

NATURALLY-OCCURRING SILICATES AS CARRIERS FOR COPPER CATALYSTS USED IN METHANOL CONVERSION

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Abstract—Bentonite- and sepiolite-supported copper catalysts have been prepared either by adsorption of Cu(II) from aqueous solutions of copper nitrate at pH ~4.5 or by adsorption of a $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex from an ammonia solution of CuSO_4 at pH ~9.5. The structure and composition of the calcined preparations have been studied by X-ray diffraction, chemical analysis, and energy dispersive X-rays. Textural characteristics have derived from the analysis of the adsorption-desorption isotherms of N_2 . All catalysts have been tested for the dehydrogenation of methanol to methyl formate. For this reaction, bentonite-based catalysts were found to have very little activity, which indicates that copper located in the interlamellar spaces is inaccessible to methanol molecules. On the contrary, copper-sepiolite catalysts showed a very high specific activity even for those catalysts with a very low copper content. The chemical state of copper in the catalysts on-stream has been revealed by X-ray photoelectron spectroscopy and X-ray-induced Auger techniques. In most of the catalysts Cu^+ is the dominant copper species.

Key Words—Bentonite, Copper catalysts, Methanol dehydrogenation, Sepiolite.

INTRODUCTION

Naturally-occurring silicates are interesting materials for catalytic purposes, not only for their great abundance and low cost, but also for the particular properties and structures they show (Figueras, 1988). Among these, bentonite and sepiolite remain prominent. Bentonite is composed essentially of montmorillonite, a dioctahedral smectite of the 2:1 low charge clay mineral family. Bentonites possess several textural and chemical properties, such as high surface area, surface acidity, cation exchange capacity, and the possibility for intercalating water or other polar molecules of different kinds (Pinnavaia *et al.*, 1984; Pinnavaia, 1983). It is highly suitable for the preparation of new catalytic materials.

Sepiolite is also a 2:1 clay mineral, with the octahedral sheet populated by magnesium instead of aluminum oxide. It has a structure consisting of laths joined together at their corners, with very small channels running along the whole length of the fiber-like crystals. This channel microporosity can be exploited for catalytic and adsorption purposes (Mendioroz *et al.*, 1987).

In the present chemical and petrochemical indus-

tries, new catalytic processes yielding high molecular weight hydrocarbons from simple molecules (CO , CO_2 , CH_4 , CH_3OH) are highly desirable. In particular, methanol, which is usually obtained from syngas ($\text{CO} + \text{H}_2$), can be transformed via nonselective processes into dimethyl ether or hydrocarbons (Chang, 1983), or oxidized to formaldehyde with the concomitant appearance of water (Calkins, 1984). Another more attractive reaction of methanol is its dehydrogenation to methylformate, which can then be used in the synthesis of formic acid, dimethyl formamide, formamide, or acetic acid.

Methanol dehydrogenation to methyl formate can be conducted either in the absence (dehydrogenation) or presence (oxidation) of oxygen. Numerous catalyst systems have already been described for the latter process (Ai, 1983). However, this process presents the disadvantage that the H_2 removed from methanol is lost as valueless water. Obviously, the better alternative is direct dehydrogenation:



which yields gaseous hydrogen and methyl formate. However, the resulting yield is no higher than 40%,

since the equilibrium conversion is thermodynamically controlled. Among the catalysts proposed for the reaction described by Eq. (1), many, usually containing copper, have been investigated (Tonner *et al.*, 1984; Guerrero-Ruiz *et al.*, 1991).

The aim of this work is the design of bentonite- and sepiolite-supported copper catalysts active and selective in the direct dehydrogenation of methanol (Eq. 1). In order to explore how the copper location and its interaction with the surface of both silicates affect the selectivity to methyl formate, various copper precursors have been used in the synthesis of catalysts, and a careful structural and textural characterization of fresh and spent catalysts has been undertaken to determine the nature, as well as the role, of the active sites responsible for the reaction.

EXPERIMENTAL

Catalyst preparation

Bentonite (B), containing more than 92% montmorillonite was supplied by Minas de Gador S.A. (Spain). Sepiolite (S), more than 95% pure, was provided by Tolsa S.A. (Spain). The fine montmorillonitic fraction ($<2 \mu\text{m}$) was extracted from the bentonite by controlled sedimentation. The textural parameters of this purified fraction were: BET surface area, $87 \text{ m}^2/\text{g}$; total pore volume, $0.12 \text{ cm}^3/\text{g}$; cation exchange capacity, 1.10 meq/g . For sepiolite (S) the relevant textural characteristics were: BET surface area, $238 \text{ m}^2/\text{g}$; pore volume, $0.53 \text{ cm}^3/\text{g}$.

Copper incorporation into both bentonite and sepiolite was carried out according to the following procedures: (1) adsorption of Cu(II) from aqueous solutions of copper nitrate at a pH close to 4.5; the samples will be referred to hereafter as BAA and SAA for bentonite and sepiolite, respectively, (2) adsorption of the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex from an ammonia solution of CuSO_4 at $\text{pH} \approx 9.5$; these samples will be referred to hereafter as BAB and SAB. (All precursors were filtered, washed with distilled water and dried at 383 K), (3) incipient wetness impregnation of the solid with an ammonia solution of the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex; the sample will be referred to hereafter as BIB.

