Journal of Catalysis **184,** 134–143 (1999)
Article ID jcat.1999.2437, available online at http://www.idealibrary.com on IDEAL®

One-Step Synthesis of Methyl Isobutyl Ketone from Acetone and Hydrogen over Cu-on-MgO Catalysts

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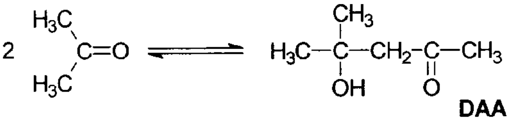
Received September 23, 1998; revised January 18, 1999; accepted January 26, 1999

The one-step synthesis of methyl isobutyl ketone (MIBK) from acetone and hydrogen over Cu-on-MgO catalysts was studied at atmospheric pressure in a fixed bed continuous flow reactor. Catalysts with various copper loadings were prepared by impregnation and coprecipitation and characterized by BET and Cu(0) surface area measurements, XRD, SAXS, thermal analysis, and basicity measurements. A 3.46% Cu-on-MgO prepared by coprecipitation, calcined at 723 K for 4 h, and pretreated in hydrogen (673 K, 1 h) showed high and stable activity and selectivity in the production of MIBK. Under the best conditions (553 K reaction temperature, 15% molar excess of hydrogen to acetone, and 1920 ml h^{-1} $gcat^{-1}$ space velocity) MIBK is formed in 45–48% yield (60–80% conversion and 60–75% selectivity) over a period of 24 h-on-stream. The results of deuterium labeling studies point to metallic sites catalyzing deuterium exchange and basic sites catalyzing dimerization of acetone, leading eventually to MIBK with high deuterium content. A comparison of deuterium contents of acetone, mesityl oxide (MO), and MIBK shows that the surface deuterium pool is highly diluted with hydrogen, formed during the exchange process. Deuterium incorporation during the saturation of the carbon–carbon double bond of MO to form MIBK, therefore, is less than expected. Formation of diisobutyl ketone with very low deuterium content is suggested to result from the involvement of strongly bound surface intermediates with long residence time not allowing exchange process. © 1999 Academic Press

Key Words: **acetone; methyl isobutyl ketone; copper on magnesia; one-step synthesis; deuterium labeling; basic surface sites.**

INTRODUCTION

4-Methyl-2-pentanone (methyl isobutyl ketone, MIBK) is an important chemical produced from acetone. It is an excellent solvent used in the manufacture of other important products (1) and in the extraction of inorganic salts, e.g., in the separation of plutonium from uranium, niobium from tantalum, and zirconium from hafnium. It is also applied in the production of paints and stabilizers. Although new, one-step processes operating in the gas phase at atmospheric pressure were introduced for the manufacture of MIBK applying supported Pd catalysts (2, 3); its large-scale commercial production is still carried out by the three-step catalytic process at moderate to high pressure (10–100 atm) in the liquid phase: acetone is transformed to diacetone alcohol (DAA) in an acid- or base-catalyzed aldol condensation (reaction 1), DAA is dehydrated to mesityl oxide (MO) in an acid-catalyzed process (reaction 2), and finally, mesityl oxide is hydrogenated on a noble metal catalyst to yield the final product MIBK (reaction 3). The problems associated with this approach are the unfavorable equilibrium of the first condensation step, the possibility of the reverse reaction of MO with water to form acetone in the second step, and the formation of a considerable amount of methyl isobutyl carbinol (MIBC) in the final hydrogenation step.



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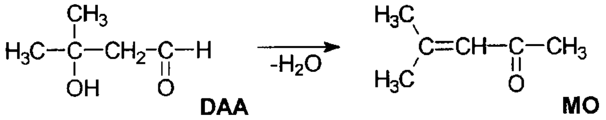

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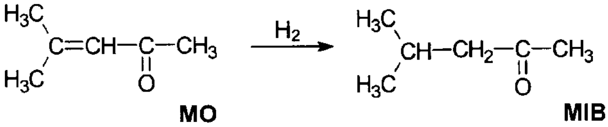

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Since the one-step process is simpler and more economical, there is still a great interest in finding new, improved catalyst systems operating in the gas phase at atmospheric pressure. Various supported metal catalysts have recently been described which can be utilized in the one-step synthesis. These include Ni supported on MgO (4), ALPON (5), or Al_2O_3 (6), and Pd-on-MgO promoted by Na (7). Pt–HZSM5 (8), Pd–HZSM5 (9), Pt–HMFI (10) and Pd or Ni supported on Mg/Al hydrotalcite (11) were also tested.

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0021-9517/99 $30.00

All these catalysts were applied at atmospheric pressure, whereas others, such as Pd-on-zirconium phosphate (12) and Pd-on-niobic acid (13) require the use of elevated pressure.

In this paper we disclose our recent observations with respect to the use of various Cu-on-MgO catalysts in the one-step, low-pressure production of MIBK from acetone in the presence of hydrogen in the gas phase. Under appropriate reaction conditions Cu-on-MgO proves to be a very promising catalyst ensuring good conversion, high selectivity, and stability in the formation of MIBK. Valuable information attained by deuterium labeling studies allows conclusions to be drawn for the interpretation of surface processes.

EXPERIMENTAL

Materials and Catalysts

$Mg(NO_3)_2 \cdot 6H_2O$ (99%, Aldrich) and $Cu(NO_3)_2 \cdot 3H_2O$ (analytical grade, Reanal, Hungary) were used for catalyst preparation. Catalyst supports also used were MgO (Fluka, light, >98%), ZnO (Haldor-Topsoe, HTZ-3, 1450/82), TiO_2 (rutile and anatase, Aldrich, 99.9%), ZrO_2 (Aldrich, 99.99%), γ-Al_2O_3 (Leuna, 5780 S), and SiO_2 (Strem, large pore). Acetone of analytical grade was purchased from Reanal (Hungary) and used as received. Hydrogen (99.999%) and helium (99.996%) were Linde products. N_2O (95%) was purified by evaporating about one third of the liquefied material resulting in an oxygen-free product suitable for measuring Cu(0) surface areas. Deuterium used in labeling studies was prepared from D_2O (99.8%, Russia) with a General Electric 15EHG2B4 generator.

