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$CuCl_2$ immobilized on amino-functionalized MCM-41 and MCM-48 as efficient heterogeneous catalysts for dimethyl carbonate synthesis by vapor-phase oxidative carbonylation of methanol

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Pure silica mesoporous molecular sieves MCM-41 and MCM-48 organofunctionalized with 3-aminopropyltrimethoxysilane and *N*-[(3-trimethoxysilyl)propyl]ethylene-diamine, respectively, were served as supports to immobilize $CuCl_2$ with conventional impregnation method. The supported copper catalysts showed a considerable enhancement in the reaction rate in heterogeneous vapor-phase oxidative carbonylation of methanol to produce dimethyl carbonate in comparison with that obtained by $CuCl_2$-supported nonfunctionalized mesoporous silicas under identical conditions. The electronic donation of the amino groups, the accessibility and dischargeability of reactants in the regular mesopores probably account for the good catalytic performance as evidenced by the characteristic studies with XRD, BET, FTIR, TG-DTA, and XPS.

KEY WORDS: MCM-41; MCM-48; amino functionalization; copper catalyst; methanol; oxidative carbonylation; dimethyl carbonate.

1. Introduction

Increasing attention has been paid to the synthesis of dimethyl carbonate (DMC) in recent years from both academic and environmental interests [1–13]. It is well known that the best way to produce DMC is by oxidative carbonylation of methanol. Although a liquid slurry process employing copper chloride catalyst has been commercialized [1], a vapor-phase process is more desirable because copper chloride is highly corrosive in the liquid phase [2]. A number of investigations have been focused on the use of a supported copper catalyst to synthesis DMC *via* vapor-phase oxidative carbonylation of methanol [3–8], and the reaction system is almost free from corrosion. The solid-state ion-exchanged Cu(I) Y-type and MCM-41 zeolites are active for the oxidative carbonylation of methanol [3,7,9], although the catalytic efficiency is low. The formation of DMC molecule from MeOH and CO requires oxidation processes involving transfer of two electrons, indicating that the factors being able to accelerate the redox cycle of the active enters like Cu(II)/Cu(I) would be beneficial for the reaction rate. The considerable enhancements in the methanol conversion and selectivity to DMC have been observed by using supported and unsupported copper-based catalysts modified with N-donor ligands [10–13]. Very recently, it was reported that the CuCl immobilized on diamide modified SBA-15 was an efficient heterogenized catalyst for the oxidative carbonylation of methanol to dimethyl carbonate [14]. Independently, we have successfully obtained an effective heterogeneous catalyst system for the vapor-phase oxidative carbonylation of methanol to produce DMC by supporting $CuCl_2$ in amino-grafted mesoporous silicas MCM-41 and MCM-48. The catalysts have been characterized by means of XRD, BET, FTIR, TG-DTA, and XPS.

2. Experimental

The mesoporous silicas of MCM-41 and MCM-48 were obtained according to the literature procedures [15]. Aminosilane-grafted mesoporous silicas were prepared respectively with 3-aminopropyltrimethoxysilane or *N*-[(3-trimethoxysilyl)propyl]-ethylene-diamine according to the methods described in literature [16]. The mono- and diamino-functionalized silicas were denoted as N- and NN-support. Immobilization of $CuCl_2$ was performed by mixing the vacuum-treated supports with an ethanol solution of $CuCl_2$ under argon for 6 h, followed by evaporation to remove the solvent under vacuum and by vacuum drying at 383 K for 12 h. The loadings of $CuCl_2$ were varied in the range of 5–20 wt% as Cu/support.

The catalytic test was performed with a fixed-bed flow microreactor in the temperature range of 373–423 K under the reaction conditions of $GHSV = 1200\,mL\ h^{-1}\ g^{-1}_{-cat}$ and $CO/CH_3OH/O_2/N_2 = 72/16/4/8$ (mol%) at 1.0 MPa. The mixture was regulated by mass-flow controllers. Methanol was introduced to the flow reactor by bubbling $CO/N_2/O_2$ mix-gas through a stainless

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saturator filled with methanol at a controlled temperature in order to obtain the molar ratio required. The outlet streamline from the reactor to a gas chromatograph was heated at about 423 K in order to avoid condensation of reaction products. The products were analyzed by an online gas chromatograph using Porapak N (3 m) and AC (3 m) columns.

