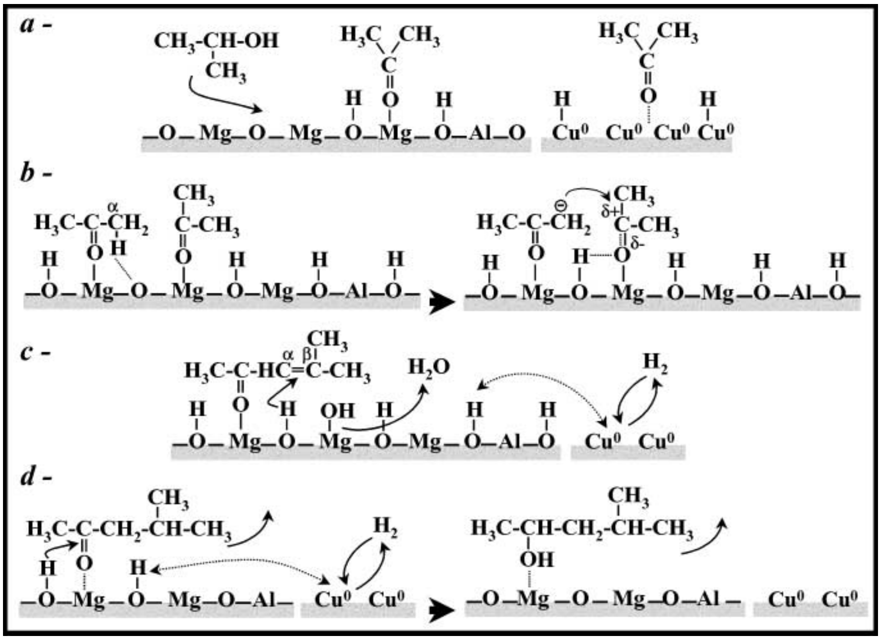
FIG. 6. Effect of the reaction atmosphere on catalyst deactivation. 2-Propanol conversion and product selectivities as a function of time on stream ($CuMg_{10}Al_7O_x$ catalyst, 473 K, 101.3 kPa total pressure). (a) H_2/2-propanol = 12, $W/F^0_{C_3H_7OH} = 3.6$ g h/mol; (b) N_2/2-propanol = 12, $W/F^0_{C_3H_7OH} =$ 0.9 g h/mol.

of H^α and H^β and on the catalyst dehydrogenating-dehydrating properties. In a previous work (19) we studied the 2-propanol conversion on MgO-based catalysts and found that 2-propanol dehydrogenation to DMK, which takes place via an anionic E_{1cB}-like mechanism on Brønsted base–Lewis acid pair sites, is significantly more rapid than its dehydration to propylene. In agreement with these results, we observe here that $M_I(M_{II})O_x$ samples form essentially DMK, the selectivity to C_3= being lower than 4% in all these basic materials (Table 2). In contrast, on alumina the 2-propanol conversion rate to C_3= is significantly higher than that to DMK. Alumina contains Al^{+3}–O^{2-} pair sites of weak basic strength, which promote the formation of propylene via E_2 elimination pathways.

Cu/SiO_2 selectively forms DMK from 2-propanol at reaction rates up to 1000 times faster than $M_I(M_{II})O_x$ oxides, thereby showing that metallic copper efficiently catalyzes alcohol dehydrogenation reactions. $CuM_I(M_{II})O_x$ samples were more active than Cu/SiO_2 for 2-propanol dehydrogenation probably because Cu is better dispersed in the



SCHEME 1. Reaction steps involved in the MIBK synthesis from 2-propanol on bifunctional $CuM_I(M_{II})O_x$ catalysts.



SCHEME 2. MIBK formation mechanism from 2-propanol on bifunctional $CuM_I(M_{II})O_x$ catalysts.

$M_I(M_{II})O_x$ matrix than on silica. 2-Propanol dehydrogenation on copper would occur via the formation of an alkoxide intermediate upon alcohol adsorption and further removal of the H^α, as has been postulated for ethanol dehydrogenation on Cu/ZnO by Chung *et al.* (25) and on Cu(110) by Wachs and Madix (26). Formation of DMK from 2-propanol on either surface Cu^0 atoms or acid–base pairs of bifunctional $CuMg_zAl_yO_x$ catalysts is illustrated in Scheme 2a.