Analytical techniques

Copper contents were determined by atomic absorption spectrometry on aliquots of the solubilized catalysts. Elementary analysis was performed with an ISI DS 130 microscope equipped with an energy dispersive X-ray analyzer (EDX), which uses a Li(Si) detector. The main components, Si, Al, Mg and Cu were analyzed using their respective $K\alpha$ lines and a Gaussian deconvolution program incorporated in the analytical system.

The structural characterization was carried out by X-ray diffraction (XRD) and infrared (IR) spectroscopy.

X-ray diffraction patterns were obtained with a Philips PW 1710 using $\text{CuK}\alpha$ radiation and a nickel filter. IR spectra were recorded with a Nicolet ZDX spectrometer using pelleted samples diluted to $\sim 2\%$ in KBr.

The chemical state of copper and the surface composition of both fresh and used catalysts in the dehydrogenation of methanol were revealed by X-ray photoelectron spectroscopy (XPS). XPS spectra were acquired with a Leybold LHS10 spectrometer provided with a hemispherical electron analyzer and a $\text{MgK}\alpha$ X-ray radiation source ($h\nu = 1253.6 \text{ eV}$). The used samples were collected in isooctane to prevent further oxidation by ambient air. All samples were pressed into small holders and placed in the turbopumped pretreatment chamber and outgassed at $\sim 10^{-6}$ Torr before they were moved into the ultrahigh vacuum chamber. The residual pressure was maintained below 8×10^{-9} Torr during data acquisition. Each spectral region was signal-averaged for a number of scans to obtain good signal-to-noise ratios. Accurate binding energies (BE) were determined by charge referencing with the $\text{Si}2p$ peak at 103.4 eV .

The BET surface area and porosity of the samples were calculated from the nitrogen adsorption isotherms at 77 K , obtained with automatic equipment (Micromeritics ASAP-2000), using 0.162 nm^2 as the cross-sectional area of the N_2 -adsorbed molecule.

Catalytic activity

Activity tests for dehydrogenation of methanol were carried out at atmospheric pressure in a 0.9 cm O.D. fixed-bed tubular glass reactor. The reaction temperature was measured by a thermocouple placed in the outer wall of the catalytic bed. The methanol was fed into the reactor by bubbling a flow of helium ($50 \text{ cm}^3 \text{ min}^{-1}$) through the saturator-condenser maintained at 293 K , which allowed for a constant methanol concentration of 12.0% in volume. A catalyst charge of $0.5\text{--}1.0 \text{ g}$ was used in each experiment. Reaction temperatures in the range $453\text{--}523 \text{ K}$ were explored at a fixed contact time until constant conversion and selectivity were reached. Reaction products were analyzed by an on-line gas chromatograph (Hewlett Packard 5840 A) equipped with a flame ionization detector and a Chromosorb 101 column for product separation. Each test was duplicated on aliquots of two different batches of the same preparation. In general, good reproducibility for the two batches and the test itself were found.

RESULTS AND DISCUSSION

Chemical analyses of copper by atomic absorption spectrometry and EDX are summarized in Table 1. It is seen that Cu loadings for samples prepared in basic media (BAB, SAB and BIB) are higher than for their homologues prepared in acid solutions (BAA and SAA).

Table 1. Copper content of the catalysts.

Catalyst	Chemical analysis	EDX
BAB	10.8	11.9
SAB	8.4	8.4
BAA	3.0	3.6
SAA	1.3	1.0
BIB	10.5	12.3

This was to be expected, as the isoelectric points of bentonite and sepiolite are very low (≈ 2) and close to that of SiO_2 (Parks, 1965). In addition, the possibility of negative polarization of their surfaces in the solution of pH 4.5 is very low, and hence also the retention of Cu^{2+} by electrostatic forces. Therefore, ionic exchange seems to be the operative process. The former process would explain the higher extent of copper incorporation in basic media in which the large differences in pH, 2 vs 9.5, result in a high degree of surface polarization, which favors Cu adsorption. In addition, Cu adsorption and exchange in bentonite may be enhanced, as this material swells in basic media, thus increasing the available surface up to 10 times that of the original material.

In many cases, Cu was not uniformly distributed on the surface, as revealed by EDX analyses at several sites of mechanically-produced flat surfaces. The only exception was the BAA sample, which showed a much more homogeneous distribution, probably resulting in a better Cu dispersion.

The chemical state of copper in dried preparations was studied by XPS. Figure 1 shows the Cu2p core-level spectra of two Cu bentonites prepared by aqueous impregnation of $\text{Cu}(\text{NO}_3)_2$ (BAA) and by adsorption of the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex (BAB). Both of them show the characteristic Cu2p doublet with shake-up satellites on the higher BE side of the principal Cu2p lines characteristic of Cu^{2+} ions (Rojas *et al.*, 1990). Even considering the presence of Cu^{2+} ions in both preparations, the chemical environment seems to be different. The most intense $\text{Cu}2p_{3/2}$ peak appears at 933.9 eV in sample BAB, while it is shifted to 935.5 eV in sample BAA. The BEs of the $\text{Cu}2p_{3/2}$ peak in the range of 933.9 eV are typical of Cu(II) coordinated to several ammonia ligands, as expected from the adsorption of the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex at pH ~ 9.5 in the BAB sample. The shift of this peak towards higher BE in sample BAA indicates a change in the coordination sphere of copper. Aquocomplexes of the type $[\text{Cu}(\text{H}_2\text{O})_x]^{2+}$, or even $[\text{Cu}(\text{H}_2\text{O})_x(\text{OH})]^+$ ($x > y$) were expected on the bentonite surface.

