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# A New Method for Preparing Ti-Si Mixed Oxides

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**Abstract:** Ti-Si mixed oxides with different $TiO_2$ content were prepared by sol-gel one step hydrolysis, using $TiCl_4$ as the precursor. The samples were characterized by BET, FT-IR and XRD. The results indicated that titanium is in fourfold coordination with oxygen in the $SiO_4^{4-}$ in mixed oxides, form the bond of Ti-O-Si, and the low titania materials are mixed on an atomic scale. The phase of anatase appeared when $TiO_2$ content is up to 80%. The mixed oxides had high specific surface areas up to 681.5 $m^2/g$. 10TiSi is a better support than $SiO_2$ in the reaction of CO oxidation.

**Keywords:** Ti-Si mixed oxide, sol-gel one step hydrolysis, $TiCl_4$.

Ti-Si mixed oxides have been extensively used as supports[1], catalysts[2] and advanced materials[3]. Chemical and physical properties of solid catalysts depend mainly on the procedures and conditions. The sol-gel process[4] is an effective route. It provides a flexibility for realizing the multi-component systems with high specific surface areas and homogeneity. No matter of numerous advantages, many deficiencies still exist in the sol-gel method, such as the different hydrolysis rates between the titanium alkoxide and silicon alkoxide. The hydrolysis rate of titanium alkoxide decreased due to chelating with the acethylactone, while the silicon alkoxide hydrolyzed in the 1st step of the two-step process. Thus the hydrolysis process became complicate.

This paper dealed with the preparation of Ti-Si mixed oxides by sol-gel one step hydrolysis using $TiCl_4$ as starting material.

## Experimental

EtOH, tetraethoxysilane, $H_2O$ and $CH_3COOH$ were mixed, $TiCl_4$ was added at 0℃. The amounts of tetraethoxysilane and $TiCl_4$ were varied to obtain the content of mixed oxides with $TiO_2$ to be 0 to 100 wt%, and the corresponding molar ratios TEOS: $TiCl_4$: EtOH: $H_2O$: $CH_3COOH$ were m : n : 7(m+n) : 10(m+n) : 2(m+n). The mixed oxides were obtained gelling at R.T. and drying at 65℃. The materials were denoted as XtiSi, where X gave the normal $TiO_2$ content in weight percentage.

The specific surface areas were determined by nitrogen physisorption at 77 K using SORPTOMIC 1990 SERIES. The XRD patterns were recorded on a Rigaku D/max

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2500 X-ray diffraction instrument with CuKα radiation over a 2θ-range of 10-80°C. FT-IR measurements were performed on a 1730 Infrared Fourier Transform Spectrometer (PERKIN- ELMER).

**Results and Discussion**

The results of the BET-surface area are listed in **Table 1**. The BET-surface area of the samples decreased with increasing the amount of $TiO_2$, and reached to maximum at 10TiSi (681.5 $m^2/g$). It is higher than that reported in the reference[4]. The reason is that the rise of Ti content favors the formation of Ti-O-Ti, which leads to the decrease of the BET-surface area. Besides, anatase has lower surface area than $SiO_2$. The amount of acetic acid also influenced BET surface area obviously. The surface area of 60TiSi$^{\#}$ prepared with less amount of acetic acid is far lower than 60TiSi.

**Table 1** $S_{BET}$ of Mixed-Oxide

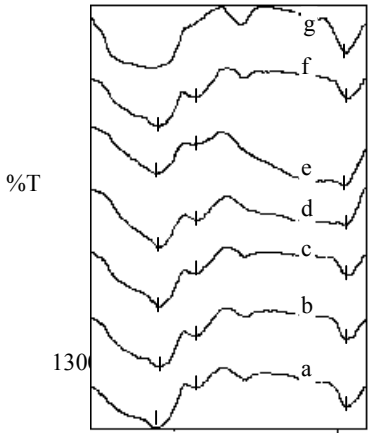
| Samples | $S_{BET}/m^2/g$ |
|---|---|
| $SiO_2$ | 700 |
| 10TiSi | 681.5 |
| 20TiSi | 670.6 |
| 40TiSi | 421.8 |
| 60TiSi | 351.5 |
| 60TiSi$^{\#}$ | 65.4 |
| 80TiSi | 193.6 |
| $TiO_2$ | 100.5 |

