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Article

Effect of Cu-ZnO-Al₂O₃ supported on H-ferrierite on hydrocarbons formation from CO hydrogenation

J. H. Flores^a, M. E. H. Maia da Costa^b, M. I. Pais da Silva^{a,*}^a Departamento de Química, Pontifícia Universidade Católica, 22453-900, Rio de Janeiro, RJ, Brazil^b Departamento de Física, Pontifícia Universidade Católica, 22453-900, Rio de Janeiro, RJ, Brazil

ARTICLE INFO

Article history:

Received 29 October 2015

Accepted 9 December 2015

Published 5 March 2016

Keywords:

Methanol synthesis catalyst

Low supersaturation precipitation

High supersaturation precipitation

Syngas

Hydrotalcite

Hydrocarbon

Dimethyl ether

ABSTRACT

Methanol synthesis catalysts based on Cu, Zn and Al were prepared by three methods and subsequently mixed with H-ferrierite zeolite in an aqueous suspension to disperse the catalysts over the support. These materials were characterized by X-ray diffraction, N₂ adsorption, transmission electron microscopy, temperature programmed reduction, NH₃ and H₂ temperature-programmed desorption, and X-ray photoelectron spectroscopy. They were also applied to the CO hydrogenation reaction to produce dimethyl ether and hydrocarbons. The catalysts were prepared by coprecipitation under low and high supersaturation conditions and by a homogeneous precipitation method. The preparation technique was found to affect the precursor structural characteristics, such as purity and crystallinity, as well as the particle size distribution of the resulting catalyst. Low supersaturation conditions favored high dispersion of the Cu species, increasing the methanol synthesis catalyst's metallic surface area and resulting in a homogeneous particle size distribution. These effects in turn were found to modify the zeolite properties, promoting both a low micropore volume and blockage of the zeolite acid sites. The effect of the methanol synthesis catalyst on the reaction was verified by the correlation between the Cu surface area and the CO conversion rate.

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1. Introduction

The Fischer-Tropsch process has long been used to produce hydrocarbons from synthesis gas (syngas, H₂/CO) obtained through methane steam reforming [1,2]. During the last decade, the synthesis of light hydrocarbons, liquefied petroleum gas in particular, from syngas via the methanol route in a single step has attracted the attention of researchers [2–8]. Liquefied petroleum gas is a mixture of propane and butanes that has favorable environmental characteristics and is currently widely used as a clean fuel. However, the methanol route to produce hydrocarbons from syngas is not still completely understood and the associated catalytic systems need to be improved.

The conversion of syngas to hydrocarbons via methanol is promoted by a hybrid material composed of a methanol synthesis catalyst (MSC) and an acidic material (silica or zeolites) [9–13]. Two challenges must be overcome to obtain high hydrocarbon yields; a highly active catalyst must be developed, together with a dehydration material having pore size and acid properties suitable for the production of hydrocarbons.

The synthesis of methanol is the first stage of the overall reaction and may represent the rate-limiting step. The optimization of this stage could therefore be the key to the whole process. Metal oxides based on Cu, Zn and Al have been extensively used as methanol synthesis catalysts or as catalysts for the steam reforming of methanol, and various groups have pre-

* Corresponding author. Tel: +55-21-35271323; E-mail: isapais@puc-rio.br

This work was supported by CAPES.

DOI: 10.1016/S1872-2067(15)61032-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 3, March 2016

pared these oxides using several different methods to improve their catalytic activities [14–17]. Studies related to methanol synthesis or the steam reforming of methanol have revealed that metallic Cu atoms serve as active sites, whereas oxidized Cu ions are inactive [14,18]. Consequently, extensive effort has been directed toward improving the dispersion of Cu metal.

A reasonable starting point for optimizing the hybrid catalysts used to synthesize hydrocarbons from syngas is the improvement of the MSC responsible for the first reaction stage. In this case, the synthesis of the precursor to the MSC plays an important role. The preparation method can affect the particle size, such that small particles of the catalyst can be dispersed over the acid component, leaving the active sites of both the catalyst and acid component readily available. Ideally, small particles of the MSC would be spread over the support, thereby avoiding blockage of the zeolite pores, decreased acidity of the support and increased diffusion hindrance.

Coprecipitation has been the method most commonly used to prepare MSCs, and has been employed to successfully synthesize layered double hydroxides (LDHs) [14,19]. In this technique, aqueous solutions of metal species (M^{2+} and M^{3+}) are mixed with a precipitating agent under specific conditions to form solid precipitates. The simultaneous precipitation of two or more cations is favored under certain combinations of pH, temperature, species concentration and addition rate [20]. In the case of catalysts based on Cu, Zn and Al, a pH of approximately 7 is typically used to simultaneously precipitate the metallic species [21]. However, the particle size of the precipitate is controlled by varying other parameters, such as supersaturation, during the precipitation. This occurs because the nucleation and growth of the solid precipitate are affected by the rate at which the reactants are mixed or the precipitating agent is added (or generated through a decomposition process such as urea hydrolysis).

