

A Novel Way to Prepare TiO_2 and $\gamma\text{-Al}_2\text{O}_3$ Supported Catalysts with Large Surface Areas

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Several TiO_2 and $\gamma\text{-Al}_2\text{O}_3$ supported catalyst systems were prepared by a novel way and characterized by X-ray diffraction, Raman spectroscopy and BET surface area measurement. The results show: (1) all the samples, including $\text{MoO}_3/\text{TiO}_2$, WO_3/TiO_2 , $\text{V}_2\text{O}_5/\text{TiO}_2$, $\text{FeSO}_4/\gamma\text{-Al}_2\text{O}_3$, $\text{Al}_2(\text{SO}_4)_3/\gamma\text{-Al}_2\text{O}_3$, $\text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ and so on, prepared by impregnating $\text{TiO}_2 \cdot \text{H}_2\text{O}$ or pseudo-boehmite $\text{AlO}(\text{OH})$ with the active components then calcining at a high temperature exhibit much larger surface areas than that of pure TiO_2 or $\gamma\text{-Al}_2\text{O}_3$ calcined at the same temperature; (2) the surface area of the sample increases with the increase in the coverage of active component on the surface of the support; (3) when the content of active component reaches its utmost monolayer dispersion capacity, the surface area of the sample is the largest, and then decreases when the content of active component exceeds its dispersion threshold.

Keywords Monolayer dispersion, large surface area, TiO_2 supported systems, $\gamma\text{-Al}_2\text{O}_3$ supported systems

Introduction

In the majority cases, fine thermostability and large surface area are targets to pursue in the preparation of catalyst. In recent years, ZrO_2 and TiO_2 as catalyst supports are attracting much attention for their special properties.¹⁻³ However, it is very difficult to obtain ZrO_2 or TiO_2 supported catalysts with high surface areas by the traditional method, *i. e.* impregnating the pre-calcined oxide support with the solution of active component then calcining again, because the surface area of ZrO_2 or TiO_2 obtained by heating hydrous zirconia or titania at 773—873 K is not

very large and will decrease further when impregnated with the solution of an active component and calcined again. This disadvantage limits its applications greatly.

It has been reported by our group that many oxides and salts can disperse spontaneously onto surfaces of supports as monolayers.⁴ This principal has been proved to be a widespread phenomenon by the results of more than one hundred systems.⁴⁻⁸

In our work and the reports of other authors we noticed that some catalysts with high surface areas could be obtained by impregnation method using hydrous oxides as the supports, such as $\text{MoO}_3/\text{TiO}_2$,⁹ $\text{SO}_4^{2-}/\text{ZrO}_2$,^{10,11} $\text{CrO}_3/\text{ZrO}_2$ ¹² and CuO/ZrO_2 ¹³ *etc.* Some other work showed that monolayer dispersed compounds could act as surface modifiers to improve the thermostability of the catalyst or the texture of the support.¹⁴⁻¹⁷ On the basis of above work, we did systematic research and reported a new way to prepare zirconia-supported catalysts with high surface areas,¹⁸ that is, dispersing a layer of oxide or salt onto the surface of $\text{Zr}(\text{OH})_4$ only dried at 383 K or ZrO_2 obtained by calcining $\text{Zr}(\text{OH})_4$ at a relatively low temperature, then calcining again at a required temperature. The resultant catalysts possessed much higher surface areas than those of the catalysts prepared by the traditional method. It was also found that there was good correlation between the surface coverage and the surface area of the sample. For ZrO_2 -supported catalysts, the universality of this preparation method was proved by the results of seven kinds of systems in Ref. 18. The mechanism responsible

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for this phenomenon can be chiefly concluded as follows. The layer of an active component dispersed on the surface of a support suppresses the surface diffusion and segregates the particles of the support from each other, therefore the crystalline growth as well as inter-crystalline sintering is hindered during the calcination at high temperature, and then sample with much higher surface area can be obtained.

In this work, the method above mentioned was applied to the preparation of several kinds of important catalytic systems based on titania, including $\text{MoO}_3/\text{TiO}_2$, WO_3/TiO_2 , $\text{V}_2\text{O}_5/\text{TiO}_2$, $\text{SO}_4^{2-}/\text{TiO}_2$, $\text{NiSO}_4/\text{TiO}_2$ and NiO/TiO_2 . The results showed that this method was very effective to improve the surface areas of the catalysts. Besides, in order to further certify the universality of this phenomenon, several $\gamma\text{-Al}_2\text{O}_3$ -supported systems were also investigated and affirmative results were obtained.

