CATALYTIC OXIDATION OF CO ON THE SILICA AEROGELSCONTAINING NANOCLUSTERS OF METALS

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SUMMARY: A series of silica aerogels containing metal Cu or Co in nanoscale have been prepared by sol-gel process and supercritical drying. The resulting aerogels were characterized using TEM, XRD, elemental analysis and nitrogen adsorption analysis. Their catalytic behavior for oxidation of CO have been investigated. The results indicate that Cu-SiO_2 or Co-SiO_2 aerogels have high activity at 100°C-400 °C, whereas the pure SiO_2 aerogels has no activity for this reaction.

KEYWORD: Aerogels, catalyst, CO

INTRODUCTION

Catalytic Oxidation of CO is the major effective way to reduce pollution from automobile exhaust. Currently, noble metal catalysts are predominantly used because of their high activity and long lifetime. At the same time, there has been an understandable desire to replace noble metal catalysts with cheaper, more plentiful substitutes. As these types of pollution control measure are more widely adopted internationally, along with the increasing number of automobiles in operation, the desire to identify a noble metal substitute becomes even more compelling. Transition metal (Cu or Co) is one possible alternative, which has attracted increasing attention. Normally, transition metals are supported on Al_2O_3. In recent years, Cu ion-exchanged ZSM-5 has been widely studied [1]. It appears that Cu-ZSM-5 is among the best catalysts to eliminate automobile exhausts. But Cu-ZSM-5 is not sufficiently active for practical use and has stability problems[2]. Silica aerogels are sol-gel derived nano-porous materials. Taking advantage of their great specific areas, their high selectivity, their open loose textures and their chemical inertness, silica aerogels were made as an important support for active phases in catalysts or even as catalysts per se [3]. When transition metals are incorporated in aerogels framework, the potential exists for new and very effective catalysts [4]. However, few papers about application of metal-containing silica aerogels as catalysts for oxidation of CO was found. In this report, Silica aerogels containing transition metal clusters in nanoscale have been prepared by sol-gel process and supercritical drying. The resulting aerogels were characterized using TEM, XRD and nitrogen adsorption analysis and the catalytic oxidation of CO over them has been studied also.

EXPERIMENTAL

The silica aerogels containing metal clusters in nanoscale were prepared in the following way. The required amount of $Si(OC_2H_5)_4$ mixed with 1-propanol. $Cu(NO_3)_2$ or $Co(NO_3)_2$ was dissolved in the required stoichometric amount of water and HCl. The latter solution was added into the alkoxied-alcohol solution and the liquid mixture obtained was stirred for 60 min resulting in hydrolysis and subsequent polymerization. The solutions obtained were maintained at 60°C until gelled. After gelation, the samples were evacuated under supercritical conditions with respect to alcohol in an autoclave. Then, aerogels were reduced at 500°C for 3 hours in pure flowing hydrogen. Details about the preparation of these samples have been given elsewhere [5]. The resulting aerogels are characterized using transmission electron microscopy (TEM), XRD, elemental analysis and nitrogen adsorption analysis.

Catalytic activity measurements were carried out in a fixed bed continuous flow reactor. The reactor was a quartz tube heated by an electric furnace. The $CO+O_2+N_2$ gas mixtures was passed through the catalyst bed at atmospheric pressure. The composition of the effluents was analyzed by a gas chromatography with a thermal conductivity detector. The activity of the catalysts for $CO-O_2$ reaction was indicated by the conversion of CO at an assigned- temperature and the lowest temperature at which conversion of CO was complete.

RESULTS AND DISCUSSIONS

Characterization of aerogels containing nanoclusters of metals

A series of silica aerogels containing Cu or Co in nanoscales were obtained in this report. Table 1 summarizes the metal content of aerogel catalysts and their specific surface areas. It is shown that aerogel catalysts with metal content in the range from 1% to 10% have high specific surface areas (up to 800m^2/g). Moreover, the surface areas of pure silica aerogels are higher than that of metal-containing ones. Figure 1 Shows the XRD spectra of pure silica aerogels and $Cu-SiO_2$ aerogels(2.45 wt%) after reduction in flowing hydrogen at 500°C . Three peaks are observed in spectra of $Cu-SiO_2$ aerogels (Fig.1a) while no peak was found in that of silica aerogels (Fig.1b). It is obvious that pure SiO_2 aerogels are amorphous. The peaks appearing in Figure 1a are due to the metal Cu embedded in amorphous silica matrix. The formation of Cu metal in the zero valence state was evident by reduction at 500°C. The intensity of the peak increased with increasing reduction temperature, which may caused by the increase in particle size. For $Co-SiO_2$ aerogels, XRD measurements also indicated the presence of metal Co in framework of silica aerogels. It's not stated in detail here.

Table 1. Properties of silica aerogels containing Cu or Co prepared in this paper.

