Copper-catalyzed Selective Oxidation of Methane to Formaldehyde by Oxygen

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Cu/SBA-15 exhibited the highest activity for the selective oxidation of methane to formaldehyde by oxygen among various M/SBA-15 catalysts (M = V, Cr, Mn, Fe, Co, Ni, Cu, Mo, and W) containing small amount of M (M/Si = 1/13200). Formaldehyde space-time yield reached 870 g $\mathrm{kg_{cat}}^{-1}$ h^{-1} over the Cu/SBA-15 under the conditions maintaining single-pass formaldehyde yield higher than 1%. The turnover frequency for HCHO formation was 5.6 s^{-1} under the same conditions, significantly higher than other catalysts reported so far.

The selective oxidation of methane to useful oxygenates such as methanol and formaldehyde is one of the most challenging themes in catalysis research.[1] The significance of developing efficient catalysts for direct conversion of methane to liquid fuels or valuable chemicals has been perceived for a long time and has escalated in recent years because of the increasing demand for the decrease in the dependency on oil. A large number of heterogeneous catalysts have been reported for the selective oxidation of methane to formaldehyde, but the productivity is still too low for commercial exploitation.[2] On the other hand, methane monooxygenases in biological systems can catalyze the selective oxidation of methane to methanol with high efficiency under mild conditions.[3,4] While the dinuclear iron center in the soluble methane monoxygenase is responsible for methane oxidation,[3] copper is the active center in the particulate methane monoxygenase.[4] It would thus be a promising route to design and synthesize iron- or copper-containing heterogeneous catalysts with appropriate structures of active sites for the selective oxidation of methane. Many studies have shown that iron-containing heterogeneous catalysts can catalyze the conversion of methane to formaldehyde by oxygen, and the high dispersion of iron sites on/in a matrix such as silica or by counteranions in an iron compound such as $FePO_4$ is believed to play pivotal roles in obtaining high formaldehyde selectivities because iron oxides only catalyze the complete oxidation of methane.[5–7] On the other hand, there are few reports succeeding in exploiting copper-based catalysts for partial oxidation of methane.[8] In this paper, for the first time, we show that copper sites with extremely high dispersions can function efficiently for the selective oxidation of methane to formaldehyde.

We chose SBA-15, a typical mesoporous silica, which possesses large surface areas and ordered porous channels, as the supporting matrix for copper sites. We have revealed that SBA-15 is a promising support for selective oxidation of CH_4 possibly because of its larger pore diameter (ca. 5 nm) and more inert property without any acid sites, which allow the rapid desorption of HCHO.[9] SBA-15 was prepared with the same procedure as reported previously.[9] A pluronic P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$) and tetraethyl orthosilicate were used as the template and the silicon source, respectively. After hydrothermal synthesis at 308 and 370 K, SBA-15 was recovered by filtration, washing, drying, and finally calcination in air at 923 K for 6 h. Transition-metal (denoted as M) species were introduced into SBA-15 by an impregnation method with ethanolic solution of respective transition-metal salts, followed by drying and calcination at 923 K. XRD measurements clarified that the hexagonal mesoporous structure of SBA-15 was not altered after the introduction of transition-metal species. No segregation of transition-metal oxide particles was observed from TEM observations. Catalytic reactions were carried out with a fixed-bed flow reactor (quartz tube) operated at atmospheric pressure. The products were analyzed by on-line gas chromatography. CH_4 conversions and product selectivities were calculated on the basis of the amount of carbon-containing products formed and that of CH_4 remaining in the effluent.[7b]

Figure 1 compares the catalytic performances of various M/SBA-15 containing a small amount of M (M/Si = 1/13200) for the selective oxidation of CH_4 at 898 K. SBA-15 showed a very low CH_4 conversion (0.3%) under the conditions used in Figure 1. The introduction of vanadium, cobalt, nickel, molybdenum, and tungsten into SBA-15 with a M/Si ratio of ca. 1/13200 did not significantly increase CH_4 conversions. Although SBA-15-supported MoO_x and VO_x clusters with loading amounts of 5 and 3% catalyzed the selective oxidation of CH_4 to HCHO with good yields,[9a,9b] the Mo or V sites with such a low concentration were almost inactive for oxidation of CH_4. On the other hand, chromium, manganese, iron, and copper considerably enhanced the conversion of CH_4 to HCHO. Among these transition metals, copper showed the highest CH_4 conversion (3.8%) and HCHO yield (1.6%). Over the Cu/SBA-15 catalyst, the selectivities to HCHO, CO, and CO_2 were 42, 45, and 13%, respectively, under the conditions of Figure 1.