Experimental

Sample preparation

$\text{TiO}_2 \cdot \text{H}_2\text{O}$ was prepared by dropping aqueous solution of NH_4HCO_3 and $\text{NH}_3 \cdot \text{H}_2\text{O}$ into $\text{Ti}(\text{SO}_4)_2$ solution with subsequent filtering and washing until no SO_4^{2-} could be detected. The resultant was dried at 383 K, its composition was determined as $\text{TiO}(\text{OH})_2$ or $\text{TiO}_2 \cdot \text{H}_2\text{O}$ by weight-loss analysis. $\text{TiO}_2 \cdot \text{H}_2\text{O}$ prepared in different batch possessed different surface area after calcination. The comparison of surface area was based on the same system using the same $\text{TiO}_2 \cdot \text{H}_2\text{O}$.

$\text{MoO}_3/\text{TiO}_2$, WO_3/TiO_2 , $\text{V}_2\text{O}_5/\text{TiO}_2$, $\text{SO}_4^{2-}/\text{TiO}_2$, $\text{NiSO}_4/\text{TiO}_2$, NiO/TiO_2 samples were prepared by impregnating $\text{TiO}_2 \cdot \text{H}_2\text{O}$ with solutions of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, $(\text{NH}_4)_2\text{W}_4\text{O}_{13}$, NH_4VO_3 , H_2SO_4 , NiSO_4 and $\text{Ni}(\text{NO}_3)_2$, respectively, then drying and calcining at designed temperature for 4 h.

$\text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$, $\text{Al}_2(\text{SO}_4)_3/\gamma\text{-Al}_2\text{O}_3$ and $\text{FeSO}_4/\gamma\text{-Al}_2\text{O}_3$ samples were prepared by impregnating pseudo-boehmite $\text{AlO}(\text{OH})$ with solutions of K_2CO_3 , $\text{Al}_2(\text{SO}_4)_3$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, respectively, with subsequent drying and calcining.

For comparison, some samples were also prepared by impregnating TiO_2 or $\gamma\text{-Al}_2\text{O}_3$ calcined at 773 K with the solutions of respective active components then drying and calcining at designed temperature for 4 h.

Sample characterization

X-ray diffraction was carried out on a BD-86 X-ray diffractometer, employing Ni-filtered Cu K_α radiation.

The surface areas of the samples were measured using BET method by N_2 adsorption at 77 K. All the specific surface areas were normalized to the values per gram support for the comparison with each other.

Raman spectra were obtained on a Jobin-Yvon U-1000 monochromator. The 514.5 nm line of a Spectra-Physica Model Stabilite-2016 Ar^+ laser was used for excitation. A laser power of 100 mW and the spectral slit width of 1 cm^{-1} were applied.

Results

$\text{MoO}_3/\text{TiO}_2$ system

It has been found that MoO_3 can disperse onto the surface of TiO_2 and form a quite complete monolayer.¹⁹⁻²¹ Fig. 1 is the XRD patterns of some $\text{MoO}_3/\text{TiO}_2$ samples calcined at 773 K. It can be seen that the sample with a MoO_3 content of 0.20 g $\text{MoO}_3/\text{g TiO}_2$ has almost the same XRD pattern as that of the support, which indicates that all the MoO_3 in the sample is in a monolayer dispersed state.⁴ The characteristic peaks of crystalline MoO_3 begin to show up in the sample of 0.25 g $\text{MoO}_3/\text{g TiO}_2$, then the intensity of the peak increases with increasing MoO_3 content. This means that the monolayer dispersion capacity of MoO_3 on the surface of TiO_2 is approximate to 0.25 g $\text{MoO}_3/\text{g TiO}_2$.

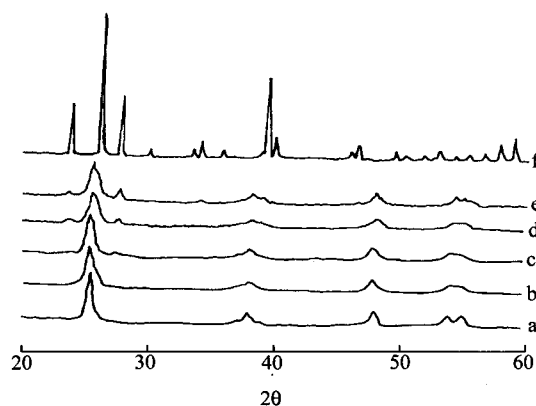


Fig. 1 XRD patterns of $\text{MoO}_3/\text{TiO}_2$ samples calcined at 773 K for 4 h. MoO_3 content (g/g TiO_2): a. 0; b. 0.20; c. 0.25; d. 0.30; e. 0.35; f. pure MoO_3 .