X-ray diffraction patterns of the copper bentonites show a decrease of the basal spacing of the pure bentonite ($d = 1.47$ nm), irrespective of the nature of the complex, i.e., aminocomplex and aquocomplex. Such a decrease can be attributed to the substitution of Cu^{2+} for Ca^{2+} or Na^+ ions in the montmorillonite layers,

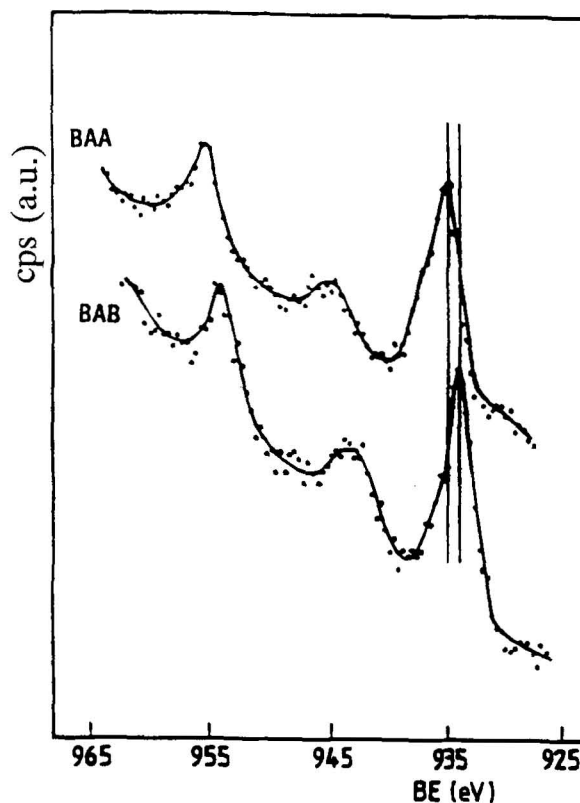


Figure 1. XPS spectra of bentonite-supported precursors.

since these ions exhibit a larger hydration capacity than Cu^{2+} . In addition, sample BAB shows diffraction lines corresponding to CuO, which may result from dehydration of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ or $\text{Cu}(\text{OH})_2$ species. Finally, the copper sepiolite shows no diffraction peaks for copper species, except sample SAB, for which the lines of CuO are clearly distinguished.

The IR spectra of the bentonite samples show bands at 3200 cm^{-1} , attributable to N–O bonds, and at 1364 cm^{-1} , assigned to SO_4^{2-} , which are more intense in BIB than in the respective BAB sample. The IR spectra of the sepiolite-supported precursors show a small decrease in the 3570 cm^{-1} peak. This may be ascribed to the stretching vibrations of dioctahedral OH bonded to Mg^{+2} (Serna *et al.*, 1975), and can be explained in terms of Mg^{+2} substitution by Cu^{+2} during active phase incorporation. Also, the 1423 cm^{-1} peak corresponding to NH_4^+ is observed for the SAB sample.

In order to determine how preparation methods affect the textural characteristics of bentonite and sepiolite carriers, adsorption-desorption isotherms of N_2 at 77 K have been completed. Figure 2a sums up these isotherms for the BAB and BAA preparations, as well as for the bentonite counterpart. All of them are similar, showing H3-type hysteresis loops ascribed to slit-shaped mesoporosity, as in between plate-like particles

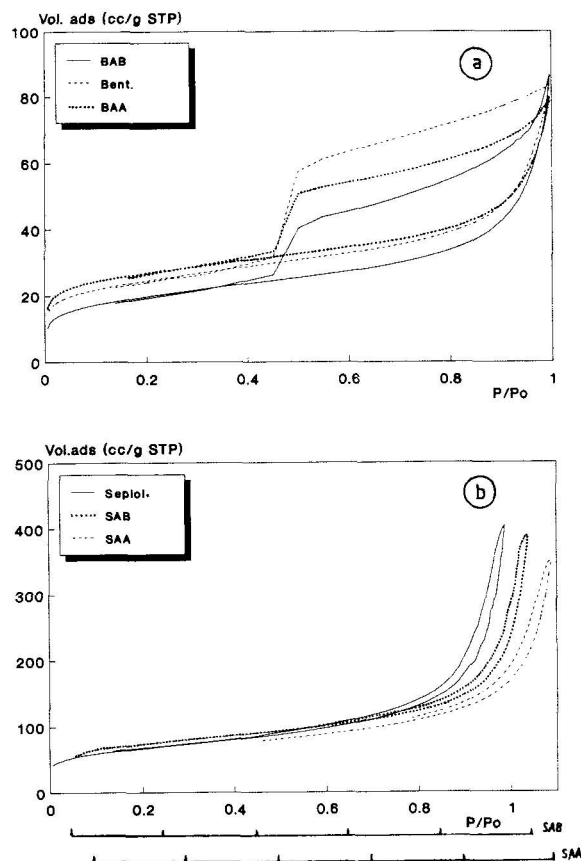


Figure 2. N_2 adsorption-desorption isotherms. a) Bentonite-supported catalysts, b) Sepiolite-supported catalysts.