**Figure 1** shows the FT-IR spectra of the Ti-Si mixed oxides. The spectra revealed three major absorption bonds at about 1070, 950 and 460 $cm^{-1}$ (**Figure 1**, b.c.d.e), which represent the characteristic bonds of Si-O-Si asymmetric stretching (near 1070 $cm^{-1}$), Ti-O-Si asymmetric stretching (around 950 $cm^{-1}$) and Ti-O stretching (near 460 $cm^{-1}$), respectively. The absorption bond at about 950 $cm^{-1}$ is associated with titanium in fourfold coordination with oxygen in the $SiO_4^{4-}$ structure. $SiO_2$ also give a 950 $cm^{-1}$ peak in the FT-IR spectrum which is attributed to Si-OH bond, however, this bond disappeared after thermal treatment at 600°C (**Figure 1**, g). In addition, the 950 $cm^{-1}$ absorption bond is still observed for the 20TiSi after thermal treatment at 1000°C (**Figure 1**,f). Accordingly, the 950 $cm^{-1}$ peak of Ti-O-Si mixed oxides should not be attributed to Si-OH bond, but associated with Si-O-Ti bond.

The XRD analysis is given in **Figure 2**. The specimens with $TiO_2$ content lower than 80% show only weak and broad diffraction around 2θ=25°, which is characteristic of amorphous silica. These results suggested that the low titania materials are mixed on an atomic scale, which prevent the materials from phase separation and crystallization even at elevated temperature (showed as **Figure 2**, b). The XRD of 80TiSi indicates the appearance of anatase. However, it is broader than $TiO_2$, which proves that the size of anatase crystal in 80TiSi is very small.

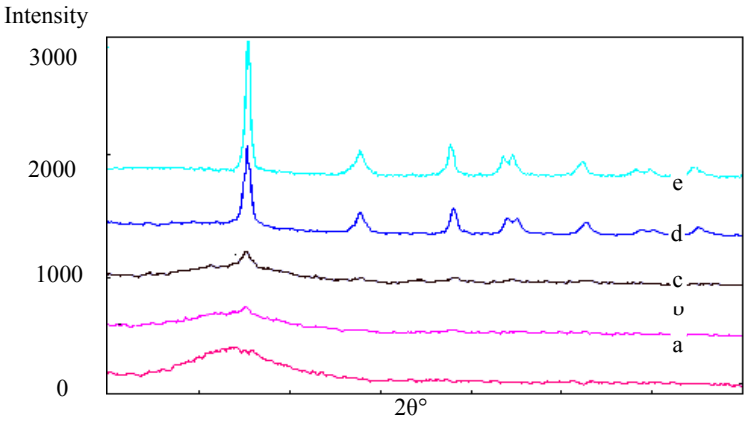
**Figure 3** shows the results of CO oxidation activities with different supports. It is obvious that 5%Co on 10TiSi has higher oxidation activity than on $SiO_2$.

**Figure 1** The FT-IR of the mixed-oxides




a. $SiO_2$ b. 20TiSi c. 40TiSi d. 60TiSi
e.80TiSi f.20TiSi-1000 g.$SiO_2$-600

**Figure 2** XRD of the mixed-oxides

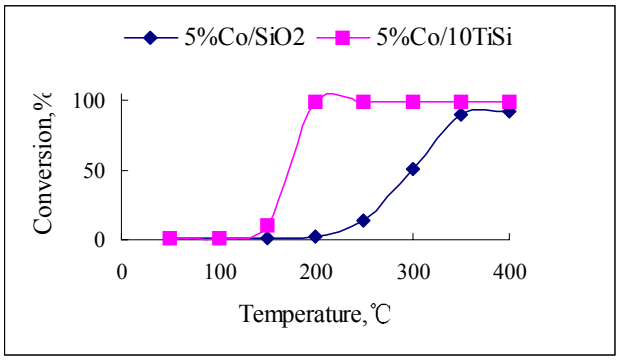



a.20TiSi b.40TiSi c.60TiSi d.80TiSi e.$TiO_2$

## Conclusion

Ti-Si mixed oxides with different $TiO_2$ content have been prepared with $TiCl_4$. The mixed oxides have high BET-surface areas, the surface area of 10TiSi came to 681.5 $m^2/g$. According to the FT-IR, thebond of Ti-O-Si appeared in all samples. XRD data showed that Ti-Si mixed oxide with $TiO_2$ content up to 60wt% existed in the form of amorphous. The anatase peak appears in 80TiSi, but its crystal size was far smaller than $TiO_2$. Mixed oxides are better supports than single oxide-$SiO_2$ in the CO oxidation reaction.

**Figure 3** Effects of supports on the CO oxidation activities of 5%Co catalyst

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