Coprecipitation at low supersaturation, referred to hereafter as conventional coprecipitation, is performed by the slow and simultaneous mixing of two solutions—one containing the divalent and trivalent metal salts and another containing an alkali metal—at a rate such that the pH is maintained at a specified value that leads to the coprecipitation of the two metallic salts. This method favors control of the charge density (that is, the M^{2+}/M^{3+} ratio) of the hydroxide layers of the resulting LDH by precisely controlling the solution pH. However, the inevitable consequence is that a wide dispersion of crystallite size is obtained after aging. The particle size of LDHs are difficult to control using the conventional coprecipitation method because the process of mixing salt and alkali solutions requires a considerable amount of time during coprecipitation at low supersaturation. As a result, the nuclei formed at the start of the addition process have a substantially longer period of time to undergo growth compared to those formed towards the end of the addition. That is, nucleation and aging occur simultaneously during the long addition process. Low supersaturation conditions tend to result in precipitates with greater crystallinity because the rate of crystal growth is higher than the rate of nucleation.

To avoid this problem, methods based on rapid mixing of

the two solutions (precipitation under high supersaturation conditions) have been developed that favor the formation of smaller particles with a narrow distribution of particle size. High supersaturation conditions during precipitation are achieved by the rapid simultaneous mixing of the aforementioned solutions. This fast mixing produces a solid precipitate with smaller particles because the metallic species and the precipitating agent are consumed instantaneously and because the nucleation rate is higher than the growth rate.

In addition to the above, a homogeneous precipitation method has been developed by Soler-Illia et al. [22] to synthesize both amorphous and crystalline metal oxide particles with uniform shapes from an aqueous medium. In their method, the decomposition of urea (CH_4N_2O) in aqueous solution is accompanied by the slow and controlled addition of ammonia (NH_3) and carbon dioxide (CO_2) to the solution. The smooth pH increase resulting from the degradation of urea in conjunction with the active release of OH^- and CO_3^{2-} ions usually leads to the precipitation of particles with a well-controlled particle morphology. Therefore, this homogeneous precipitation method based on the generation of the precipitating agent via urea hydrolysis is an attractive technique because it is based on control of the nucleation rate, which is considered to be the main parameter governing the particle size. The decomposition rate of urea depends on the temperature, and the particle size distribution can therefore be tuned by changing the reaction temperature.

Following the generation of methanol, methanol dehydration to form dimethyl ether (DME) and hydrocarbons takes place on porous acidic materials such as zeolites [23]. H-ferrierite is a highly acidic material that has demonstrated excellent dehydration performance, as reported by Prasad et al. [24] and Flores et al. [25].

The present study focused on understanding the effect of the MSC component of the hybrid MSC/zeolite catalyst system on hydrocarbon production from syngas. It is important to study the MSC because its behavior as a hybrid catalyst component is different from its characteristics when used alone, largely because it is widely dispersed over a support. In the work reported herein, an MSC catalyst was prepared using three methods based on different nucleation rates and then dispersed on a H-ferrierite zeolite using a wet physical mixture.

2. Experimental

2.1. Catalyst preparation

H-Ferrierite zeolite with a Si/Al ratio of 10 was prepared from commercial NaK-ferrierite provided by Toyo Soda Manufacturing (720 KOA) by repeated ion exchange with NH_4NO_3 solutions at 90 °C followed by calcination under N_2 at 400 °C for 4 h.

MSCs based on Cu-Zn-Al at a 55:30:15 atomic ratio were prepared by three methods. The first catalyst was prepared by coprecipitation at low supersaturation based on the slow, simultaneous mixing of two aqueous solutions over a period of 45 min. One solution contained Cu, Zn and Al nitrates (1 mol/L)

and the other contained Na_2CO_3 (1.5 mol/L). The slow mixing was performed with vigorous stirring at 70 °C while maintaining the pH at approximately 7 ± 0.2 . The resulting solid was aged for 1 h at 70 °C and subsequently washed with warmed water (1 L) to eliminate residual Na.

A second catalyst was prepared by the rapid mixing (over a period of several seconds) of the aforementioned solutions, previously heated to 70 °C. The solid product was aged at 70 °C for 1 h and washed under the same conditions used in the first method.

A third MSC was prepared employing a homogeneous precipitation method. A solution containing Cu, Zn and Al nitrates (0.05 mol/L) and urea (0.5 mol/L) was prepared and heated to 90 °C. After the urea had hydrolyzed, the precipitate was aged for 1 h. The resulting solid was then washed with warm water (1 L).

Each of the three MSCs was subsequently suspended in deionized water and mixed with an aqueous H-ferrierite zeolite suspension at room temperature for 1 h and then filtered. The resulting solid was dried at 90 °C for 12 h and then calcined at 400 °C for 4 h under a N_2 atmosphere flowing at 50 mL/min, using a heating rate of 5 °C/min. The samples prepared under low and high supersaturation conditions (slow and fast mixing) are termed CP1 and CP2, respectively, while the sample prepared by homogeneous precipitation is referred to as HP.

2.2. Characterization

N_2 adsorption measurements were performed using a Micromeritics ASAP 2010 instrument, heating the samples to 250 °C. The surface areas were calculated according to the method of Brunauer-Emmett-Teller (BET).

X-ray diffraction (XRD) analyses of uncalcined and calcined samples were carried out with a Rigaku diffractometer equipped with a $\text{Cu } K_\alpha$ radiation source operated at 40 kV and 30 mA. Patterns were acquired over the 2θ range from 5° to 60° using a step size of 2°/min and Bragg-Brentano geometry. The XRD data were analyzed by the Rietveld refinement method using the TOPAS software package and subsequently compared with standard ICDD patterns.