Seven catalyst samples with 5% nominal copper loading used in preliminary pulse reactor studies were prepared by impregnating various supports with $Cu(NO_3)_2 \cdot 3H_2O$ using the incipient wetness technique. Detailed studies in a continuous flow reactor were carried out with Cu-on-MgO catalysts with 2, 5, and 7% nominal loadings prepared by impregnation (Cu-on-MgO/imp) using the incipient wetness technique, or by coprecipitation (Cu-on-MgO/cop) following the procedure described earlier (14). The resulting precipitates were filtered, washed, and dried at 393 K for 24 h. Catalyst precursors thus prepared were calcined at 723, 773, or 813 K in air for 4 h (calcination temperatures are shown in parenthesis in the denomination of catalyst samples).

Methods of Catalysts Characterization

Elemental analysis. Copper content of the catalysts were determined with a Jobin-Yvon ICP-AES spectrometer with samples prepared by dissolving the catalysts in 0.05 molar nitric acid solution.

Surface area measurements. BET surface areas were determined using nitrogen adsorption at 77 K after a pretreatment of the samples at 573 K for 0.5 h under vacuum. The Cu(0) surface area of the catalysts was measured by N_2O titration based on the reaction of nitrous oxide with surface Cu(0) species applying the GC pulse method (363 K, small sample size, large excess of N_2O) (15, 16).

Basicity measurements. Decomposition of 2-methyl-3-butyn-2-ol in pulse microreactor experiments was used to characterize the basicity of catalysts and catalyst supports (17). After the appropriate pretreatment (0.1 g sample size; oxides = 673 K, 1 h, 30 ml helium min^{-1}; 5% copper-containing supported catalysts = 673 K, 1 h, 30 ml hydrogen min^{-1}, then 473 K, 1 h, 30 ml helium min^{-1}), the samples were treated with 2-μl pulses of the reactant at 473 K in helium (30 ml min^{-1}). Under these conditions the products of cleavage (acetone and acetylene) were formed in approximately equal amounts. The average values determined in five pulses are used to compare the basicity of samples.

X-ray measurements. The catalyst samples prepared by coprecipitation exhibiting the best catalytic performance were studied by XRD (Philips PW 1820/1830 equipment, Cu$K\alpha$ radiation, $\lambda = 0.154$ nm, Al sample holder). Data processing was performed with a PW 1877 Philips software. Small angle X-ray scattering (SAXS) measurements were carried out with a PKCEC/3 Kompakt Kratky Kamera (Philips PW 1830 X-ray generator, 50 kV, 40 mA, 0.5-mm thick Cu sample holder).

Thermal analysis. Measurements were performed using a MOM Derivatograph-Q (Hungary) operating in the 283–1273 K temperature range (sample size = 0.1 g, temperature ramp = 12° min^{-1}).

Methods of Catalytic Studies

Pulse experiments for preliminary testing were carried out with copper-containing catalysts with various supports at 573 K in hydrogen (catalyst quantity = 0.1 g, activation = 673 K, 1 h, 30 ml min^{-1}).

A Pyrex glass microreactor (8 mm I.D., vertical position, fritted glass catalyst holder) was used for the catalytic measurements in flow experiments. Acetone was fed into a stainless steel evaporator kept at 353 K by a motorized syringe pump, mixed with appropriate amounts of hydrogen and helium controlled by mass flow controllers (Aalborg, GFM17) and then the mixture was introduced into the reactor. Except where noted otherwise, the general reaction conditions were as follows: catalyst quantity = 0.25 g, activation of catalyst = 673 K, 1 h, 30 ml min^{-1} hydrogen flow, acetone feeding rate = 1.33 ml h^{-1} $gcat^{-1}$, acetone/hydrogen molar ratio = 0.75. The temperature was controlled to an accuracy of $\pm 0.5^\circ$ by a microprocessor-based controller (Selftune plus, LOVE Controls Corp.). The effluents were sampled by a heated pneumatic sampling device automatically controlled by a DataApex

Chromatography Station for Windows 1.5 which was also used for processing GC data. Reaction products were subjected to GC analysis (Shimadzu 8A equipment, thermal conductivity detector, CWAX 20M column, 393 K, 30 ml min^{-1} helium carrier gas). Products were identified by comparison of their retention times with authentic samples and by mass spectrometry (HP 5890 GC + HP 5970 mass selective detector, 60 m HP-1 column). The same equipment was used for the analysis of deuterium-labeled compounds.

RESULTS

Catalyst Characterization

Characteristic data of the copper-on-magnesia catalysts determined by various chemical and physical methods are collected in Table 1. These include BET surface areas and various data obtained by SAXS measurements, as well as Cu(0) surface areas measured by N_2O titration. BET surfaces of catalysts prepared by coprecipitation are significantly higher and they decrease with increasing calcination temperature. The surface area values obtained by SAXS (S_p (18) and S'_p calculated according to Jánosi (19)) for selected catalysts are somewhat lower. The difference may be due to capillary condensation occurring during the BET measurement. S/V is the relative inner surface according to Porod (18), i.e., the surface of unit volume. The theoretical values for the D_s surface fractal dimensions may be between 2 and 3. The measured values that are close to 3 indicate that the samples are of rather rough surface.

Cu(0) surface areas, naturally, increase with increasing loading and the highest value was found for a 3.46% Cu-on-MgO/cop catalyst calcined at medium temperature (773 K).