(de Boer, 1958). This is in agreement with the morphology. No important differences in the loop width is observed among the samples, showing a mesoporosity unaffected by active phase incorporation, and a microporosity and surface area moving slightly towards higher values in BAA, and to lower ranges in BAB, with respect of the original bentonite. Similarly, the isotherms for SAB and SAA, and also for their sepiolite homologue (Figure 2b), denote an important mesoporosity. Here, the hysteresis loop is of the H1 type ascribed to cylindrical pores, as expected from the needle-like morphology of the material (de Boer, 1958). Mesoporosity is not changed by active phase incorporation, as in the former material, and only small changes in surface area are observed in SAB as compared to the original material.

Table 2 summarizes the textural parameters of the samples. As can be seen, no significant changes are produced upon Cu incorporation through adsorption from solution, the change being more important in the samples prepared from basic media. The exception is the BIB sample, in which surface area and pore volume have almost disappeared. Since the crystal structure of

Table 2. Textural characteristics of supports and precursors.

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)
Bentonite	87	0.12
BAA	98	0.11
BAB	69	0.12
BIB	1	0.01
Sepiolite	238	0.53
SAA	245	0.47
SAB	281	0.51

bentonite is preserved in the BIB sample, as revealed by its XRD pattern, it can be reasonably inferred that most of the copper is deposited at the edges of the silicate sheets, thus blocking the entrance of the N_2 molecule. In agreement with this, mercury porosimetry for this sample shows that more than 80% of the porosity is due to pores larger than 48 nm.

Catalytic activity

All catalysts were tested in the dehydrogenation of methanol (Eq. 1) after *in situ* preconditioning. Two different treatments have been followed in order to activate the samples. The first was the decomposition of the precursors in a helium flow at 573 K for 12 hr. As has been reported (Rodríguez-Ramos *et al.*, 1991), the formation of methyl formate occurs on metallic copper, which means that a reduction of the oxidized precursors is likely with the H_2 evolved (Eq. 1) upon exposure to the reactant ($CH_3OH + He$) mixture. The second pretreatment consisted of the reduction of oxidized precursors in a hydrogen flow at 573 K for 12 hr, which is sufficient for complete reduction of copper precursors.

Under the experimental conditions used in this study, the major reaction products were methyl formate and dimethyl ether, as well as minor amounts of methane. Carbon balances also included carbon oxides produced either by the degradation of methyl formate or by methanol decomposition. All the results presented in this work were obtained under steady-state conditions.

The specific activities of the various copper-containing catalysts are shown in Figure 3. As can be observed, the activity of the BIB catalyst is extremely low. This is consistent with the low surface area of the sample, from which large copper particles are expected to be formed after preconditioning and/or on-stream. Under such conditions, surface acid sites must be likewise inaccessible, and therefore low dimethyl ether yields are found. Another observation derived from Figure 3 is the low specific activity of bentonite-based (BAB and BAA) catalysts. This behavior could, in principle, be explained on the basis that Cu located in the interlamellar spaces becomes inaccessible to reducing gases after the decomposition-reduction pretreatments of the Cu aquo- (BAA) and amino- (BAB) complexes. Hence, reduction has not been produced. The sintering