The technique used for the temperature-programmed desorption of H_2 (H_2 -TPD) was adapted from that of Mühler et al. [26], and the results were used to determine the Cu surface area. The measurements were performed using a conventional TPD apparatus equipped with a Baltzer quadrupole mass spectrometer. Calcined samples were dried using pure He at 150 °C for 1 h and then reduced under pure H_2 (60 mL/min) at 250 °C for 1 h at a heating rate 10 °C/min. The samples were subsequently cooled to 0 °C for 1 h using an ice bath, after which they were further cooled to -196 °C for 1 h using liquid nitrogen. The gas was then switched to He at a flow of 50 mL/min for 30 min at the same temperature, after which the cooling bath was removed and the sample was heated to 350 °C. H_2 desorption was monitored at $m/z = 2$. Temperature-programmed desorption of NH_3 (NH_3 -TPD) measurements were carried out using the same apparatus. The calcined sample (600 mg) was dried at 400 °C for 2 h under He flowing at 50 mL/min. The sample was

then cooled to 175 °C and exposed to an NH_3/He mixture (3.84 %; 300 mL/min) for 1 h. After adsorption, the sample was purged with He for 1 h at 175 °C at a flow rate of 30 mL/min. The sample was finally heated to 1000 °C at a heating rate of 10 °C/min, and the NH_3 -TPD data were collected using $m/z = 17$.

X-ray photoelectron spectroscopy (XPS) was performed using a VG Alpha110 hemispherical analyzer, with sample excitation via $\text{Al } K_\alpha$ (1486.6 eV) radiation. The surface of each calcined sample was positioned at 90° with respect to the electron analyzer. The $\text{Cu } 2p$, $\text{Zn } 2p$, $\text{Al } 2p$, $\text{O } 1s$ and $\text{C } 1s$ energy regions were recorded for each sample, and the respective binding energy (BEs) were calibrated using the $\text{C } 1s$ line at 284.6 eV as an internal reference. The spectra were deconvoluted employing the least squares fitting routine incorporated into the Casa XPS software package. A Gaussian/Lorentzian product function was used in conjunction with Shirley background subtraction.

The temperature-programmed reduction experiments (H_2 -TPR) were conducted using 1.53% H_2 in Ar at a flow rate of 20 mL/min, in conjunction with heating from room temperature to 600 °C at 5 °C/min. The H_2 concentration was determined using a thermal conductivity detector (TCD)

2.3. Activity of catalysts

The catalytic activity measurements were carried out in a fixed-bed, stainless-steel reactor with a diameter of 12.7 mm. The reaction products were analyzed with an on-line gas chromatograph equipped with a TCD in the case of non-flammable products (CO , CO_2) and simultaneously with a flame ionization detector (FID) for flammable products such as methanol, DME and hydrocarbons. Two columns were used in series: a Carboxen 1010 PLOT capillary column and a SUPEL-Q PLOT fused silica capillary column; each column was 30 m long.

The samples were reduced at 250 °C using a heating rate of 10 °C/min under pure H_2 at a flow rate of 50 mL/min. The reaction was carried out at 350 °C, 2 MPa and at a W/F of 10.2 (g·h)/mol using a feed gas ratio (H_2/CO) of 2.

3. Results and discussion

3.1. Structural and textural properties

The XRD patterns of the hybrid catalysts before calcination are shown in Fig. 1. Hydrotalcite-phase peaks, which are in good agreement with the literature [27], were generated by the CP1 and CP2 samples, serving as the main precursor phase for the MSC. The hydrotalcite peaks were less intense in the CP2 pattern than in the CP1 pattern, indicating that the CP2 was less crystalline. Hydrotalcite peaks were also observed in the XRD pattern of the HP, but with low intensity. The pattern generated by the precursor HP sample showed well-defined, intense peaks that were attributed to Cu-hydroxynitrate. The patterns of each sample also contained H-ferrierite-phase peaks, labeled as “F” in Fig. 1.

Although the $(\text{Cu}+\text{Zn})/\text{Al}$ molar ratio in each of the samples was close to 3 (Table 1), a ratio that favors the formation of highly pure hydrotalcite-like structures, malachite peaks were

Fig. 1. XRD patterns of the precursor hybrid catalysts.

nonetheless observed in the XRD patterns of samples CP1 and CP2 [28]. The lower crystallinity of the hydrotalcite phases observed in the case of the CP2 is attributed to the greater nucleation rate during the precipitation process for this specimen, which favors the formation of smaller crystallites. In contrast, the highly intense precursor peaks in the pattern of the CP1 sample confirmed that larger crystallites were produced by the high nuclei growth rate favored by the low supersaturation conditions.

The nucleation rate applied during the precipitation process was observed to exert a significant effect in the case of the HP sample. The precursor phase of this sample had the lowest degree of crystallinity among the three materials assessed, demonstrating that the nucleation rate was highest when using this method. However, it is also possible that the steady increase in pH during the urea decomposition process used to generate the precipitating agent could have affected the formation of the Cu-hydroxynitrate precursor phase, which appears to be favored at low pH values during urea hydrolysis. As the pH was increased because of the formation of CO_2 by urea decomposition, the hydrotalcite phase would also be expected to form.