Surface areas of the samples were measured by a BET nitrogen-adsorption method at 77 K using a TriStar 3000 machine. XRD patterns were measured on a Rigaku Rotaflex D/Max-C diffractometer using Cu Kα radiation. XPS spectra were measured on a Quantum 2000 ESCA spectrometer by using Al Kα radiation (1253.6 eV) with X-ray power of 250 W (accelerating voltage 15 kV). The binding energy was referred to 284.6 eV for C 1s. FTIR spectra were measured on a Perkin Elmer Spectrum 2000 instrument with an MCT detector at a resolution of 4 cm^{-1}. TG-DTA measurements were made on a Netzsch STA 449C thermal analysis.

3. Results and discussion

Table 1 presents the performances of the supported $CuCl_2$ catalysts for the oxidative carbonylation of methanol. The results showed a considerable enhancement in the DMC production on $CuCl_2$/N- (or NN-) mesoporous silicas, but very low reaction rate with $CuCl_2$/mesoporous, amorphous, and amino functionalized silicas as catalysts. Figure 1 shows the reaction STY ($g\,g_{-Cu}^{-1}\,h^{-1}$) as a function of copper loading in the $CuCl_2$/N-MCM-41 and $CuCl_2$/NN-MCM-41 catalysts. The STY increased with increasing copper loading, and reached the maximum values of 4.36 and 4.27 $g\,g_{-Cu}^{-1}\,h^{-1}$, respectively, at 10 wt%Cu in the two catalysts used. Above this loading the reaction STY dropped. The $CuCl_2$/N-(or NN-)MCM-41 and MCM-48 catalysts with 10 wt% of copper loading presented a stable performance for the DMC synthesis at 403 K, keeping no changes in both the methanol conversion and the DMC yield during the experimental running of 10 h.

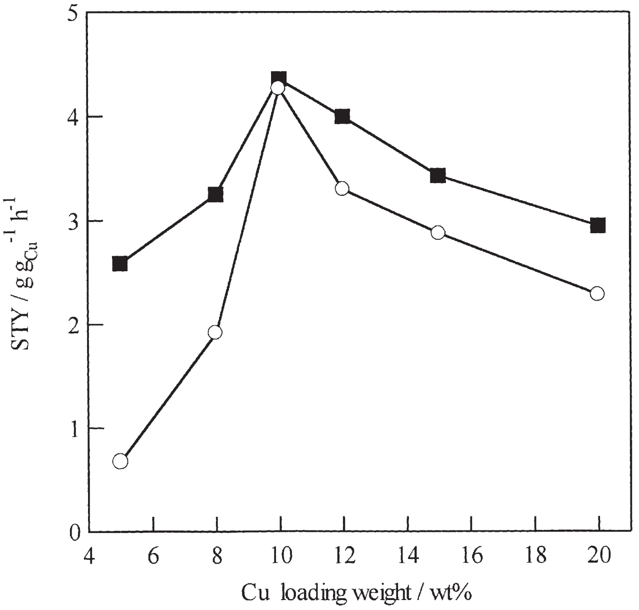

Figure 1. Variations of the reaction STY with copper loading in the $CuCl_2$/N-MCM-41 and $CuCl_2$/NN-MCM-41 catalysts. ■: $CuCl_2$/N-MCM-41; ○: $CuCl_2$/NN-MCM-41. Reaction conditions are the same as in table 1.

The curves of nitrogen-adsorption isotherms for MCM-41 and MCM-48 contained linear to step-shaped uptakes at partial pressures between 0.1 and 0.8, which were indicative of the presence of mesopores. Upon grafting 3-aminopropyl-trimethoxysilane to the framework walls, for instance, significant decreases in the surface area, pore volume, and pore size were observed due to the graft of amino groups in the framework channels as shown in table 1. Infrared spectra (not shown) of MCM-41 and MCM-48 showed that the

Table 1

Catalytic performance of 10 wt% $CuCl_2$ supported on ordered mesoporous silicas with and without aminofunctionalization for the vapor-phase oxidative carbonylation of methanol at 403 K[a]

