Photocatalytic reactions on chromium containing mesoporous silica molecular sieves (Cr-HMS) under visible light irradiation: decomposition of NO and partial oxidation of propane

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Cr-containing mesoporous silica molecular sieves (Cr-HMS) containing tetrahedrally coordinated isolated chromium oxide (chromate) moieties can operate as an efficient photocatalyst for the decomposition of NO and the partial oxidation of propane with molecular oxygen under visible light irradiation.

Highly dispersed transition metal oxides incorporated within the framework of zeolites and mesoporous molecular sieves show unique reactivities not only for catalytic reactions[1] but also for photocatalytic reactions.[2] In particular, highly dispersed transition metal oxides such as titanium,[3] vanadium[4] and molybdenum[5] exhibit high photocatalytic reactivities for various reactions. However, these metal oxides can operate as efficient photocatalysts only under UV light irradiation and exhibit no photocatalytic reactivity under visible light irradiation. To establish the clean photocatalysis system using the most environmentally ideal energy source—solar light—it is vital to develop a photocatalyst that can operate efficiently under visible light irradiation.

In the present study, chromium-containing mesoporous silica molecular sieves (Cr-HMS) have been prepared and characterized by various spectroscopic methods (XRD, EXAFS, EPR, UV–VIS, photoluminescence) and their photocatalytic reactivities under UV and visible light irradiations have been investigated. It has been found that chromium oxide (Cr-oxide) highly dispersed on the mesoporous silica can adsorb and utilize visible light in photocatalytic reactions such as the decomposition of NO into N_2 and O_2 and the partial oxidation of propane with O_2.

Cr-HMS mesoporous molecular sieves (0.02, 0.2, 1.0, 2.0 wt% as Cr) were synthesized using tetraethyl orthosilicate and $Cr(NO_3)_3{\cdot}9H_2O$ as the starting materials and dodecylamine as a template.[6,7] Calcination of the sample was carried out in a flow of dry air at 773 K for 5 h. Prior to spectroscopic measurements and photocatalytic reactions, the catalysts were degassed at 723 K for 2 h, heated in O_2 at the same temperature for 2 h and then finally evacuated at 473 K for 2 h to 10^{-6} Torr. The photocatalytic reactions were carried out with the catalysts (100 mg) in a flat-bottomed quartz cell (80 ml) connected to a conventional vacuum system (10^{-6} Torr range). Photocatalytic reactions were carried out under UV ($\lambda > 270$ nm) or visible light ($\lambda > 450$ nm) irradiation at 273 K using a high pressure mercury lamp (310–400 nm, 29 W m^{-2}; 360–480 nm, 44 W m^{-2}) through water and colored filters. The photocatalytic decomposition of NO was carried out on a starting amount of 135 μmol and the products in the gas phase were analyzed by GC. For the photocatalytic oxidation of propane with O_2, reactions were carried out on mixtures containing 240 μmol propane and 180 μmol O_2, and products in the gas phase and the products desorbed from the catalysts by heating to 573 K were also analyzed by GC.

The results of the XRD analysis indicated that the Cr-HMS have a mesopore structure[7] and that the Cr-oxide moieties are highly dispersed in the framework of HMS, while no other phases are formed. Cr-HMS exhibited a sharp and intense pre-edge peak in the XANES region which is characteristic of Cr-oxide moieties in a tetrahedral coordination.[8] In the Fourier transforms of EXAFS spectra, only a single peak due to the neighboring oxygen atoms (Cr–O) were observed, showing that Cr ions are highly dispersed in the Cr-HMS. Analysis of EXAFS spectra of Cr-HMS indicated that tetrahedrally coordinated Cr-oxide (chromate) moieties having two terminal C=O bonds existed as in an isolated state [two oxygen atoms (Cr=O) at 1.57 Å and two oxygen atoms (Cr–O) at 1.82 Å]. The EPR technique was also applied to investigate the coordination state of the Cr-oxide species by monitoring the Cr^{5+} ions formed under UV irradiation of the catalyst in the presence of H_2 at 77 K. After photoreduction with H_2 at 77 K, Cr-HMS exhibited a sharp, axially symmetric signal at around $g = 1.9$ $g_{\parallel} = 1.880$, $g_{\perp}$ 1.945), attributed to the isolated mononuclear Cr^{5+} ions in tetrahedral coordination.[9]

As shown in Fig. 1, the UV–VIS spectra of the Cr-HMS catalysts exhibit three distinct absorption bands at around 250, 360 and 480 nm which can be assigned to charge transfer from O^{2-} to Cr^{6+} of the tetrahedrally coordinated Cr-oxide moieties.[10] Without Cr ion, HMS exhibit no absorption band above 220 nm. The absorption bands assigned to the absorption of dichromate or Cr_2O_3 cluster cannot be observed above 550 nm, indicating that tetrahedrally coordinated Cr-oxide species exist in an isolated state. Cr-HMS exhibited photoluminescence spectra at *ca.* 550–750 nm upon excitation of the absorption (excitation) bands at *ca.* 250, 360 and 480 nm. These absorption and photoluminescence spectra are similar to those obtained with well defined, highly dispersed Cr-oxides anchored on to Vycor glass or silica[11] and can be attributed to the charge transfer processes on tetrahedrally coordinated Cr-oxide moieties involving an electron transfer from O^{2-} to Cr^{6+} and a reverse radiative decay, respectively.