Following calcination, the precursor phases were transformed into metal oxide phases, as shown in Fig. 2. CuO peaks are observed in the XRD patterns of all of the samples. These peaks are smallest and broadest in the pattern generated by CP1, followed by CP2, indicating the presence of segregated phases. In the HP pattern, these peaks are more intense and narrower, suggesting larger crystallite size. Zeolite peaks are

Fig. 2. XRD patterns of the calcined hybrid catalysts.

observed in all of the samples, confirming the crystalline integrity of the H-ferrierite.

The Rietveld refinement of the XRD patterns obtained for the calcined catalysts revealed that CuO was the main crystalline phase (Table 1). The absence of crystalline ZnO during the Rietveld refinements of samples CP1 and CP2 was ascribed to the segregation of this phase. This behavior can also be explained by considering the calcination temperature. According to Behrens et al. [29], oxide phases do not crystallize until the carbonation step at temperatures higher than 500 °C. Following calcination, at 330 °C, an amorphous material is obtained. However, the ZnO crystalline phase observed in the HP sample can be attributed to the precursors formed during the synthesis. Furthermore, the CuO crystallite size was determined to be smaller in samples CP1 and CP2 than in sample HP, indicating the influence of the Cu-hydroxynitrate precursor phase.

The specific surface area and micropore area of the hybrid catalysts are summarized in Table 1. These results correspond to the combination of the two components of the hybrid catalysts: the methanol synthesis catalyst and the zeolitic support. Consequently, the textural properties of the hybrid catalysts are a mixture of those of both components. Based on these results, the higher specific surface area observed for the CP2 sample is attributed to the preparation method, which likely favored a well-dispersed MSC over H-ferrierite.

The micropore area attributed to the zeolitic component of the hybrid catalyst revealed partial blockage of the microporous zeolite by the MSC, since the micropore area of the H-ferrierite was 288 m^2/g . The N_2 adsorption isotherms of the calcined hybrid catalysts are shown in Fig. 3, and several differences are evident among the samples. The hysteresis ob-

Table 1
Chemical compositions and structural properties of the calcined catalysts.

Hybrid catalyst	Chemical composition (wt%)			(Cu+Zn)/Al molar ratio	Crystalline phases composition (wt%)			CuO crystallite size (nm)	Specific area (m^2/g)	
	Cu	Zn	Al		CuO	Cu_2O	ZnO		S_{BET}	S_{M}
CP1	26	14	5.4	3.1	31.0	1.1	—	15.0	114	72
CP2	25	14	5.7	2.9	37.0	11.1	—	14.6	192	69
HP	27	13	6.1	2.8	26.3	—	27.4	19.4	110	72

M—Micropore.

Fig. 3. Textural properties of the calcined hybrid catalysts. (a) N_2 adsorption isotherms; (b) Pore size distributions.

served above 0.8 p/p_0 was ascribed to N_2 condensation in the spaces between the particle agglomerates of the MSC. Consequently, a relationship exists between the volume of N_2 adsorbed at high relative pressures in the hybrid catalysts and the presence of agglomerates of this component over the zeolite.

Each of the pore size distribution profiles indicate pores that are 20 Å or less in size, and thus represent the micropores of the zeolite. Sample CP1 generated a profile consistent with a zeolite, indicating that no mesopores associated with spaces between particle agglomerates of the MSC were present. The distribution profile of the HP sample contains a wide peak at 60 Å, indicating the presence of particle agglomerates, while the profile of the CP2 sample suggests a different pore size distribution. Thus the presence of agglomerates of the MSC was confirmed by these results, indicating the formation of particles of differing size on the support. The absence of mesopores in the CP1 sample is likely a consequence of the high dispersion of the MSC. This sample would therefore represent a good model of a hybrid catalyst in which the MSC is well dispersed over the dehydration component.

3.2. Morphology

TEM images of the hybrid catalysts are shown in Fig. 4. Small dark particles dispersed over the zeolite are observed in each of the samples. These particles correspond to the MSC and exhibit different sizes and morphologies. Very small spherical particles (< 5 nm) are seen in sample CP1 (Fig. 4(a)). No ag-

glomerates of metallic oxide particles are present, demonstrating that the MSC particles were widely dispersed over the support. This result confirms the results of the XRD and textural properties analyses.

In contrast, quasi-spherical particles of different sizes (5–17 nm) as well as agglomerates of these particles (see arrow) are evident in the case of sample CP2 (Fig. 4(b)). The size distributions of the heterogeneous particles and the agglomerate particles in this sample are consistent with the textural results. The preparation method used to synthesize this sample, based on a high nucleation rate, favors the formation of small particles but did not result in a homogeneous, narrow particle size distribution. This result is attributed to the continuous aggregation of the nuclei during aging, which promotes the growth of the particles and results in particles with different sizes.

Small particles of the MSC spread over the zeolitic support are also observed in the HP sample (Fig. 4(c)), in addition to a heterogeneous particles size distribution. Many of the particles in this specimen are larger than those observed in the CP1 and CP2. Agglomerates are not present, although the dispersion is not as homogeneous as that in sample CP1.

3.3. XPS results

The XPS results obtained for the calcined samples are provided in Fig. 5. The Cu 2p core-level spectra are displayed and detailed spectroscopy data are summarized in Table 2. The peak at approximately 933.8 eV, corresponding to Cu 2p_{3/2}, and

Fig. 4. TEM images of calcined samples. (a) CP1; (b) CP2; (c) HP.