XRD spectra of the precursor of a 3.46% Cu-on-MgO/cop catalyst before calcination, and those calcined at various temperatures are given in Fig. 1. It is to be seen that the main component of the dry precipitate is $Mg_5(CO_3)_4(OH)_2 \cdot 4\,H_2O$ (hydromagnesite, Fig. 1A). This decomposes into MgO at elevated temperature with peak intensities sharply increasing with increasing temperature of calcination (Fig. 1B). Diffraction peaks due to copper species are not detected which may be attributed to the low copper concentration of the sample. The results of thermal analysis of the same material before calcination, namely the stepwise loss of water and carbon dioxide, also supports the above structure (20).

Pulse Microreactor Studies

In preliminary experiments seven copper catalysts with various supports were studied in pulse experiments to test their performance in the transformation of acetone to MIBK in the presence of hydrogen. The basicity of both the supports and the catalysts was also determined by studying the transformation of 2-methyl-3-butyn-2-ol. The cleavage of this probe molecule to yield acetone and acetylene (reaction 4) was suggested to correlate with basicity (17).

$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-C\equiv CH \xrightarrow[\text{sites}]{\text{basic}} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{O}{\|}}{C}} + HC\equiv CH$$

[4]

In addition, acid sites were shown to catalyze dehydration to 3-methyl-3-buten-1-yne and skeletal isomerization to 3-methyl-2-butenal, whereas the formation of additional products (3-hydroxy-3-methyl-2-butanone and 3-methyl-3-buten-2-one) was attributed to the presence of acid–base pairs (17, 21).

TABLE 1

Characteristic Data on the Copper-on-Magnesia Catalysts Determined on Samples Calcined at 773 K

Catalyst samples	Cu content (weight %)	BET surface ($m^2\,g^{-1}$)	Cu(0) surface ($m^2\,g^{-1}$)	D_s[a]	S/V (nm^2)[a]	S_p ($m^2\,g^{-1}$)[a]	S'_p ($m^2\,g^{-1}$)[a]
Impregnated							
2% Cu/MgO	1.94	57	0.46				
5% Cu/MgO	3.96	42	0.7 (0.21)[b]				
7% Cu/MgO	5.82	43.5	2.12				
Coprecipitated							
2% Cu/MgO	2.49	105	1.06				
5% Cu/MgO	3.46	186[c]	1.49[c] (1.29)[b]	2.85[c]	0.06477[c]	114.3[c]	103.6[c]
		154	4.38[d]	2.61	0.0423	68.2	83.9
		108[e]	3.49[e]	2.67[e]	0.04672[e]	72.2[e]	88.5[e]
7% Cu/MgO	7.64	159	1.73				

[a] Values determined by SAXS. See text.
[b] *In situ* measurements after reaction (558 K, 2 h, 20 ml hydrogen min^{-1}).
[c] The catalyst precursor was calcined at 723 K.
[d] This corresponds to a dispersion of 20% and a mean particle size of 5.3 nm, assuming spherical particles.
[e] The catalyst precursor was calcined at 813 K.

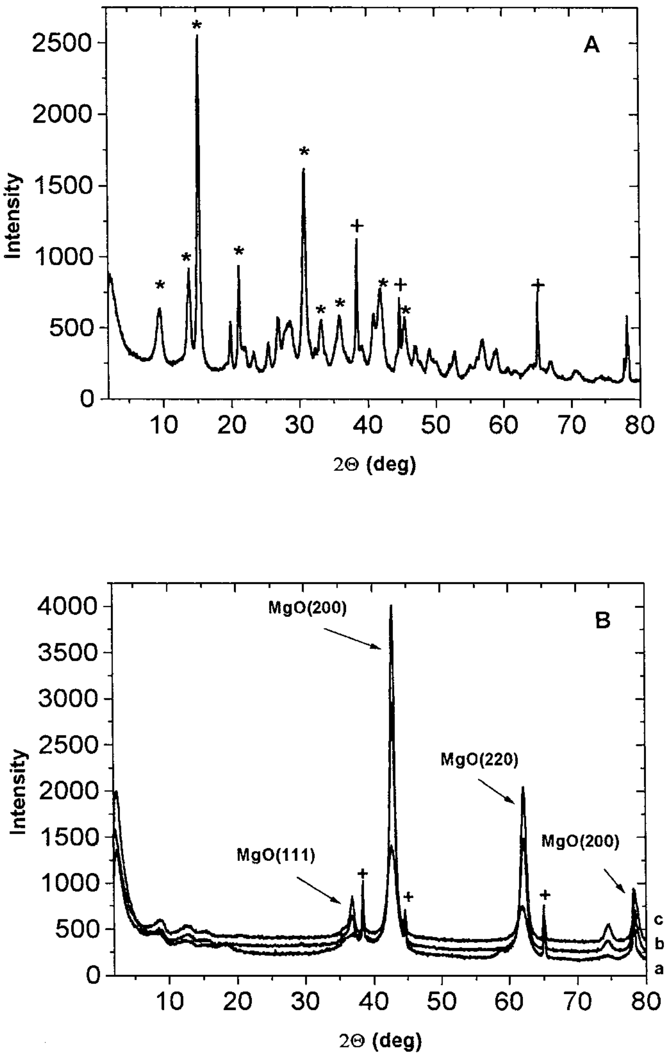

FIG. 1. The XRD diffractograms of a 3.46% Cu-on-MgO/cop catalyst precursor. (A) Before calcination; (B) calcined at (a) 723 K, (b) 773 K, and (c) 813 K. $^*Mg_5(CO_3)_4(OH)_2 \cdot 4\,H_2O$ (JCPDS card 25-513), +Al (sample holder), MgO crystal faces: JCPDS card 4-829.