However, when copper is supported on protonic HY zeolite 2-propanol is converted essentially to C_3= because the rate of 2-propanol dehydration on strongly Brønsted acid sites is significantly higher than that of 2-propanol dehydrogenation to DMK on metallic copper. Bifunctional Cu/Brønsted acid catalysts will not promote efficiently, then, the MIBK synthesis from 2-propanol. Propylene formation from 2-propanol on strong Brønsted acid sites occurs via a unimolecular E_1 mechanism in which a carbonium ion intermediate is involved (C–O bond cleavage) with no alkoxide formation (27).

In the second reaction step, DMK is converted to MO via an aldol condensation reaction (Scheme 1). Acetone condensation is a bimolecular reaction between adjacent acetone species adsorbed on medium-strength Brønsted base–weak Lewis acid pair sites (18, 28). Strong basic sites such as low-coordination O^{2-} anions present lower condensation rates because isolated O^{2-} hindered accommodation of anionic intermediates. Surface $O^{\delta-}$ Brønsted basic site abstracts the α-proton of the adsorbed DMK molecule forming a carbanion intermediate, which reacts with the carbonyl group of a second DMK molecule (Scheme 2b). Then, formation of α,β-unsaturated mesityl oxide and release of a water molecule occur, followed by the fast hydrogenation of MO to MIBK, as depicted in Scheme 2c. Gas-phase H_2 is dissociatively adsorbed and activated on Cu^0 atoms of $CuM_I(M_{II})O_x$ catalysts. The resulting surface hydrogen atoms migrate to the basic site and hydrogenate the C=C of the MO molecule. It appears that hydrogen activation and migration take place faster than the α,β-unsaturated intermediate desorption, thereby favoring the complete hydrogenation of MO to MIBK; no traces of gaseous MO were detected on our $CuM_I(M_{II})O_x$ catalysts, even at high conversion levels. However, MIBK is delivered to the gas phase before the C=O function is totally hydrogenated to MIBC (Scheme 2d), giving rise to MIBK/MIBC selectivity ratios of about 1.5 (Table 2) when catalytic tests are performed at high H_2 partial pressures ($P_{H_2} = 93.5$ kPa).

Bifunctional catalysts containing a dehydrogenating–hydrogenating metal supported on basic solids are potential catalytic materials for catalyzing the MIBK synthesis from 2-propanol. Metallic copper shows high 2-propanol dehydrogenation rates to DMK and also promotes the MO hydrogenation to MIBK. The rate-limiting step in the MIBK synthesis reaction mechanism is probably the DMK aldol condensation to MO which occurs on medium-strength Brønsted base–weak Lewis acid pair sites. The $CuMg_{10}Al_7O_x$ catalyst contains in intimate contact highly dispersed Cu^0 crystallites with proper Al^{3+} Lewis sites and Mg^{+2}–O^{2-} basic pairs and efficiently combines the active sites required for consecutive reactions leading to MIBK.

4. CONCLUSIONS

The one-step synthesis of MIBK from 2-propanol can be satisfactory carried out at mild temperatures and atmospheric pressure on catalytic materials containing in intimate contact the metallic and acid–base sites required for consecutive reactions leading to MIBK. The best results are obtained on copper-mixed oxide bifunctional catalysts in which Cu^0 atoms are finely dispersed in a matrix of moderately basic properties. At reasonable low contact times and depending on the reaction atmosphere, 2-propanol conversions between 70 and 100% can be reached, giving a reaction product mixture with up to 25 wt% MIBK and other valuable oxygenates, such as DMK, MIBC, and DIBK. These are promising results considering that in the commercial high-pressure synthesis process from acetone, MIBK concentrations are about 30 wt%, with acetone conversions lower than 40%.

Surface Cu^0 atoms efficiently promote 2-propanol dehydrogenation to acetone but do not form consecutively any C_6 condensation product because the C–C bond-forming reaction takes place on active acid–base pair sites.

Catalysts consisting of copper supported on strongly basic (Mg or Mg–Ce oxides) or acidic (Al oxide) solids are less selective for MIBK synthesis than are those containing copper on moderately basic Mg–Al oxides because the rate-limiting aldol condensation step requires an appropriate balance of medium-strength Brønsted base–weak Lewis acid sites. Bifunctional copper/strongly Brønsted acid catalysts convert 2-propanol essentially to propane and are therefore unsuitable for MIBK synthesis.

The $CuMg_{10}Al_7O_x$ catalyst is active and selective for MIBK formation from 2-propanol and does not show appreciable deactivation onstream, either in N_2 or H_2. Higher 2-propanol conversion rates are obtained in nitrogen, probably reflecting a negative order with respect to H_2 in the reaction kinetics. However, at similar conversion levels the selectivity to C_6 compounds (MIBK and MIBC) is lower in nitrogen because the aldol condensation products are more easily formed and released to the gas phase in hydrogen.

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