Fig. 5. Cu $2p_{3/2}$ XPS spectra of the calcined hybrid catalysts.

the satellite peak at approximately 942.3 eV confirm that the oxidation state of Cu in the hybrid catalysts was 2+.

The surface Cu/Zn ratio, the Cu $2p_{3/2}$ BE, the satellite/main peak intensity ratio and the FWHM (full-width at half-maximum) of the Cu $2p_{3/2}$ are summarized in Table 2. A decrease in the surface Cu/Zn atomic ratio was observed in the catalysts compared to that in the bulk. This difference has previously been reported by Okamoto et al. [30] and by Dai et al. [31] following surface enrichment with Zn, and is explained by Dai as being due to the isomorphous substitution of Cu by Zn [31]. The Zn-rich surface suggests that amorphous copper oxide was likely formed via the dissolution of Zn^{2+} ions into the surface layer of CuO, resulting in the surface of the calcined catalyst being amorphous. The results obtained for the HP sample indicate that the degree of isomorphous substitution of Cu was higher in this sample. A surface Cu/Zn atomic ratio similar to that of the bulk would indicate a homogeneous dissolution of Cu^{2+} ions into ZnO.

The Cu $2p_{3/2}$ BE of sample CP1 was lower than that reported in the literature (933.8 eV) [32]. According to Okamoto et al. [30], lower BE values indicate new Cu species. Lima et al. [33] have stated that the satellite peak structure provides information about the bonding characteristics of the Cu^{2+} ions in the catalyst. Okamoto et al. [30] have asserted that a decrease in the satellite peak provides evidence of the formation of a new Cu phase. The satellite/main peak ratios are provided in Table 2, and it can be seen that the CP1 and CP2 exhibit lower ratios. These low satellite peak intensities are ascribed to the presence

Table 2
XPS results of the hybrid catalysts.

Sample	Cu $2p_{3/2}$	Zn $2p_{3/2}$	I_s/I_m^a	FWHM (Main)	Cu/Zn	
					Surface ^b	Bulk ^c
CP1	933.0	1022.8	0.25	3.2	1.10	1.91
CP2	933.9	1022.5	0.24	3.2	0.98	1.84
HP	934.1	1022.7	0.29	3.4	0.82	2.14

^a Satellite/main peak ratio.

^b Surface Cu/Zn atomic ratios determined using the following expression: $Cu/Zn = (S_{Cu}/S_{Zn}) \times 1/0.88$, where 0.88 represents the relative atomic sensitivity factor and S_{Cu} and S_{Zn} represent the Cu and Zn peak areas, respectively.

^c Molar ratio.

of Cu^{2+} ions dissolved substitutionally into the ZnO lattice.

The smaller FWHM values observed in the CP1 and CP2 samples can be interpreted in terms of distortion of the CuO square-planar symmetry. Distortion toward a highly distorted octahedral symmetry, induced by weak coordination with the nearest neighbor or additional O^{2-} ions, results in greater delocalization of 3d electrons, reducing the FWHM of the Cu 2p-core band.

The narrow FWHM spectrum can also be explained by assuming that the Cu^{2+} ions were dissolved into the ZnO lattice and coordinated by four O^{2-} anions in T_d symmetry. Therefore, the observed Cu^{2+} species were dissolved substitutionally into the ZnO lattice. Similar results were reported by Moretti et al. [32], suggesting that the Cu ions were dispersed on the ZnO surface and that the increase in the covalence of the Cu–O bonding and of the CuO/ZnO interface could decrease the satellite peak intensity and increase the mean peak intensity. This behavior can be confirmed by a decrease in the FWHM mean peak intensity.

From these results, two types of interactions between CuO and ZnO are thought to occur in the catalysts. The first interaction forms an amorphous phase, while the other results in a dissolved phase. The CP1 catalyst evidently contains a higher concentration of this dissolved phase, and should exhibit higher activity as a consequence of the greater Cu^{2+} dispersion on the surface structure [33].

3.4. NH_3 -TPD

The NH_3 -TPD profiles show three desorption peaks (Fig. 6), attributed to NH_3 desorption from weak, medium and strong acid sites, respectively [34–36]. NH_3 desorbs from the weak acid sites at approximately 270 °C, and these sites are contributed by the zeolite and the MSC (inset to Fig. 6). The medium and strong acid sites show desorption at temperatures of 325 and 450 °C, respectively, attributed to NH_3 desorption from the zeolite surface [10,24]. The acid site concentrations were calculated from the NH_3 -TPD data and are shown in Table 3, where T1, T2 and T3 indicate weak, medium and strong sites,

Fig. 6. NH_3 -TPD profiles of the hybrid catalysts. Inset: Typical MSC sample.

Table 3

Acidity properties of the hybrid catalysts.

Hybrid catalyst	Number of acid sites ($\mu\text{mol/g}$)		
	T1	T2	T3
CP1	0.95	2.06	3.51
CP2	1.03	2.18	3.33
HP	1.08	2.52	3.43

respectively. Each of the samples exhibited a high concentration of strong acid sites, demonstrating that these sites were not fully blocked by the MSC [25].