Figure 2 shows correlations between the basicity of the oxides and the corresponding oxide-supported copper catalysts as measured by the yield of cleavage products in the transformation of 2-methyl-3-butyn-2-ol and the activity of copper catalysts in the reaction of acetone to yield MIBK. The two catalysts that were prepared by using MgO and ZnO, the two most basic supports, exhibit the highest activity. In the case of Al_2O_3 and SiO_2 the transformation of the probe molecule to cleavage products was not selective. Other products indicating the presence of acidic sites and amphoteric character were also detected with a combined yield of 11 and 4%, respectively. The behavior of Cu-on-Al_2O_3 is especially interesting. With this catalyst the yield of MIBK is low despite the relatively high basicity values. The reason for this is that Al_2O_3 exhibits acidic properties (catalyzes dehydration of 2-methyl-3-butyn-2-ol). As a result, products of decomposition (hydrocarbons) are formed in high amounts in the transformation of acetone resulting in the observed low selectivity in the formation of MIBK.

Studies in a Flow Reactor

On the basis of the above observations detailed studies were decided to be carried out with catalysts supported on MgO exhibiting the best catalyst performance. The six Cu-on-MgO catalyst samples with various copper loadings prepared by impregnation or coprecipitation were subjected to a screening process. During these measurements the effects of catalyst preparation and pretreatment (the calcination temperature of catalyst precursor, the temperature and duration of catalyst activation in hydrogen) and the reaction variables (reaction temperature, acetone to hydrogen molar ratio, space velocity) were all tested to find the best catalysts and reaction conditions.

Selected examples of these results are collected in Tables 2 and 3. The tables list the major and characteristic compounds formed and detected. Under certain conditions additional dimeric and trimeric products (2-methyl-1-pentene, 4-methyl-1- and 4-methyl-2-pentenes, 2,6-dimethyl-1-heptene, and 2,6-dimethyl-3-heptenes) were also identified in smaller, usually negligible amounts. Cyclic

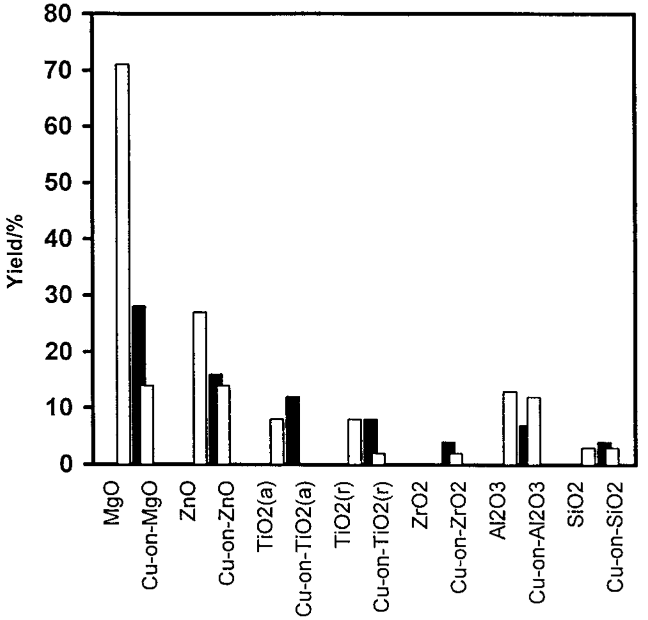

FIG. 2. Basicity of the supports and the 5% Cu-on-oxide catalysts as measured by the cleavage of 2-methyl-3-butyn-2-ol and the activity of the 5% Cu-on-oxide catalysts (prepared by impregnation, calcined at 773 K) in the transformation of acetone to MIBK (results of pulse experiments; see Experimental for details). ❐, Yield of cleavage products (acetone + acetylene), ■, yield of MIBK.

TABLE 2

Effect of Reaction Temperature on Conversion, Reactivity, and Selectivity (Catalyst = 3.96% Cu-on-MgO/imp(773), Acetone/Hydrogen = 0.12, GHSV = 4800 ml h^{-1} $gcat^{-1}$)[a]

	Temperature (K)		
	423	473	543
Conversion (mol%)	85	65	43
Reactivity (mol h^{-1} $gcat^{-1}$)	0.0154	0.0118	0.0078
Selectivity			
MIBK	7	23	50
MO	21	12	7
MIBC	3	11	13
DIBK[b]	0	2	4
2-propanol	68	53	23
C9+[c]	0	0	1

[a] Values were determined at 8 h-on-stream.

[b] Diisobutyl ketone.

[c] Mainly 3,5,5-trimethylcyclohex-2-enone (isophorone), 3,3,5-trimethylcyclohexanone and 3,3,5-trimethylcyclohexanol and some unknown compounds.

trimeric compounds, mainly isophorone (3,5,5-trimethylcyclohex-2-enone) formed from 2,6-dimethyl-hepta-2,5-diene-4-one via intramolecular Michael-addition and its partially or completely hydrogenated derivatives, 3,3,5-trimethylcyclohexanone and 3,3,5-trimethylcyclohexanol, respectively, were also detected.

The data show that reaction temperatures around 543 K (Table 2) and a slight excess of hydrogen relative to acetone (Table 3) give satisfactory catalyst activity and selectivity to MIBK. One of the major side-reactions is the hydrogenation of MIBK to MIBC. Although higher final conversions could be reached at lower temperatures, selectivities to MIBK were very low due to extensive hydrogenation of acetone to 2-propanol and increasing amounts of MO. Similar overhydrogenation was observed in a large excess of hydrogen (not shown) whereas increasing amounts of MO were detected in experiments in increasing hydrogen deficiency (Table 3).

TABLE 3

Effect of Acetone to Hydrogen Molar Ratio on Conversion, Reactivity, and Selectivity (Catalyst = 3.96% Cu-on-MgO/imp(773), $T = 573$ K, GHSV = 4800 ml h^{-1} $gcat^{-1}$)[a]

	Acetone/hydrogen molar ratio		
	0.75	1.5	2.6
Conversion (mol%)	23	12	10
Reactivity (mol h^{-1} $gcat^{-1}$)	0.0041	0.0043	0.0035
Selectivity (%)			
MIBK	83	35	16
MO	3	41	71
MIBC	6	5	0
DIBK	3	0	0
C9+[b]	4	19	13

[a] Values were determined at 4 h-on-stream.