Support	S_{BET} ($m^2\,g^{-1}$)	Pore size (nm)	N/Cu[b] (mol/mol)	MeOH conversion (%)	Selectivity (%)		STY ($g\,g_{-Cu}^{-1}\,h^{-1}$)
					MeOH/DMC	CO/DMC	
SiO_2	321	7.2	0.0	1.7	96.1	29.6	0.60
N-SiO_2	208	6.3	2.5	1.9	97.3	34.1	0.67
NN-SiO_2	73	6.2	5.3	1.5	96.7	31.9	0.53
MCM-41	1117	3.5	0.0	3.9	97.9	32.6	1.37
N-MCM-41	560	2.7	2.5	12.6	97.5	53.5	4.36
NN-MCM-41	379	2.5	5.3	11.9	98.4	62.1	4.27
MCM-48	1373	2.5	0.0	2.9	96.5	25.4	1.02
N-MCM-48	858	2.3	2.5	10.2	96.0	29.9	3.60
NN-MCM-48	476	2.0	5.2	10.5	95.2	37.8	3.71

[a] Reaction condition: reaction temperature = 403 K; total pressure = 1.0 MPa; catalyst weight = 1.0 g; copper loading weight = 10 wt%; CO/$CH_3OH/O_2/N_2$ = 72/16/4/8; GHSV = 1200 h^{-1}.

[b] Estimated from XPS data.

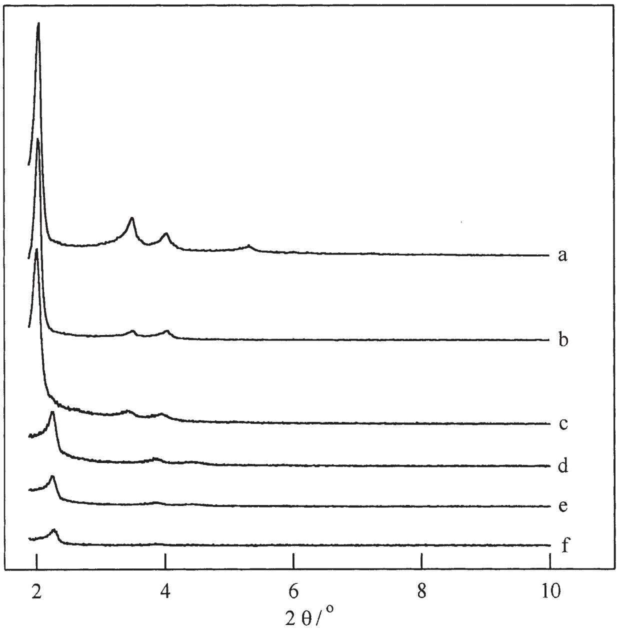

Figure 2. XRD patterns for the as-prepared supports and catalysts. (a) MCM-41, (b) N-MCM-41, (c) NN-MCM-41, (d) 10 wt% $CuCl_2$/MCM-41, (e) 10 wt% $CuCl_2$/N-MCM-41; (f) 10 wt% $CuCl_2$/NN-MCM-41.

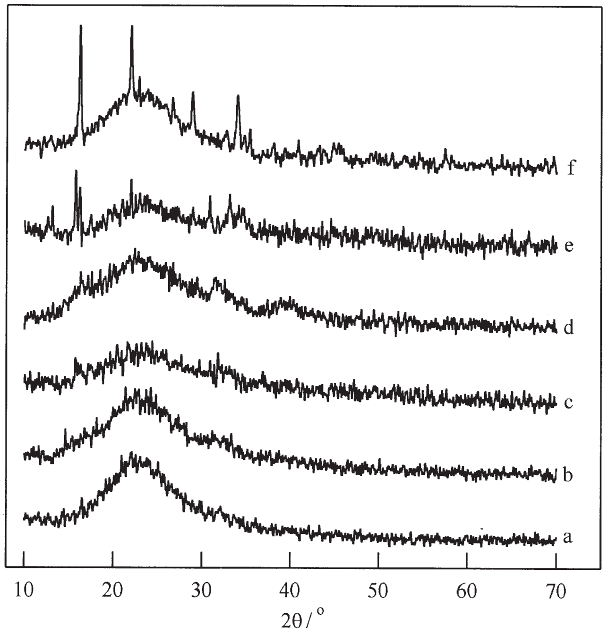

Figure 3. XRD patterns for the as-prepared $CuCl_2$/N-MCM-41 catalysts; copper loading (wt%): (a) 0.0, (b) 5.0, (c) 10.0, (d) 15.0, (e) 20, (f) 10.0 wt% $CuCl_2$/MCM-41.