Kobayashi et al. reported that iron was the best catalyst for HCHO formation among several transition-metal ions doped

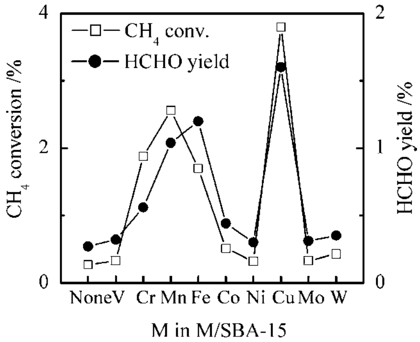

Figure 1. Catalytic performances of various M/SBA-15 (M/Si = 1/13200) for the oxidation of CH_4 by O_2. Reaction conditions: catalyst, 0.10 g; $T = 898$ K; $P(CH_4) = P(O_2) = 33.8$ kPa; total flow rate, 120 mL min^{-1}.

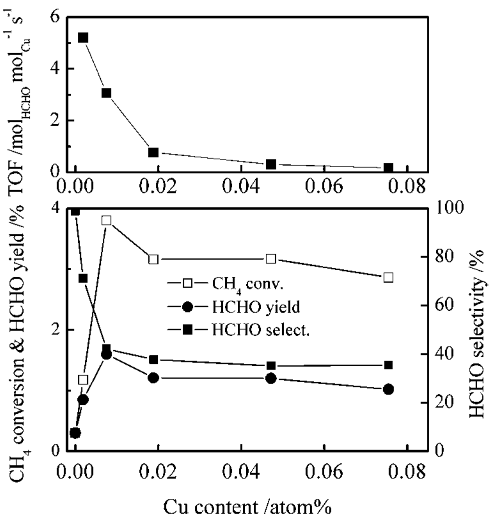

Figure 2. Effect of copper content on catalytic performances of Cu/SBA-15 catalysts. Reaction conditions: catalyst, 0.10 g; $T = 898$ K; $P(CH_4) = P(O_2) = 33.8$ kPa; total flow rate, 120 mL min^{-1}.

into a silica with a ratio of metal ion to silica being 5/10000, and copper only exhibited a lower activity.[5a] Our result in Figure 1 confirms that iron is really a good catalyst for the conversion of CH_4 to HCHO by O_2, and this coincides with the current consensus that highly dispersed iron can be a good selective oxidation catalyst.[5,6,10] However, our present result clearly reveals that copper can also function efficiently for the selective oxidation of CH_4 to HCHO with O_2 by using SBA-15 as the supporting matrix.

We have investigated the catalytic behaviors of Cu/SBA-15 samples with different copper contents. As shown in Figure 2, while HCHO selectivity decreased, CH_4 conversion and HCHO yield increased remarkably with increasing copper content from 0 (pure silicious SBA-15) to 0.0076 atom % (Cu/Si = 1/13200). Further increases in copper content decreased both CH_4 conversion and HCHO yield. Moreover, the turnover frequency (TOF) for HCHO formation evaluated on the basis of copper (HCHO formation on SBA-15 alone was subtracted) decreased significantly as copper content increased. Thus, we believe that the extremely high dispersion of copper sites over SBA-15 accounts for the selective oxidation of CH_4 to HCHO by O_2.

We have investigated the influence of reaction conditions on catalytic performances over the Cu/SBA-15 (Cu/Si = 1/13200). As shown in Table 1, HCHO selectivity increases with decreasing the pseudo-contact time (W/F), indicating that HCHO is a primary product, and CO and CO_2 are produced from the decomposition or the consecutive oxidation of HCHO. The space-time yield (STY) of HCHO could reach 870 g kg$_{cat}^{-1}$ h^{-1} while maintaining a single-pass HCHO yield of 1.3% and HCHO selectivity of 58%. This HCHO STY value is higher than that reported for the iron-doped silica prepared by an impregnation method and is comparable to the iron-containing silica prepared by an adsorption–precipitation method.[5a,6a] It is noteworthy that the TOF obtained for HCHO formation over the present Cu-based catalyst was 5.6 s^{-1}, whereas the best TOF values for the Fe- and V-based catalysts were ca. 1.0 and 0.5 s^{-1}.[6a,11] Therefore, the copper sites highly dispersed on SBA-15 were very active for the conversion of CH_4 to HCHO.

Table 1. Catalytic performances of Cu/SBA-15 (Cu/Si = 1/13200) for selective oxidation of CH_4 by O_2[a]

W/F[b]	CH_4 conv. /%	HCHO select. /%	HCHO yield /%	STY[c]	TOF[d] /s^{-1}
0.011	1.0	74	0.74	1200	6.4
0.025	2.3	58	1.3	870	5.6
0.051	3.8	42	1.6	510	3.1
0.10	6.3	29	1.8	300	2.1

[a]Reaction conditions: $T = 898$ K; $P(CH_4) = P(O_2) = 33.8$ kPa. [b]Pseudo-contact time, unit: s g mL^{-1}. [c]Space-time yield, unit: g kg$_{cat}^{-1}$ h^{-1}. [d]TOF was evaluated from the moles of HCHO formed per mole of Cu in the catalyst per second.

In summary, we have found that the copper introduced with very small amounts into SBA-15 can efficiently catalyze the selective oxidation of methane to formaldehyde by oxygen. The extremely high dispersion of copper sites is probably very crucial for HCHO formation. The most important feature of the present catalytic system is the very high turnover frequency.

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