[b] See footnote to Table 2.

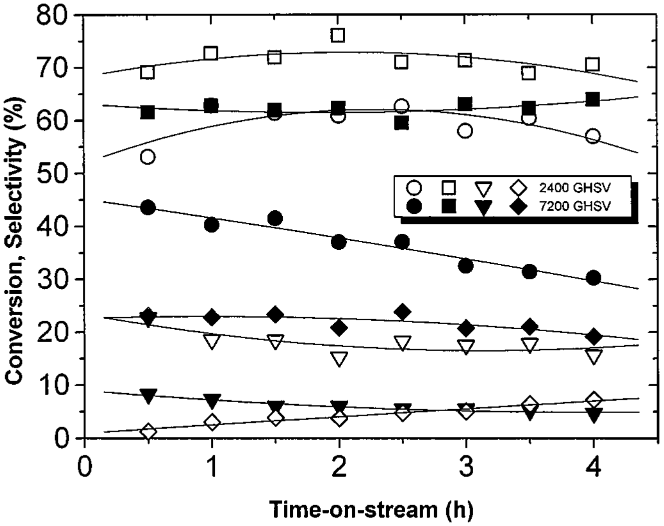

FIG. 3. Conversions and selectivities as a function of space velocity (catalyst = 3.46% Cu-on-MgO/cop(723), $T = 558$ K, acetone/hydrogen = 0.75). Circles, conversion; squares, MIBK selectivity; triangles, MIBC selectivity; diamonds, selectivity of the formation of cyclic trimers.

Results with respect to the effect of space velocity are seen in Fig. 3 which indicate that all catalyst characteristics are superior when the transformation of acetone is carried out with lower space velocity. Under these conditions both conversions and MIBK selectivities are higher, and the selectivities of the formation of cyclic trimers are lower, although MIBC selectivities are slightly higher. Moreover, the catalyst exhibits much better stability on time-on-stream.

Distinct differences can be seen between the catalytic properties of the catalysts prepared by impregnation and coprecipitation (Fig. 4). When compared under identical conditions, the catalysts prepared by coprecipitation display much better characteristics than those made by impregnation: they give much higher conversion and exhibit more stable activity, even though the selectivities of the products formed by hydrogenation of the carbonyl group (2-propanol and MIBC) are somewhat higher.

The calcination temperature of the catalyst precursor has a significant effect on catalyst performance. When the precursor was calcined at higher temperatures the resulting catalysts display better initial activities (Fig. 5). With time-on-stream, however, the activities and selectivities change and, eventually, the catalyst calcined at the lowest temperature (723 K) exhibits the best overall performance, especially when MIBK selectivity is concerned. Additional products formed with increasing selectivity with time on stream not shown are diisobutyl ketone (DIBK, 5–10%) and compounds formed via the reduction of isophorone

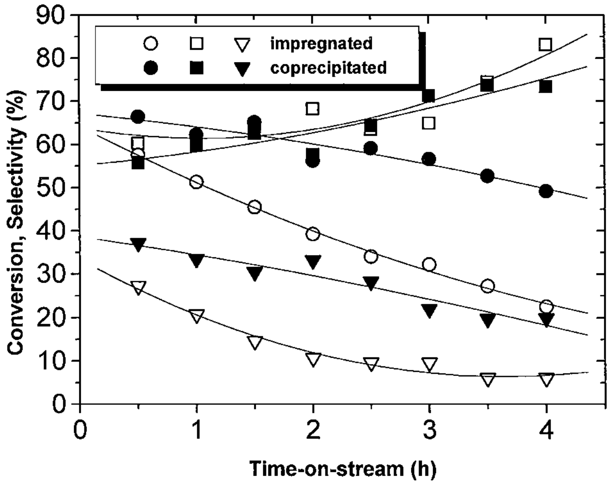

FIG. 4. Conversions and selectivities as a function of the preparation method of catalysts (catalysts = 3.96% Cu-on-MgO/imp(773) and 3.46% Cu-on-MgO/cop(773), $T = 543$ K, acetone/hydrogen = 0.75, GHSV = 4800 ml h^{-1} $gcat^{-1}$). Circles, conversion; squares, MIBK selectivity; triangles, selectivity of 2-propanol + MIBC.

(3,3,5-trimethylcyclohexanone and 3,3,5-trimethylcyclohexanol, 10–20%).

Results with respect to the effect of copper loading (Table 4) indicate that increasing copper content resulted in higher catalyst activity (increasing conversion). The stability of samples with higher copper loading was also better. MIBK selectivity, however, was decreasing due to the formation of MIBC and cyclic trimeric compounds.

TABLE 4

Effect of Copper Content of the Catalysts Prepared by Impregnation Calcined at 773 K on Conversion, Reactivity, and Selectivity ($T = 543$ K, Acetone/Hydrogen = 0.75, GHSV = 4800 ml h^{-1} $gcat^{-1}$)[a]

	Cu content (%)		
Conversion and selectivity	1.94	3.96	5.82
Conversion (mol%)	33	65	76
Reactivity (mol h^{-1} $gcat^{-1}$)	0.0029	0.0058	0.0068
Selectivity (%)			
MIBK	68	52	44
MO	4	1	0
MIBC	10	30	29
DIBK	4	6	8
C9+[b]	14	10	19

[a] Values were determined at 4 h-on-stream.

[b] See footnote to Table 2.