The MoO₃/TiO₂ samples have also been investigated with Raman spectroscopy (see Fig. 2), which gives a direct proof of the existence of monolayer dispersed MoO₃. In the sample of 0.20 g MoO₃/g TiO₂, there are only bands corresponding to the support TiO₂ (the three bands between 350 cm⁻¹ and 700 cm⁻¹) and monolayer dispersed MoO₃ (band at 950 cm⁻¹). The bands corresponding to crystalline MoO₃ (bands at 820 cm⁻¹ and 994 cm⁻¹) begin to emerge in the sample of 0.25 g MoO₃/g TiO₂. Since the sensitivity of Raman spectra for bulk MoO₃ is about 60 times higher than that for dispersed MoO₃,²² the content of bulk MoO₃ in the sample is very low. Therefore it should be considered that the result of Raman spectra is consistent with that of XRD analysis.

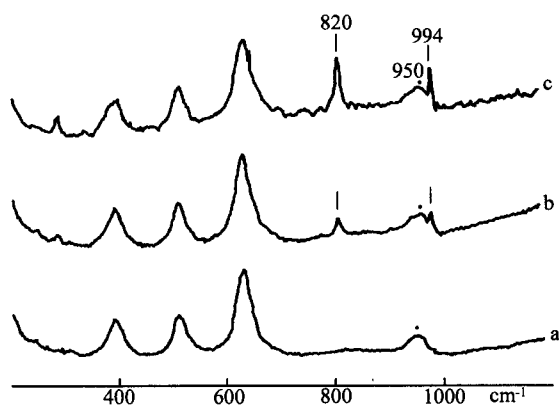


Fig. 2 Raman spectra of MoO₃/TiO₂ samples calcined at 773 K for 4 h. MoO₃ content (g/g TiO₂): a. 0.20; b. 0.25; c. 0.30.

From above results and the report of previous work,¹⁸ we can expect that the surface areas of MoO₃/TiO₂ samples would increase with increasing MoO₃ content and come up to a maximum value at near 0.25 g MoO₃/g TiO₂. This prediction has been proved by the BET surface area measurement (see Table 1, 773 K). So we can conclude that monolayer dispersed MoO₃ can greatly enhance the surface area of the support TiO₂, and the sample with the maximum surface area has a MoO₃ content near its utmost monolayer dispersion capacity. The maximum surface area is 75% higher than that of pure TiO₂.

The samples calcined at 873 K have also been studied by XRD and Raman spectroscopy, and similar results have been obtained except that the monolayer dispersion capacity of MoO₃ decreases to about 0.20 g MoO₃/g TiO₂ because of the smaller surface area resulting from the

higher calcination temperature. The results of BET surface area measurement (see Table 1, 873 K) show that the sample with the largest surface area has a MoO₃ content of 0.20 g MoO₃/g TiO₂, also near the monolayer dispersion threshold.

When the content of MoO₃ exceeds its dispersion threshold, the surplus will appear as crystalline phase and block up some pores to certain extent, so the surface area of the sample will decrease gradually. The results above show that there is a threshold effect in the influence of monolayer dispersed MoO₃ on the surface area of the sample.

Table 1 Surface areas of MoO₃/TiO₂

MoO ₃ content (g/g TiO ₂)	S (m ² /g TiO ₂)	
	773 K	873 K
0	80	62
0.10	94	74
0.20	127	104
0.25	140	72
0.30	135	70
0.32	127	65
0.37	115	—

WO₃/TiO₂ system

WO₃/TiO₂ system has also been investigated with XRD, Raman spectroscopy and BET surface area measurement, and similar results have been obtained. XRD patterns of WO₃/TiO₂ samples calcined at 873 K are shown in Fig 3. It can be seen that the sample of 0.20 g WO₃/g TiO₂ shows similar pattern as that of pure TiO₂, XRD peaks of WO₃ begin to show up in the sample of 0.25 g WO₃/g TiO₂ and then increase with increasing WO₃ content. This indicates that the monolayer dispersion capacity of WO₃ is near 0.25 g WO₃/g TiO₂. And this is also proved by the Raman spectra. The BET surface areas are listed in Table 2. It can be seen that the surface area of TiO₂ increases from 63 m²/g to 96 m²/g when the content of WO₃ reaches its monolayer dispersion threshold, which demonstrates that there is also a threshold effect in the influence of monolayer dispersed WO₃ on the surface area of the sample.