No.	catalyst	metal content (%)	specific surface area(m^2/g)
1	Cu/SiO_2	6.48	405
2	Cu/SiO_2	5.87	302
3	Cu/SiO_2	2.45	747
4	Cu/SiO_2	1.13	750
5	Co/SiO_2	3.66	568
6	SiO_2	0	878

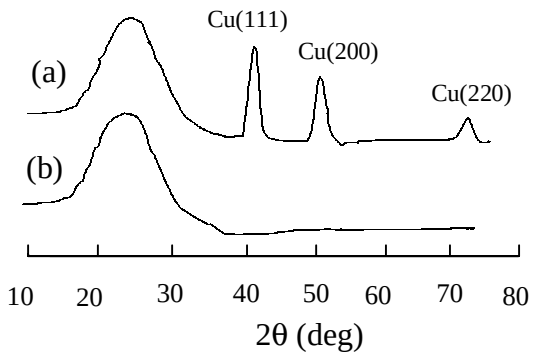
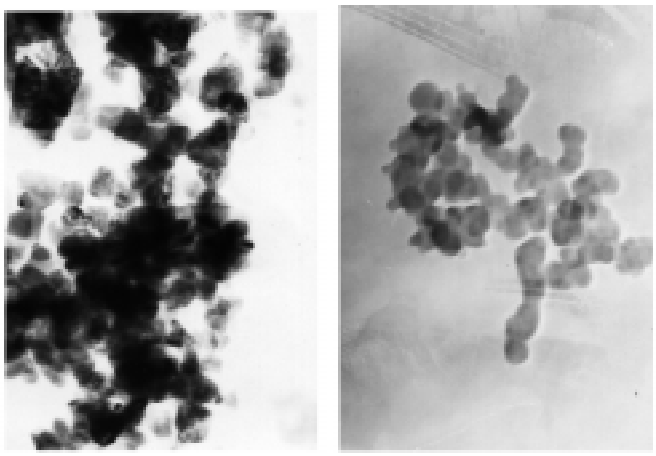


Fig.1. XRD spectra of Cu-SiO_2 aerogel (a) and pure silica aerogel (b).

Figure 2 presents TEM micrographs of the prepared silica aerogels containing a few percent of Co or Cu. It can be seen that each sample have a fine and homogeneous microstructure on the scale of a few nanometers, which is in agreement with their high surface areas. But the morphology of Cu-containing areogels is different from that of Co-containing samples.



(a)(×200000) (b)(×200000)

Figure 2 TEM micrographs of the silica aerogels containing (a) Co or (b) Cu.

The Catalytic Oxidation of CO over aerogel catalysts:

The catalytic activity of three typical samples (pure SiO_2, Cu-SiO_2 and Co-SiO_2 aerogels) for the CO oxidation was measured as a function of reaction temperature. The results are shown in Figure 3. Oxidation of CO over pure silica aerogels starts around 600°C . It is obvious that pure silica aerogels are inactive for this reaction. In contrast with pure silica sample, Cu-SiO2 and Co-SiO2 aerogels exhibit high activity at 100-400°C. The temperature dependence in figure 3 shows that silica aerogels containing Cu or Co can eliminate CO completely below 320°C. Furthermore, with the increase of reaction temperature, the catalytic activity increased rapidly. It can be concluded that the high activity of Cu-SiO_2 (or Co-SiO_2) is presumably due to the incorporation of corresponding transition metal dispersed highly in silica matrix and silica aerogel acts as a good support for transition metals in catalysts reported in this paper.

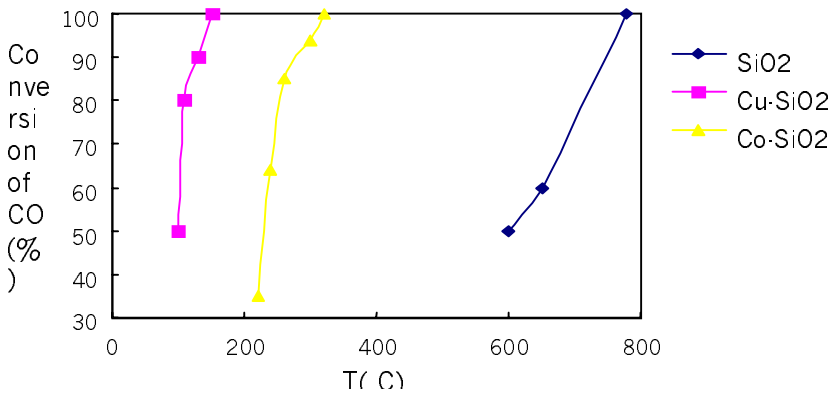


Fig 3 Relationship between CO conversion(%) and reaction temperature.

As the active phases, metal content have an important effect on the catalytic activity of metal-containing aerogels. So, the catalytic activity of CO oxidation over Cu-SiO_2 aerogels with various Cu contents was investigated. The result is depicted in Table 2. The activity of Cu-SiO_2 increased with an increase in Cu loading less than 5.87% and it doesn't increase after copper content reaches 6.48%. In comparison between various Cu-loading samples in 1-7%, the 5.87 % Cu-loading sample exhibits the highest activity for CO conversion into CO_2. It should be noteworthy that silica aerogel containing 5.87 percent of copper can eliminate CO completely at 150°C, which is comparable to some noble metal catalysts.

Table 2. Effect of copper content on activity of Cu-SiO_2 aerogels.*

No.	catalyst	metal content (%)	T_{100} (°C)
1	Cu/ SiO_2	6.48	220
2	Cu/ SiO_2	5.87	150
3	Cu/ SiO_2	2.45	260
4	Cu/ SiO_2	1.13	300
5	Cu/ SiO_2	0.90	400
6	SiO_2	0	780

- *The activity of catalysts was indicated by the lowest temperature
- for 100% oxidation of carbon monoxide T_{100} (°C)

CONCLUSIONS

From the results mentioned above, it is concluded that the silica aerogels containing Cu or Co are high active for CO oxidation.

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