When conditions of catalyst pretreatment in hydrogen are compared a small increase in conversion is brought about by increasing reduction temperature (Fig. 6). The most important change, however, is a more stable catalyst activity on time-on-stream. The increasing duration of hydrogen treatment causes significant decreases in both catalyst stability and MIBK selectivity (Fig. 7). The selectivity drop is especially significant on the catalyst reduced for 1.5 h. At 4 h-on-stream the combined selectivity of MIBK + MIBC is only 48%, the rest (not shown in the figure) being MO (25%), 3,3,5-trimethylcyclohexanone, and 3,3,5-trimethylcyclohexanol (25%), DIBK (5%), and

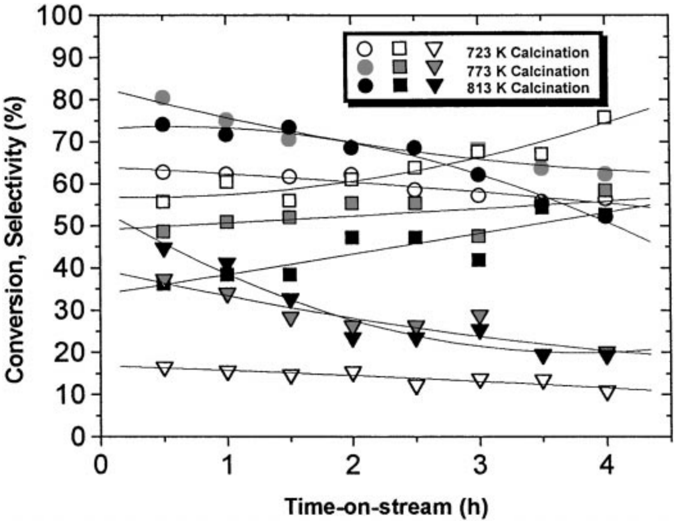

FIG. 5. Conversions and selectivities as a function of the calcination temperature of the catalyst precursor (catalyst = 3.46% Cu-on-MgO/cop, $T = 558$ K, acetone/hydrogen = 0.75, GHSV = 4800 ml h^{-1} $gcat^{-1}$). Circles, conversion; squares, MIBK selectivity; triangles, MIBC selectivity.

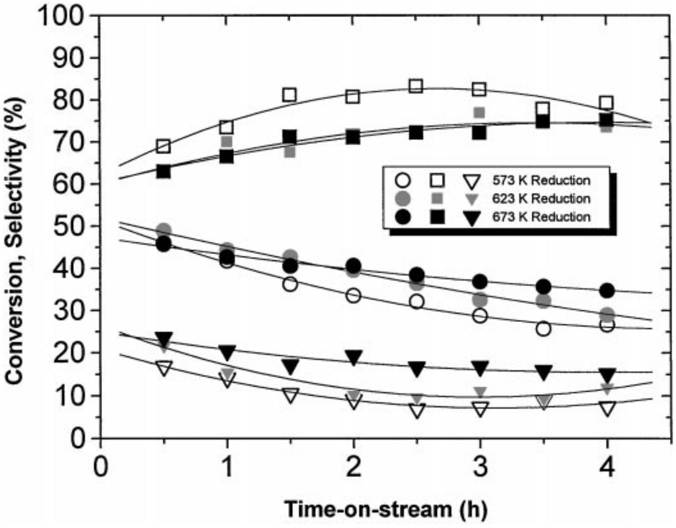

FIG. 6. Conversions and selectivities as a function of the temperature of 1-h reduction pretreatment (catalyst = 3.96% Cu-on-MgO/imp(773), $T = 558$ K, acetone/hydrogen = 0.75, GHSV = 4800 ml h^{-1} $gcat^{-1}$). Circles, conversion; squares, MIBK selectivity; triangles, MIBC selectivity.

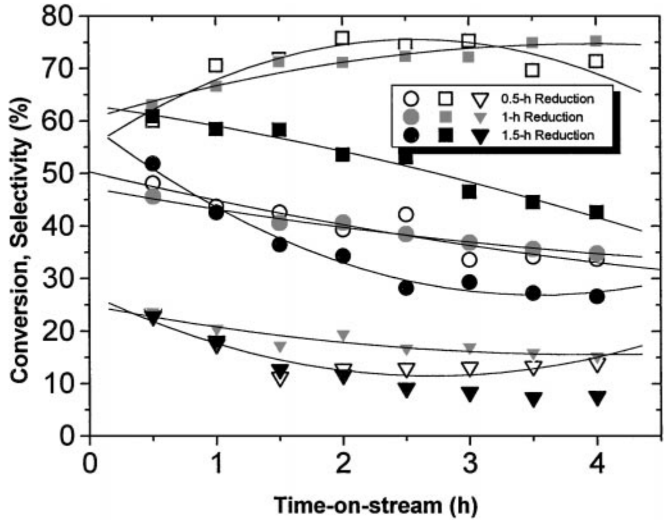

FIG. 7. Conversions and selectivities as a function of the duration of reduction pretreatment at 673 K (catalyst = 3.46% Cu-on-MgO/cop(773), $T = 558$ K, acetone/hydrogen = 0.75, GHSV = 4800 ml h^{-1} gcat^{-1}). Circles, conversion; squares, MIBK selectivity; triangles, MIBC selectivity.

2-propanol (2%). In summary, a 1-h reduction at 673 K results in a catalyst with the best performance in terms of activity, selectivity, and catalyst stability.

A thorough analysis of all the information gathered from the studies summarized above permitted us to select the best catalyst and the most satisfactory reaction conditions with respect to the production of MIBK. The 3.46% copper-on-MgO catalyst prepared by coprecipitation was found to produce MIBK in 45–48% yield (60–80% conversion and 60–75% selectivity) over a period of 24 h-on-stream (Fig. 8). Although catalyst activity was decreasing a parallel increase in MIBK selectivity could maintain a satisfactory yield throughout the catalytic run.