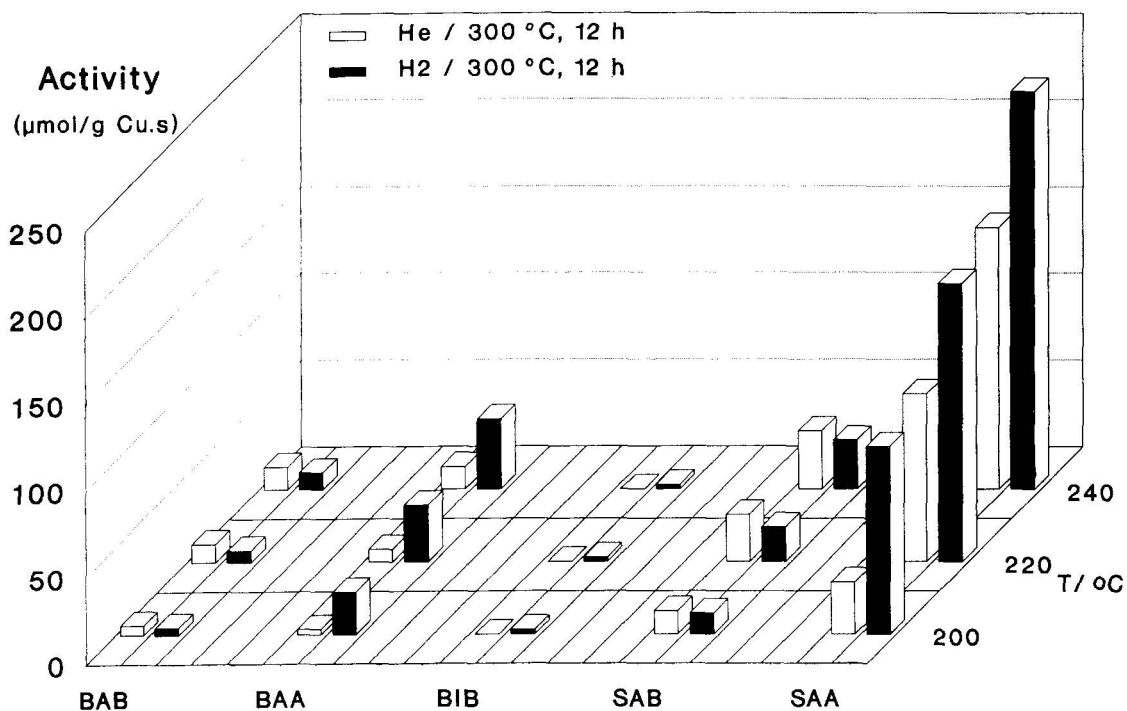


Figure 3. Methanol transformation activities for different Cu catalysts.

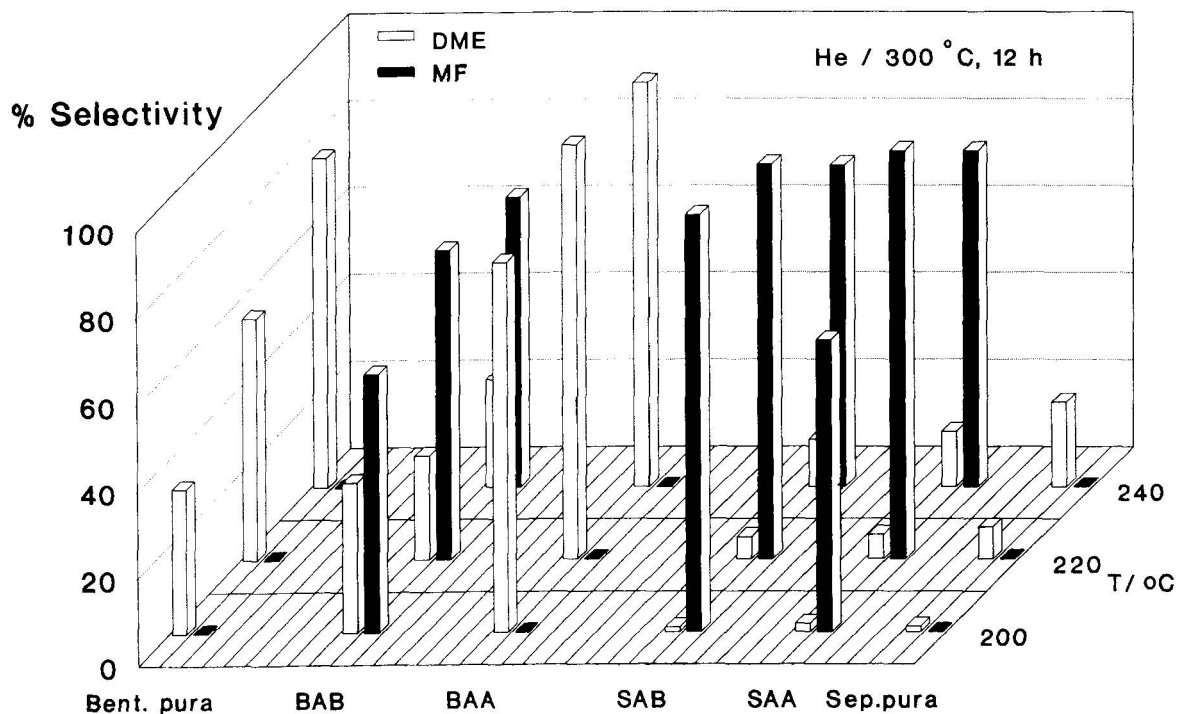


Figure 4. Catalytic selectivities to methyl formate (MF) and dimethyl ether (DME) of the different samples pretreated in helium at 573 K.