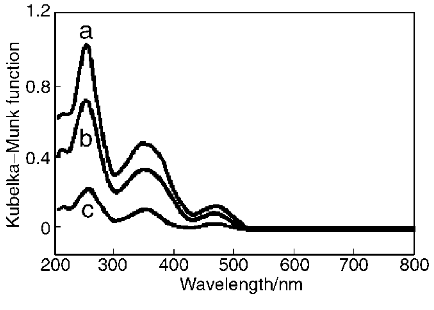

Fig. 1 The UV–VIS spectra of Cr-HMS catalysts (a) 2.0 wt%, (b) 1.0wt%, (c) 0.2 wt%, as Cr.

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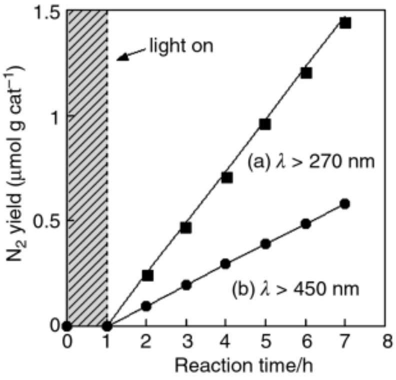

Fig. 2 The reaction time profile of N_2 formation in the photocatalytic decomposition of NO on the Cr-HMS catalyst at 273 K (2.0 wt% as Cr) under UV light irradiation (a) $\lambda > 270$ nm and visible light irradiation (b) at $\lambda > 450$ nm.

UV light irradiation ($\lambda > 270$ nm) of the Cr-HMS in the presence of NO in the gas phase at 275 K led to the photocatalytic decomposition of NO and the evolution of N_2, N_2O and O_2. The Cr-HMS also showed photocatalytic reactivity even under visible light irradiation ($\lambda > 450$ nm). As shown in Fig. 2, the N_2 yields increase linearly with the irradiation time. The reaction stopped immediately when irradiation was ceased. Formation of these reaction products was not detected under dark conditions, or from irradiation of the HMS itself without Cr-oxide. After prolonged irradiation, the amount of decomposed NO to form N_2 per total number of Cr ions included within the catalyst exceeded unity [after 96 h on the Cr-HMS (0.02 wt% as Cr)]. These results clearly indicate that the presence of both Cr-oxide species (included within the HMS) as well as light irradiation are indispensable for the photocatalytic reaction to take place and that the direct decomposition of NO to produce N_2, O_2 and N_2O occurs photocatalytically on the Cr-HMS. Although the reaction rate under visible light irradiation is less than under UV light irradiation, the selectivity for N_2 formation (97%) under visible light irradiation is higher than that of UV light irradiation (45%). These results indicate that Cr-HMS can absorb visible light and act as an efficient photocatalyst under not only UV light but also visible light irradiation, and especially, Cr-HMS can be useful to form N_2 under visible light irradiation.

The addition of NO to the Cr-HMS led to an efficient quenching of the photoluminescence spectrum of the catalyst, its extent depending upon the amount of NO added. These results indicate that the charge transfer excited state of the tetrahedrally coordinated isolated Cr-oxide moieties, $(Cr^{5+}–O^{-})^*$, easily interact with NO, and this photo-excited species plays an important role in the photocatalytic reaction under UV and visible light irradiation.

On the other hand, light irradiation of the Cr-HMS in the presence of propane and O_2 led to the photocatalytic oxidation of propane. As shown in Fig. 3, partial oxidation of propane with a high selectivity for the production of oxygen-containing hydrocarbons such as acetone and acrolein proceeds under visible light irradiation, while further oxidation proceeds mainly under UV light irradiation to produce CO_2 and CO. The selectivity of partial oxidation production under visible light irradiation observed at 12% propane conversion is higher than that observed under UV light irradiation at 26% conversion and even under UV light irradiation for the shorter reaction time with 11% conversion. These results indicate that the tetrahedrally coordinated, isolated Cr-oxide moieties in HMS can exhibit an efficient photocatalytic reactivity for the oxidation of propane under visible light irradiation with a high selectivity for the partial oxidation of propane.

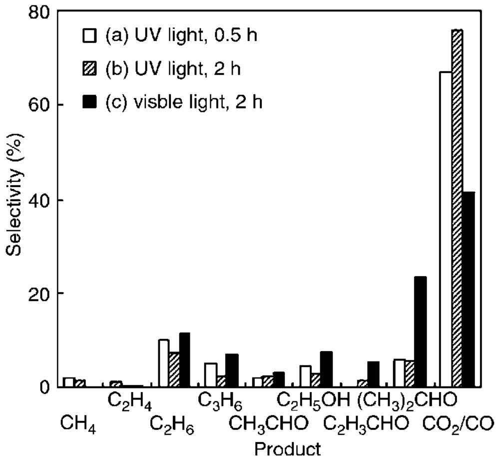

Fig. 3 The distribution of the photo-formed products in the photocatalytic oxidation of propane with O_2 on the Cr-HMS catalyst at 273 K (2.0 wt% as Cr) under UV light irradiation ($\lambda > 270$ nm) for (a) 0.5 h and (b) 2 h, and visible light irradiation ($\lambda > 450$ nm) for (c) 2 h.

The present results have clearly demonstrated that the Cr-HMS can absorb visible light and act as an efficient and selective photocatalyst under visible light irradiation. This photocatalytic system with tetrahedrally coordinated Cr-oxide moieties dispersed on mesoporous silica seems to be a good candidate for the conversion of abundant visible or solar light energy into useful chemical energy.

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