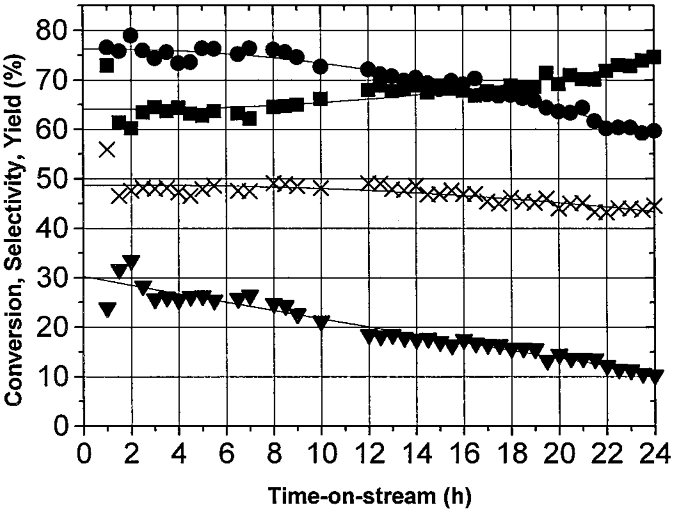

FIG. 8. Changes in conversion, selectivities, and MIBK yield as a function of time-on-stream over a 3.46% Cu-on-MgO/cop(723) catalyst ($T = 553$ K, acetone/hydrogen = 0.87, GHSV = 1920 ml h^{-1} gcat^{-1}). Circle, conversion; square, MIBK selectivity; triangle, MIBC selectivity; diamond, MIBK yield.

Deuterium Labeling Experiments

The results of studies carried out in the presence of deuterium are collected in Table 5.

A comparison of the deuterium content of unreacted acetone over MgO and copper-on-magnesia shows significant differences. Deuterium incorporation is extremely low when acetone was reacted over MgO. In sharp contrast, significant deuterium incorporation was observed over Cu-on-MgO. The dominant species is d_1 indicating that the exchange occurs in a single adsorption–desorption process. The deuterium content of the condensation product MO is about three times as high as that of acetone and the deuterium distribution is shifted to isotopomers with multiple exchange (d_2 and d_3). The average deuterium content of MIBK formed in the hydrogenation of MO, in turn, is less

TABLE 5

Relative Abundance of the Isotopomers and D Content in Deuterium-Labeled Products Calculated from their Mass Spectra (Catalyst = 3.46% Cu-on-MgO/cop(723), $T = 558$ K, GHSV = 2400 ml h^{-1} gcat^{-1}, Acetone/Deuterium = 0.75)[a]

Compound	Number of deuterium atoms	Relative abundance (%)[b]	D content per molecule
Acetone[c]	d_0	92	0.09
	d_1	7	
	d_2	1	
Acetone	d_0	49	0.62
	d_1	41	
	d_2	9	
	d_3	1	
MO	d_0	14	1.75
	d_1	24	
	d_2	35	
	d_3	27	
MIBK	d_0	22	2.67
	d_1	9	
	d_2	16	
	d_3	20	
	d_4	16	
	d_5	10	
	d_6	5	
	d_7	2	
	d_8	1	
DIBK	d_0	84	0.69
	d_1	1	
	d_2	1	
	d_3	2	
	d_4	4	
	d_5	4	
	d_6	4	

[a] Analyses were carried out with samples collected in 2-h runs.

[b] Values corrected by the natural isotope abundance.

[c] Results of reaction carried out over MgO.

than expected by supposing the addition of one deuterium molecule to the carbon–carbon double bond. A highly surprising observation is the very low deuterium content of DIBK with dominant species of multiple exchange.

DISCUSSION

Catalytic Studies

In terms of the necessary technology required, the one-step synthesis of MIBK from acetone and hydrogen is less complicated than the traditional three-step process practiced in industry. However, when the chemistry involved is considered the one-step process has also its drawbacks. As the experimental results of the present study indicate, numerous by-products may be formed as a result of secondary transformations. Nevertheless, our findings also show that it is possible to achieve acceptable levels of conversion and selectivity through the correct choice of experimental variables and by fine tuning catalyst characteristics.

The condensation of acetone to produce DAA in the first step of the synthesis of MIBK is typically catalyzed by bases. Our choice of MgO as the support, therefore, is warranted by its well-known basic properties. With the application of various probe molecules (e.g., 2-propanol (22), methyloxirane (23), and 2-methyl-3-butyn-2-ol (17)) magnesia has been proven to be one of the most basic oxides. This high basicity, in turn, is also responsible for the formation of high molecular weight by-products which are produced in various inter- and intramolecular condensation and addition processes of the intermediates (24). These compounds, and 2-propanol and MIBC, formed as a results of overhydrogenation, are the main by-products resulting in decreased selectivities of the formation of MIBK. High molecular weight condensation products, in addition, are the primary reason for catalyst deactivation.

The results of comparative studies with the two sets of catalysts used in the present report show that catalysts prepared by coprecipitation usually exhibit better performance than those made by impregnation. The former have higher BET surface areas and higher specific Cu(0) surfaces and exhibit higher activities (Fig. 4). It is even more important from a practical point of view that their stability is always higher (Fig. 4). This high stability is possibly attributed to a more intimate interaction between the metal and the support resulting form the coprecipitation method. This assumption is well illustrated by the results of surface area measurements: the decrease in Cu(0) surface area during reaction under otherwise identical experimental conditions is much smaller for a catalyst prepared by coprecipitation (Table 1).

Metal loading and the conditions for catalyst pretreatment also significantly affect catalyst performance. Although conversion increases with copper loading the concomitant increase in MIBC selectivity results in a significant drop of MIBK selectivity (Table 4). This change can be accounted for by an increase in the hydrogenation activity of the catalysts with higher copper loadings due to the increase in specific copper surface area (Table 1). Catalyst pretreatment in hydrogen before reaction affects primarily the activity of the working catalyst. Pretreatment at higher temperature obviously leads to more fully reduced catalysts and, therefore, higher and more stable activity (Fig. 6). The marked drop in activity after prolonged hydrogen treatment (Fig. 7), in turn, may be a result of sintering of metal particles. Additionally, the poisoning effect of the high molecular weight condensation products also has to be taken into account. As it was pointed out the selectivity of the formation of cyclic trimers increases significantly with reaction time. Moreover, other high molecular weight compounds, namely tetramers (isoxylitones), mesitylene, and 3,3,6,8-tetramethyltetralone (a pentamer), are also known to be formed in the base-catalyzed transformation of acetone (24). Though not found in our case, these products, even when formed in undetectably low amounts, may accumulate on the catalyst surface contributing to the decreasing activity on time on stream.