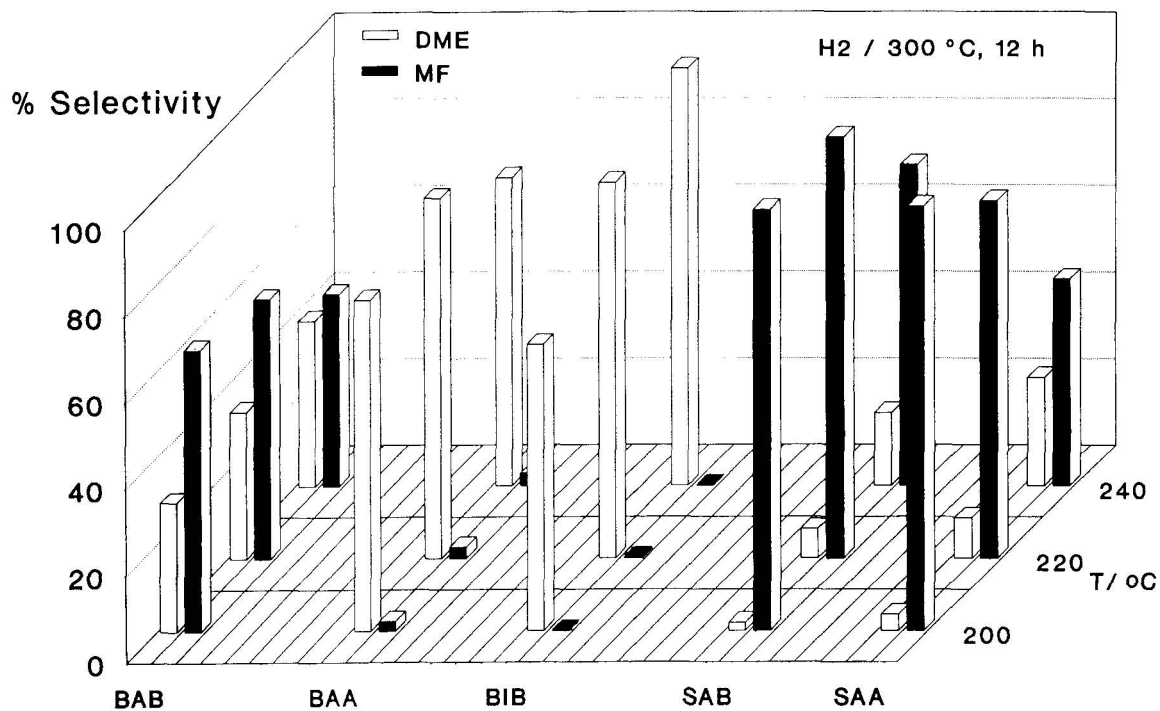


Figure 5. Catalytic selectivities to methyl formate (MF) and dimethyl ether (DME) of the different samples pretreated in hydrogen at 573 K.

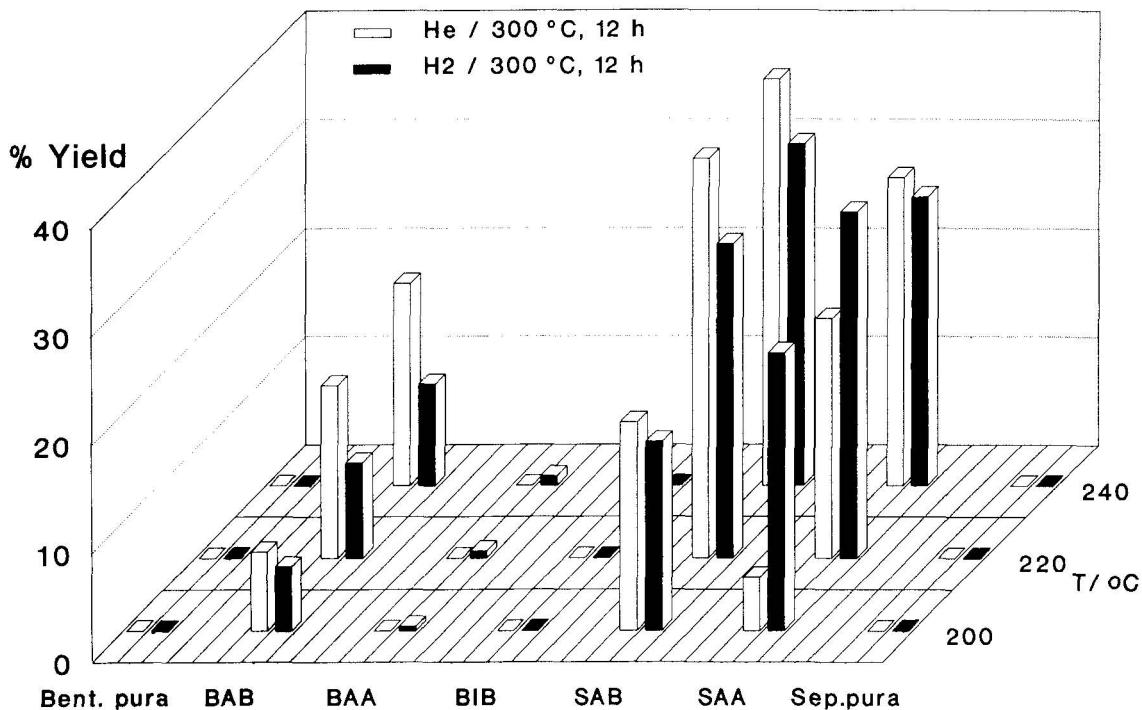


Figure 6. Catalytic yield to methyl formate (MF) of the different samples.

Table 3. XPS analysis of catalysts used in the dehydrogenation of methanol.

Sample	Cu2p _{3/2} (eV) ¹	CuL ₃ VV (eV) ²	α _x (eV) ³
BAB	934.2	—	—
BAA	933.9	908.7	1848.4
SAB	933.5	910.1(911.8)	1848.8(1851.5)
SAA	932.5	911.3	1848.6
BIB	933.1	—	—

¹ Si2p at a BE of 102.6 eV was taken as internal reference.

² Most intense X-ray induced Auger transition.