bands at 2928, 2858, 1669, 1604, 1458, and 1352 cm^{-1} appear at the expense of the band at 3742 cm^{-1} after silylation, which are assigned to C–H asymmetric stretching, C–H symmetric stretching, NH_2 scissor, CH_2 scissor, and CH_3 bending vibrations respectively. The band positions are similar to those reported in the literature [17]. The presence of the CH_3 bending mode suggested a small amount of remaining of OCH_3.

Figure 2 compares the X-ray diffraction patterns of the mesoporous silicas before and after functionalization with 3-aminopropyltrimethoxysilane, and after immobilization of $CuCl_2$, respectively. In the pattern of MCM-41, a dominant (100) peak with small (110) and (200) reflections, are attributed to the 2D-hexagonal structure (*p6mm*). Aminosilane grafting to MCM-41 and further $CuCl_2$ immobilizing on an aminosilane-grafted one caused a considerable decrease in the XRD intensity. The reflections due to higher indices almost disappeared. These changes shown in figure 2 are due to a partial loss of the space correlation of the pores. This kind of resultant disorder in silica mesostructures has been commonly observed in studies of silylation and immobilization of mesoporous silicas [16]. No destruction of the mesoporous structures was observed by the XRD studies after the experimental running of 10 h. Large-angle XRD patterns are shown in figure 3. Almost no XRD lines for $CuCl_2$ appeared for the $CuCl_2$/N-(and NN-) MCM-41 catalysts with copper loadings below 10 wt%. TG-DTA analysis (not shown) revealed that the amino groups began to decompose at temperature above 573 K, while the $CuCl_2$/N- (and NN-)mesoporous silicas gave massive mass loss at temperature around 473 K under air. The results mean that the catalysts are stable at the reaction temperature.

Figure 4 shows Cu 2p XPS spectra for the as-prepared $CuCl_2$/MCM-41, $CuCl_2$/N-MCM-41 and $CuCl_2$/NN-MCM-41 catalysts. There were two intense peaks at 934.9/954.7 eV for $CuCl_2$/MCM-41 (figure 2(a)) assignable to $Cu^{2+}2p_{3/2}$ and $2p_{1/2}$, along with corresponding Cu(II) satellite peaks at 942.3–944.8 eV. At the surfaces of $CuCl_2$/N- and NN-MCM-41 the Cu 2p XPS spectra were similar, exhibiting two peaks

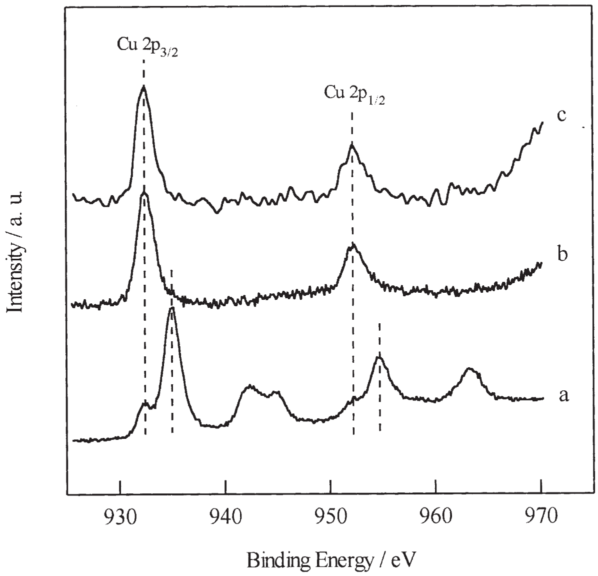

Figure 4. Cu 2p XPS spectra for the as-prepared catalysts with 10 wt%-Cu: (a) $CuCl_2$/MCM-41; (b) $CuCl_2$/N-MCM-41; (c) $CuCl_2$/NN-MCM-41.