It appears that calcination temperature affects activity in a similar way. Calcination of the catalyst precursor at high temperature results in catalysts exhibiting high initial hydrogenation activity. This is manifested in the high selectivity of the formation of 2-propanol and MIBC (Fig. 5). This activity, however, drops rapidly with time on stream with a parallel decrease in overall catalyst activity. This latter phenomenon may be explained by the unfavorable contribution of basic sites of the samples calcined at high temperature. As XRD results show peak intensities of MgO sharply increase with increasing temperature of calcination (Fig. 1B). This as well as the decreasing BET surface (Table 1) bring about increasing basic site densities. The accumulation of the increased amounts of high molecular weight by-products formed on such catalyst samples may be the primary reason for the observed catalyst deactivation.

The effect of reaction variables may be summarized as follows. The formation of MIBK in high yields requires high reaction temperature, a slight excess of hydrogen, and low space velocity. Although higher conversions are achieved at low temperature (Table 2), the thermodynamics of the ketone–secondary alcohol equilibrium are unfavorable and the hydrogenation of acetone to produce 2-propanol becomes the main transformation direction. Since hydrogen is required in equimolar amount in the last, hydrogenation step of MIBK formation (reaction 3), an appropriate amount of hydrogen is an obvious requirement: in addition to low conversions the intermediate MO becomes the main product under conditions of hydrogen deficiency (Table 3). Finally, low space velocity naturally ensures high conversion and overhydrogenation becomes more significant (Fig. 3). The main disadvantage of applying higher space velocity is the increased amount of condensation products and, consequently, a marked decrease in catalyst stability.

Deuterium Labeling Experiments

It is known that MgO after prolonged thermal activation at very high temperatures (773–1070 K) under vacuum exhibits high activity in deuterium exchange processes (25–27). The pretreatment conditions employed in our case (673 K in deuterium for 1 h) are not sufficiently severe enough to activate MgO. This explains why only an insignificant amount of deuterium was found in unreacted acetone on pure magnesia (Table 5).

Deuterium exchange in acetone, in turn, does take place on copper-on-magnesia. Obviously, the exchange reaction requires deuterium atoms, i.e., the dissociation of D_2 which is a highly activated process on copper. Evidence for such activation over copper-on-silica catalysts was found by infrared spectroscopy (28). An additional important feature of the exchange process is a break after d_3. A similar phenomenon was observed in the exchange of acetone over rhodium and platinum suggesting a tendency for completion of exchange of a single methyl group (29). The surface species to account for this is η^1 acetone weakly bound to the surface via one of the oxygen lone pairs. The resulting geometry with one methyl remote from the surface and the other adjacent allows rapid multiple exchange via an $\alpha\gamma$ intermediate (30).

The deuterium content and distribution in MO indicates that once formed it participates in further exchange processes but with a lower probability than acetone due to the lower number of exchangeable hydrogens. Similarly, the deuterium content of MIBK is less then expected. In fact, it is very close to that calculated on the assumption of the incorporation of only a single deuterium atom to MO in the final hydrogenation step. This testifies to the fact that the surface deuterium pool is highly diluted as a result of the H–D exchange process and hydrogen atoms thus formed remain in the adsorbed state on the surface and are used up in the subsequent addition reaction. This is in agreement with the observation of Chester *et al.* who found that exchange between surface and gas phase hydrogen/deuterium over Cu-on-MgO occurs slowly as compared with platinum (31). The results of this exchange study are in harmony with the assumption that the characteristic reactions leading to the formation of MIBK are the condensation of acetone molecules taking place on basic sites dominant on the surface of MgO and the hydrogenation of the intermediate MO on copper metal sites.

The most dramatic observation coming from the deuterium labeling studies is the unexpectedly low deuterium content of DIBK. It is evident, therefore, that neither MO nor MIBK both with significant amounts of deuterium is the intermediate in the formation of DIBK. Rather, the latter should be formed with the involvement of different surface active sites. It appears that there exist certain active sites which are able to strongly adsorb acetone. Due to strong binding acetone molecules adsorbed on such sites do not participate in the exchange process. Having a long residence time condensation may occur on both methyl groups without the desorption of surface intermediates. With the present set of data in hand it is not yet possible to identify these sites. However, it is tempting to suggest that sites of the oxide–metal interface called adlineation sites may be responsible for the observed phenomenon. Such sites of specific geometry and electronic properties have been shown to exhibit peculiar catalytic activity (see, e.g., (32)).

CONCLUSIONS

It has been shown that Cu-on-MgO catalysts are active in the one-step synthesis of MIBK from acetone and hydrogen at atmospheric pressure in the gas phase. Catalysts prepared by coprecipitation are superior to those prepared by impregnation: they exhibit high and stable activity and selectivity to MIBK. With the best catalyst after appropriate pretreatments yields of MIBK as high as 45–48% could be attained. Important information was gathered from the results of transformations in deuterium. The dominant reaction leading to the formation of MIBK appears to be the condensation of acetone molecules taking place on basic sites of MgO. DIBK with very low deuterium content, in turn, may be formed on active sites capable of the strong adsorption of acetone. Due to the slow exchange between surface hydrogen formed during the exchange process and gas phase deuterium, the former plays a major role in the saturation of the carbon–carbon double bond of MO to form MIBK with lower than expected deuterium content.

ACKNOWLEDGMENTS

The authors thank Dr. G. Mulas (University of Sassari) for carrying out the XRD measurements. Professors I. Kiricsi and I. Dékány are acknowledged for the use of instrumentations (BET, thermal analysis, and SAXS XRD measurements).

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