³ Modified Auger parameter.

of copper particles cannot be dismissed, since XRD patterns of these catalysts after on-stream, display clear diffraction lines of metallic Cu. In addition, if one compares catalytic activities of BAB and BAA catalysts it seems that H₂-reduction provokes an enhancement of catalyst activity after He pretreatment in the BAA sample, while minor changes are observed with either pretreatment in the BAB sample. The greater activity of the BAA catalyst pre-reduced in hydrogen can be explained in terms of catalyst reduction, owing to its low Cu-content and a stronger interaction of Cu²⁺ ions with the carrier. A similar reasoning can be applied to the sepiolite-supported catalysts. As the SAB catalyst possesses a high Cu-content, the steady-state activity is almost constant, irrespective of catalyst pretreatment. On the other hand, the SAA catalyst, with a lower Cu-content, and a stronger metal-support interaction, requires strongly reducing conditions to achieve complete reduction of Cu²⁺ ions, resulting in higher metal dispersion. Finally, the very high specific activity of the SAA catalyst is not surprising when one realizes that the copper phase can reach a high degree of dispersion as a consequence of its interchange with terminal Mg²⁺. The contribution of sepiolite alone (derived from a blank experiment) to the overall activity is insignificant, since its activity under the reaction conditions used in this work is extremely low.

The dimethyl ether and methyl formate selectivities of all the catalysts pretreated in helium are shown in Figure 4. From this figure it is clear that sepiolite-supported catalysts are highly selective toward dehydrogenation, while dehydration is the principal reaction in bentonite-based preparations.

Participation of the Cu-free bentonite surface on the dehydration reaction is important, as significant amounts of dimethyl ether have been found in a blank experiment with bentonite alone. The only exception is the BAB catalyst, whose methyl formate selectivity is still greater than that of dimethyl ether, as expected from its very high Cu-content, together with the lack of acidic centers "neutralized" during active phase incorporation. A similar behavior is observed with catalysts pre-reduced in hydrogen (Figure 5). As already noted above, dehydrogenation of methanol to methyl

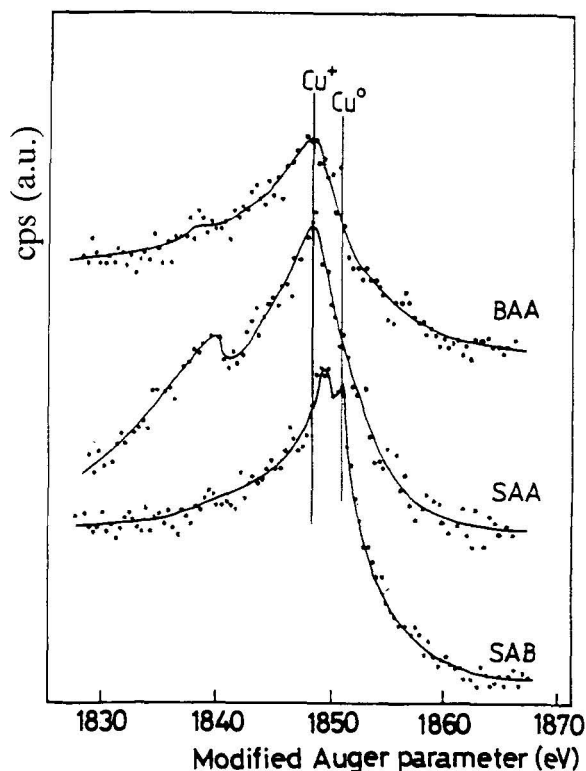
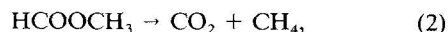


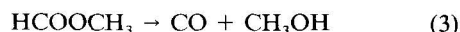
Figure 7. CuL₃VV X-ray-induced Auger lines of various copper-supported catalysts.

formate (Eq. 1) is an equilibrium reaction, for which the maximum theoretical yield under the experimental conditions used in this study does not exceed 40% (Morikawa *et al.*, 1980). Note that, irrespective of pretreatment, Cu-sepiolite catalysts (SAA and SAB) are very efficient catalysts in the dehydrogenation reaction (Figure 6), and approach the theoretical yield.

The selectivity to methyl formate decreases with increasing reaction temperature. This can be due to several factors: (1) the thermal decomposition of methyl formate to a methane by-product (Hirose *et al.*, 1982):



(2) to subsequent decarbonylation:



(Cant *et al.*, 1985), or (3) to thermal noncatalytic decomposition of methanol to CO plus 2H₂ (Hirose *et al.*, 1982). The extent of this last reaction is not important below 513 K.

The chemical state of copper in the spent catalysts has been revealed by XPS. The BEs of the Cu2p_{3/2} peak appear at slightly lower values than in oxidized preparations (Table 3), and no satellite structure was observed on the high BE side. Both findings exclude the

presence of Cu^{2+} in spent catalysts, hence Cu^+ and/or Cu^0 must be formed during prereduction or on-stream.

Owing to the small differences in the BE of the $\text{Cu}2p$ peaks of Cu^+ and Cu^0 , the differentiation between both copper species by XPS technique alone becomes extremely difficult, if not impossible. Measurement of the most intense $\text{Cu}L_{3VV}$ X-ray-induced Auger line is, however, conclusive. Figure 7 summarizes these transitions for three spent samples. The abscissa of this plot is referred to as the modified Auger parameter (α'_A) (Gaarenstam and Winograd, 1977; Sheffer *et al.*, 1989), as defined by the equation:

$$\alpha'_A = h\nu + \alpha_A = h\nu + (\text{KE}_{LMM} - \text{KE}_{\text{Cu}2p_{3/2}}), \quad (4)$$