3.5. TPR results

TPR measurements were carried out to investigate the reducibility of the Cu species in the Cu/ZnO/Al₂O₃ catalysts prepared by various methods [37]. The TPR profiles of the Cu/ZnO/Al₂O₃ catalysts are provided in Fig. 7. The profiles of the samples prepared by coprecipitation at low supersaturation (CP1) and by homogeneous precipitation (HP) exhibit two reduction peaks, whereas the profile of the sample prepared by coprecipitation at high supersaturation (CP2) has only one. The reduction profiles with two peaks are attributed to the reduction of two types of CuO. The peak at lower temperature is ascribed to the reduction of dispersed CuO in a solid CuO-ZnO solution [38], whereas the peak at higher temperature can be attributed to the reduction of bulk-like CuO phases [39–44]. Profiles with two peaks are not always observed, and the CP2 sample profile is believed to result from the reduction of bulk-like CuO phases, including large clusters and bulk CuO [45–49]. TEM results for the CP2 revealed the presence of large MSC particles even in the presence of a high concentration of the CuO phase. In any event, highly dispersed Cu species do not exhibit a single reduction step.

With respect to the reduction temperatures, the CP1 and HP samples were reduced at lower temperatures compared with the CP2 sample. A higher reduction temperature indicates a stronger interaction between the Cu species and the support. Some authors have reported that highly dispersed CuO generates TPR signals at much lower temperatures than those of bulk CuO [50]. Nevertheless, a similar shift of the reduction maximum toward higher temperatures has been previously reported by Robinson and Mol [51] in a TPR study of the interaction of CuO and ZnO. They attributed this phenomenon to the presence of a specific type of strong interaction between CuO and the ZnO lattice.

The greater reducibility observed for the CP1 and HP samples is attributed to various factors, such as better dispersion of

Fig. 7. TPR results of the hybrid catalysts.

the MSC over the zeolitic support, smaller particles sizes, or the broad distribution of Cu²⁺ species in the oxide mixture formed by Cu, Zn and Al.

3.6. Catalytic performance of hybrid catalysts

The catalytic activity results are shown in Table 4. The CO conversion data verified that the Cu sintering normally observed at reaction temperatures above 300 °C was minimized by the use of highly dispersed Cu species. In these trials, the application of lower reaction temperatures was not considered because the methanol-to-hydrocarbon conversion to produce C₃–C₄ hydrocarbons is favored by temperatures above 350 °C [12]. Different CO conversions were observed among the hybrid catalysts, due to the MSC component responsible for promoting the first transformation stage of syngas to methanol. The CO conversion was greatest in the case of the CP1 sample, followed by the CP2 and HP. Methanol was not observed among the products, suggesting that the methanol was completely converted during the second stage of the reaction. The CO conversion observed when using the CP1 was higher than that reported by Fujimoto et al. [52], who used a hybrid catalyst at 375 °C (33.9 %). However, Ge et al. [5] obtained CO conversions between 70% to 80% at 375 °C and 5.1 MPa.

Hydrocarbons and CO₂ were the main products detected in addition to DME, with C₂–C₃ products accounting for the majority. The active species obtained from methanol conversion are the carbene (CH₂) and carbenium (C_nH_{2n+1}⁺) ions, and that the stability of carbenium ions increasing with increasing carbon number. The methyl cation (CH₃⁺), which is the most active carbenium ion, reacts with carbene (:CH₂) to produce an ethyl cation (C₂H₅⁺), after which the C₂H₅⁺ reacts with carbene to

Table 4

Cu surface areas and catalytic trial results.

Hybrid catalyst	S_{Cu} (m ² /g)	X_{CO} (%)	Product (mol%)			Hydrocarbons distribution (mol%)					
			HC	DME	CO ₂	C1	C2	C3	C4	C5	C6+
CP1	16.9	54.4	40.3	17.0	42.7	8.5	42.2	14.5	7.7	4.4	22.6
CP2	13.0	42.6	40.2	21.8	38.0	7.6	66.1	5.0	4.0	2.5	14.9
HP	10.2	32.8	41.0	15.8	43.2	9.8	38.6	14.3	8.9	5.2	23.4

Trial conditions: W/F = 10.2 (g·h)/mol, 2.0 MPa, 350 °C, H₂/CO = 2.

generate $C_3H_7^+$ and then $C_4H_9^+$. This is the typical route by which hydrocarbons are generated. The reaction between carbenium ions takes place inside the zeolite through a mechanism involving deprotonation and hydrogenation. The former process produces olefins and is favored at higher temperatures because it is endothermic, while the second generates paraffins and is exothermic.

It was not determined if the hydrocarbons obtained during the catalytic tests were paraffins or olefins. However, based on the temperature at which the reactions were conducted, the products were most likely olefins [53]. The CP1 and HP samples produced C2 and C3 in higher proportion, while the CP2 sample gave a greater proportion of C1–C2. Overall, C2 was the main hydrocarbon produced by the hybrid catalyst, and so chain growth was not favored, likely due to the pore sizes available in the H-ferrierite zeolite. The partial blocking of pores by the MSC may have limited the diffusion of the reaction products [54].