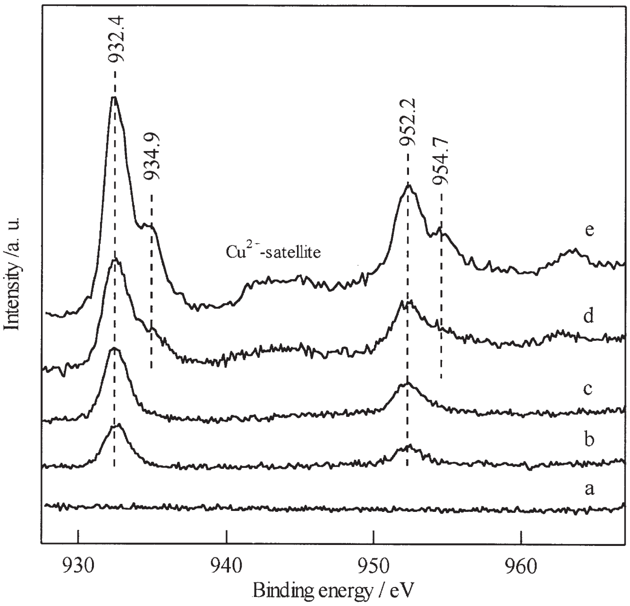

Figure 5. Cu 2p XPS spectra for the as-prepared $CuCl_2$/N-MCM-41 catalysts; copper loading (wt%): (a) 0.0, (b) 5.0, (c) 10.0, (d) 15.0, (e) 20.0.

centered at 932.4 and 952.2 eV. The peaks are attributable to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ levels of $Cu^{0-\delta+}$ species, which may be due to the formation of the mono/bi/multidentate copper complexes with nitrogen ligands. The N/Cu ratio decreased with the Cu-loading weight, as expected, and approximately reached 2.5 : 1 and 5.3 : 1 (molar ratio) in the cases of 10 wt% $CuCl_2$/N- and NN-MCM-41, respectively, as estimated by XPS data. Figure 5 shows the Cu 2p XPS spectra for the as-prepared $CuCl_2$/N-MCM-41 catalysts with different copper loadings. The catalysts with copper loadings of 5 and 10 wt% possessed only copper species with electronical richness due to the coordination by the amino groups. Whereas, for the catalysts with copper loading above 10 wt%, the XPS Cu 2p peaks for Cu^{2+} species appeared in addition to the peaks for copper species ligated with amino groups. The observation is coincided with the XRD results as shown in the figure 3. The results indicated that the amino groups at the surfaces of mesopores were electronically donors to $CuCl_2$ and the copper species thus formed were principally responsible for the oxidative carbonylation of methanol to produce DMC. Therefore, the increase in the reaction efficiency of the catalysts $CuCl_2$/N-(or NN-)mesoporous silicas can be understood by a strong coordinative interaction between the copper species and the amino moieties in the ordered mesoporous silicas.

4. Conclusions

We have demonstrated that the $CuCl_2$ supported on amino-functionalized ordered mesoporous silicas MCM-41 and MCM-48 by simple and versatile scheme of impregnation are excellent candidates for the vapor-phase oxidative carbonylation of methanol to DMC. The catalysts are reusable and air stable. The characterization by using XRD, BET, FTIR, and XPS methods indicated that the one-dimension pores with diameters of 2 ~ 3 nm in the mesoporous silicas were suited to accommodating the amino groups and $CuCl_2$, leaving an appropriate space for diffusion and reactions of the reactant molecules. Interaction between $CuCl_2$ and amino-functional groups in the ordered mesoporous silicas caused stabilization of Cu(I) species that are active for the oxidative carbonylation of methanol to DMC. The highest reaction rates on $CuCl_2$/N-MCM-41 and $CuCl_2$/NM-MCM-41 catalysts were achieved in the copper loading 10.0 wt%. The results of the comparative studies of $CuCl_2$ supported on nonamino-functionalized silicas implied that the redox capability of copper species ligated with amino groups in the supports may be responsible for the enhancement in reaction rate in the oxidative carbonylation of methanol to DMC.

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