in which the Auger parameter, α_A , represents the difference between kinetic energies of the emitted Cu_{LMM} electron and photoemitted $\text{Cu}2p_{3/2}$ electron. As shown in Figure 7, and summarized in Table 3, three samples exhibited the α'_A parameter at about 1848.6 eV, which is typical for Cu^+ species. Only the SAB catalyst showed a less-intense peak at 1851.5 eV, which can be reasonably assigned to metallic copper. At variance with this, are the mixed-oxide catalyst, $\text{LaMn}_{0.4}\text{Cu}_{0.6}\text{O}_3$ (Rodríguez-Ramos *et al.*, 1991) and the Cu/SiO_2 (Guerrero-Ruiz *et al.*, 1991) catalysts. These two catalysts when used in methanol dehydrogenation showed the modified Auger parameter (α'_A) at 1850.9 eV, which closely corresponds with the value expected for Cu^0 . Consequently, from the analysis of the experimental data it is evident that the stabilization of Cu^+ or Cu^0 depends mainly on the chemical nature of the environment. In the case of silicates it seems that small copper particles can interact with surface hydroxyl groups, thus accomplishing copper stabilization at a higher oxidation state than metallic copper, i.e., Cu^+ .

CONCLUSIONS

In the light of our results, we conclude that the incorporation of copper into the interlamellar spaces of bentonite makes an important part of it inactive, either by nil-reduction or by sintering in the steam generated through reduction. The acidic function is predominant, and thus, selectivity to dimethyl ether is obtained. In contrast, copper-loaded sepiolites constitute a class of interesting catalysts for this reaction; the metallic function addressing the yield to methyl formate.

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REFERENCES

- Ai, M. (1983) The reaction of formaldehyde on various metal oxide catalysts: *J. Catal.* **83**, 141–150.
- de Boer, J. H. (1958) *The Structure and Properties of Porous Materials*: Butterworths, London, p. 68.
- Calkins, W. N. (1984) Chemicals from methanol: *Catal. Rev. Sci. Eng.* **26**, 347–358.
- Cant, N. W., Tonner, S. P., Trimm, D. L., and Wainwright, M. S. (1985) Isotopic labeling studies of the mechanism of dehydrogenation of methanol to methyl formate over copper based catalysts: *J. Catal.* **91**, 197–207.
- Change, C. D. (1983) Hydrocarbons from methanol: *Catal. Rev. Sci. Eng.* **25**, 1–118.
- Figueroa, F. (1988) Pillared clays as catalysts: *Catal. Rev. Sci. Eng.* **30**, 457–499.
- Gaarenstam, S. W. and Winograd, N. (1977) Initial and final state effects in the ESCA spectra of cadmium and silver oxides: *J. Chem. Phys.* **67**, 3500–3506.
- Guerrero-Ruiz, A., Rodríguez-Ramos, I., and Fierro, J. L. G. (1991) Dehydrogenation of methanol to methyl formate over supported copper catalysts: *Appl. Catal.* **72**, 119–137.
- Hirose, A., Takahashi, K., Takezawa, N., and Kobayashi, H. (1982) Steam reforming of methanol on copper-silica catalysts. Effect of copper loading and calcination temperature on the reaction: *Appl. Catal.* **4**, 127–134.
- Mendioroz, S., Pajares, J., Benito, J., and Pesquera, C. (1987) Texture evolution of montmorillonite under progressive acid treatment: Change from H_3 to H_2 type of hysteresis: *Langmuir* **3**, 676–681.
- Morikawa, Y., Takagi, K., and Moro-oka, Y. (1980) Dehydrogenation of methanol to form methyl formate over cupric ion-exchanged form of fluoro tetrasilicic mica: *Proc. 8th Int. Congr. Catal.* **5**, 188–197.
- Parks, G. A. (1965) The isoelectric points of solid oxides, solid hydroxides and aqueous hydroxo-complex systems: *Chem. Rev.* **65**, 177–198.
- Pinnavaia, T. J. (1983) Intercalated clay catalysts: *Science* **220**, 365–371.
- Pinnavaia, T. J., Tzou, M., Landau, S. D., and Raythatha, R. M. (1984) On the pillaring and delamination of smectite clay catalysts by polyoxo cations of aluminum: *J. Mol. Catal.* **27**, 195–212.
- Rodríguez-Ramos, I., Guerrero-Ruiz, A., Rojas, M. L., and Fierro, J. L. G. (1991) Dehydrogenation of methanol to methyl formate over copper-containing perovskite-type oxides: *Appl. Catal.* **68**, 217–228.
- Rojas, M. L., Fierro, J. L. G., Tejuca, L. G., and Bell, A. T. (1990) Preparation and characterization of $\text{LaMn}_{1-x}\text{Cu}_x\text{O}_3$ perovskite oxides: *J. Catal.* **124**, 41–51.
- Serna, C. and Fernandez, T. (1975) Adsorción de hidrocarburos en sepiolita. II. Propiedades de superficie: *Ann. Quím.* **71**, 371–376.
- Sheffer, G. R. and King, T. S. (1989) Differences in the promotional effects of the group 1A elements on unsupported copper catalysts for carbon monoxide hydrogenation: *J. Catal.* **116**, 488–497.
- Tonner, S. P., Trimm, D. L., and Wainwright, M. S. (1984) Dehydrogenation of methanol to methyl formate over copper catalysts: *Ind. Eng. Chem. Prod. Res. Dev.* **23**, 384–388.

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