3.7. Discussion

The method used to synthesize the MSC had the greatest impact on CO conversion. The results indicate that the MSC supported on the H-ferrierite zeolite was more active, resulting in greater CO conversion. The high activity toward the conversion of CO into methanol of this material was evidently due to several characteristics, including (1) small particle size, (2) better dispersion of the MSC over the zeolitic support, (3) greater dispersion of Cu species on the MSC, and (4) overcoming the thermodynamic constraints to methanol synthesis through the transformation of methanol to DME or hydrocarbons. This is considered a driving force for higher CO conversion.

During precipitation of the catalyst prepared under low supersaturation conditions or under slow mixing (sample CP1), the pH was controlled (ca. 7), allowing the formation of a highly active catalyst. With this method, high homogeneity and good dispersion of the active sites are favored because the Cu^{2+} , Zn^{2+} and Al^{3+} ions are immediately and simultaneously precipitated. Consequently, the resulting solid exhibited a homogeneous distribution of metals [32]. Later, during the aging process, dissolution/re-precipitation events in Cu- and Zn/Al-rich phases favored the formation of crystalline hydrotalcite, resulting in a final material with a homogeneous distribution of metals at the microscopic level [32]. Furthermore, small particles of the MSC were formed after calcination and were widely spread over the zeolite H-ferrierite, as verified by TEM observations.

In the case of the high supersaturation or fast mixing method (sample CP2), the simultaneous precipitation of metallic ions was also favored. In addition, although a narrow particle size distribution was not observed, Cu species appeared to have been homogeneously distributed in the oxide mixture after calcination. The metals precipitated simultaneously even at a high addition rate, thereby enabling the homogeneous distribution of Cu species.

In the conventional homogeneous precipitation method, the

Fig. 8. CO conversion rate as a function of Cu surface area.

pH is not controlled; thus, the initial pH of the solution is very low and increases during the urea hydrolysis. Consequently, the different metals do not precipitate simultaneously. Rather, Cu^{2+} precipitates prior to the Zn^{2+} and Al^{3+} , and the desired microscopically homogeneous distribution of the metal species is not achieved [20]. Furthermore, other precursor phases can be favored. This fact is confirmed by the Cu surface areas reported in Table 4. Samples in which the homogenous distribution of the metallic species was favored exhibited higher Cu surface areas. This surface area was directly correlated with the CO conversion (Fig. 8), confirming that Cu particles served as the active sites for methanol formation from syngas.

It is apparent that the heterogeneous particle size distribution of the MSC observed in the case of sample CP2 did not affect the distribution of active sites, in contrast to the TPR results. XRD patterns of the reduced samples presented in Fig. 9 showed that, despite the CP2 sample containing large particles of $CuO/ZnO/Al_2O_3$ that were not well spread over the zeolite, this sample did not exhibit large crystallites of the Cu phase (Table 5). Furthermore, the Cu crystalline phase content found in sample CP2 was similar to that observed in the CP1. In contrast, the CP2 showed a greater tendency towards deactivation compared to the CP1 and HP samples, as confirmed by the XRD patterns of the catalysts after reaction. The Cu phase peak corresponding to the (111) plane in the CP2 pattern was very weak in relation to the corresponding peaks in the CP1 and HP

Fig. 9. XRD patterns of the reduced hybrid catalysts.

Table 5

Structural properties of reduced and used hybrid catalysts.

Sample	Reduced						Used					
	Crystalline composition (%)				Cu lattice constant (Å)	Crystallite size (nm)	Crystalline composition (%)				Cu lattice constant (Å)	Crystallite size (nm)
	Cu	Cu ₂ O	CuO	ZnO			Cu	Cu ₂ O	CuO	ZnO		
CP1	71.7	2.0	4.8	21.5	3.6066	9.2	35.5	19.6	44.8	1.0	3.6188	8.5
CP2	69.1	1.0	10.6	19.3	3.6240	10.7	6.5	19.6	49.3	24.5	3.6082	5.0
HP	81.5	0	0.4	18.1	3.6284	12.2	22.8	12.7	62.2	2.3	3.6030	13.1

samples (Fig. 10). Consequently, the proportion of Cu the phase was very low, as verified by the Rietveld refinement results (Table 5).

In contrast, the precipitation under low supersaturation conditions favored the formation of catalysts with small particles sizes and well-dispersed Cu active sites, resulting in the enhancement of other characteristics, such as structural stability. After 6 h of reaction, the CP1 still exhibited a higher level of Cu crystalline phase. In addition, a slight decrease of the crystallite size was observed, indicating that no sintering of Cu particles occurred (Table 5).

The main reaction mechanism of CO hydrogenation to light hydrocarbons via methanol/DME is thought to proceed as summarized in the following equations. CO is first hydrogenated to form methanol over the MSC (1), after which methanol dehydration results in the formation of DME (2). Further dehydration results in the formation of hydrocarbons over the zeolite (3) while, simultaneously, a shift reaction occurs between CO and water over the Cu-based components (4) to form CO₂ [55].

The four reaction steps show synergistic effects, as confirmed by Li and Fujimoto [56,57]. The conversion of methanol to hydrocarbons overcomes the equilibrium limitations associated with methanol synthesis from syngas. As well, the zeolite acid sites act as active sites for DME formation. The protons on the zeolite surface promote carbenium hydrogenation and this effect can be enhanced by the hydrogen spilled over the zeolite surface. The CO₂ formed by the water-gas shift reaction can

react with hydrogen to form methanol via another reaction route, although the reactivity is lower. The resulting H₂O affects the reaction on the zeolite surface by suppressing the adsorption of protons or carbenium ions, although the spillover of hydrogen allows methanol conversion to hydrocarbons. In short, the methanol formed from syngas is converted to DME, which is then transformed into hydrocarbons (C1–C7) via chain growth that is significantly promoted by the spillover of hydrogen.

The balance between hydrogenating and acidic functionalities could be the key to obtaining highly active hybrid catalysts. Such catalysts should provide the maximum conversion of methanol, primarily formed from syngas on Cu sites, into the final hydrocarbon products on acidic sites [58]. This characteristic of a hybrid catalyst can be controlled through adjusting the ratio of its hydrogenating and acidic components. Thus, for a hybrid catalyst, there is no single ideal component ratio. Another strategy to obtain active hybrid catalysts is to improve the dispersion of the MSC over the acidic component (the zeolite) so as to enhance the catalytic properties of both components.

Optimization of the MSC must favor the first stage of the global reaction to efficiently transform the syngas into methanol. According to the results obtained here, the MSC affects the CO conversion. Therefore, the benefits of optimizing the MSC are potentially greater. As an example, small particles of the MSC dispersed homogeneously over the zeolite surface, as well as Cu species well distributed over the oxide mixture (Cu-ZnO-Al₂O₃), can favor greater hydrocarbon production from syngas. This occurs for the following reasons: (1) the well-dispersed Cu species result in greater methanol formation; (2) widely dispersed MSC particles retard the sintering of Cu crystallites; (3) small particles result in reduced blocking of both the zeolite micropores and strong acid sites; and (4) well-dispersed, small particles increase the extent of proximity between the two active sites (that is, Cu and acid sites), thereby promoting increased production of hydrocarbons.

4. Conclusions

Different preparation methods to synthesize MSCs were found to affect their textural, structural and morphological properties. In addition, precipitation under low supersaturation conditions was verified to favor hydrotalcite precursor formation with highly dispersed metallic ions and a homogeneous particle size distribution. Aggregation of the nuclei during aging was observed in samples precipitated from highly supersaturated solutions, giving a heterogeneous particle size

Fig. 10. XRD patterns of the used hybrid catalysts.

distribution. However, the structural characteristics of the MSC prepared under high supersaturation conditions were not affected; consequently, highly dispersed Cu species were also observed. In the homogenous precipitation method, the precipitation conditions influenced the precursor formation and poorly dispersed Cu species were obtained.

We also verified that the effect of an MSC on the overall reaction is directly related to the CO conversion, the first stage of hydrocarbon production, because of the variations in the metallic Cu surface area. A direct correlation between the Cu surface area and CO conversion rate was determined. In addition, an optimized MSC was found to affect the zeolitic properties, avoiding blockage of the micropores and acid sites as well as favoring the proximity between the active sites involved in the global reaction.

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Graphical Abstract

Chin. J. Catal., 2016, 37: 378–388 doi: 10.1016/S1872-2067(15)61032-4

Effect of Cu-ZnO-Al₂O₃ supported on H-ferrierite on hydrocarbons formation from CO hydrogenation

J. H. Flores, M. E. H. Maia da Costa, M. I. Pais da Silva*
Pontifícia Universidade Católica, Brazil

Catalysts consisting of Cu/Zn/Al supported on H-ferrierite zeolite prepared by coprecipitation under low supersaturation conditions exhibit a greater degree of Cu species dispersion, well-dispersed particles and reduced blockage of the zeolite acid sites.

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H型镁碱沸石负载对Cu-ZnO-Al₂O₃催化剂上CO加氢生成烃类的影响

J. H. Flores^a, M. E. H. Maia da Costa^b, M. I. Pais da Silva^{a,*}

^a里约热内卢天主教大学生物化学系, 里约热内卢22453-900, 巴西

^b里约热内卢天主教大学物理系, 里约热内卢22453-900, 巴西

摘要: 采用三种不同方法制备了Cu-Zn-Al基甲醇催化剂, 然后在水相悬浮液中与H型镁碱沸石混合分散, 以制得负载型甲醇催化剂。运用X射线衍射、N₂吸附-脱附、透射电镜、程序升温还原、NH₃程序升温脱附、H₂程序升温脱附和X射线光电子能谱对催化剂进行了表征。考察了催化剂催化CO加氢反应生成二甲醚和烃类的性能。该催化剂是在低和高过饱和度条件下采用共沉淀法和均匀沉淀法制得的。制备方法对前驱体的结构特性(如纯度、结晶度和催化剂颗粒粒径分布)有显著影响。低过饱和度的沉淀条件有利于Cu物种的高度分散, 增加了催化剂中金属的比表面积, 所得催化剂粒径分布均匀。这些效应进而会影响分子筛的性质, 导致其微孔孔体积较小, 分子筛酸性位被堵塞。通过Cu比表面积和CO转化速率之间的关联可考察甲醇催化剂的性能。

关键词: 甲醇合成催化剂; 低和高过饱和度下沉淀; 合成气; 镁碱沸石; 烃类; 二甲醚

收稿日期: 2015-10-29. 接受日期: 2015-12-09. 出版日期: 2016-03-05.

*通讯联系人. 电话: +55-21-35271323; 电子信箱: isapais@puc-rio.br

基金来源: CAPES项目.

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).