FeSO₄/γ-Al₂O₃ systems

FeSO₄/γ-Al₂O₃ system A is prepared by impregnat-

ing γ - Al_2O_3 calcined at 773 K for 4 h with the solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and followed by drying at 393 K and calcining at 773 K for 4 h. $\text{FeSO}_4/\gamma\text{-Al}_2\text{O}_3$ system B is prepared by impregnating pseudo-boehmite $\text{AlO}(\text{OH})$ with the solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ followed by drying at 393 K and calcining at 773 K for 4 h. XRD analysis shows that after calcining, FeSO_4 is converted to a mixture of $\text{Fe}_2(\text{SO}_4)_3$ and Fe_3O_4 , and that for system B the monolayer dispersion capacity of iron species corresponds to about 0.14 g $\text{FeSO}_4/\text{g}\gamma\text{-Al}_2\text{O}_3$. The BET surface areas of these two systems are listed in Table 3 and Table 4 respectively.

Table 2 Surface areas of WO_3/TiO_2

WO_3 content (g/g TiO_2)	S ($\text{m}^2/\text{g TiO}_2$)	
	873 K	
0	63	
0.10	70	
0.15	72	
0.20	87	
0.25	96	
0.30	84	

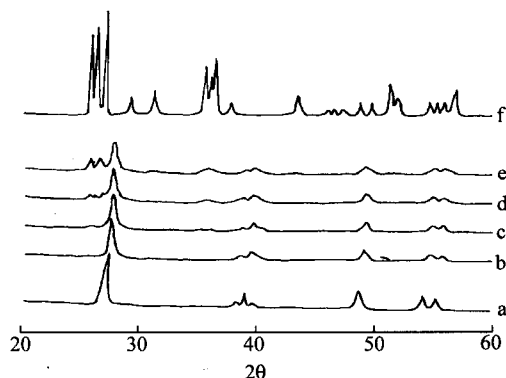


Fig. 3 XRD patterns of WO_3/TiO_2 samples calcined at 873 K for 4 h. WO_3 content (g/g TiO_2): a. 0; b. 0.20; c. 0.25; d. 0.30; e. 0.35; f. pure WO_3 .

Table 3 Surface areas of $\text{FeSO}_4/\text{Al}_2\text{O}_3$ (A)

FeSO_4 content (g/g $\gamma\text{-Al}_2\text{O}_3$)	S ($\text{m}^2/\text{g } \gamma\text{-Al}_2\text{O}_3$)	
0	238	
0.06	238	
0.13	227	

It can be seen that the surface areas of the samples in $\text{FeSO}_4/\gamma\text{-Al}_2\text{O}_3$ system A are lower than those of the

samples in $\text{FeSO}_4/\gamma\text{-Al}_2\text{O}_3$ system B. For system B, the sample with a content of 0.14 g $\text{FeSO}_4/\text{g}\gamma\text{-Al}_2\text{O}_3$ which corresponds to the dispersion threshold has the largest surface area of 361 m^2/g . These results are similar to the results of above systems, which proves that monolayer dispersed iron species can enhance the surface area of the sample.

Table 4 Surface areas of $\text{FeSO}_4/\text{Al}_2\text{O}_3$ (B)

FeSO_4 content (g/g $\gamma\text{-Al}_2\text{O}_3$)	S ($\text{m}^2/\text{g } \gamma\text{-Al}_2\text{O}_3$)	
0	238	
0.02	236	
0.06	260	
0.10	289	
0.14	361	
0.15	340	
0.17	260	
0.19	250	

$\text{Al}_2(\text{SO}_4)_3/\gamma\text{-Al}_2\text{O}_3$ and other systems

$\text{Al}_2(\text{SO}_4)_3/\gamma\text{-Al}_2\text{O}_3$ and four TiO_2 -supported samples are also prepared by this method and their surface areas are measured. The results are listed in Table 5. Clearly all the samples show larger surface areas compared with those of pure supports calcined at the same temperature, which demonstrates the effect of the monolayer dispersed species on the increase in surface areas of the samples.

Table 5 Surface areas of some samples

Sample	Content of active component (g/g support)	S ($\text{m}^2/\text{g support}$)
$\text{Al}_2(\text{SO}_4)_3/\gamma\text{-Al}_2\text{O}_3$	0	270
	0.03	328
	0.08	334
	0.19	304
TiO_2	0	80
$\text{SO}_4^{2-}/\text{TiO}_2$	0.02	94
$\text{NiSO}_4/\text{TiO}_2$	0.11	112
NiO/TiO_2	0.09	125
$\text{V}_2\text{O}_5/\text{TiO}_2$	0.05	136

$\text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ system

From the results of above-mentioned systems, we can see that using hydrous oxides instead of calcined oxides as supports in the catalyst preparation is really a novel way to

obtain catalysts with large surface areas. The authors imagine that if the active component can be washed away from the sample after calcination, pure oxide support with large surface area would be obtained, and it can be used in the preparation of other kind of supported catalyst.

In order to prove this imagination, $K_2CO_3/\gamma-Al_2O_3$ samples are prepared by this novel method (impregnating pseudoboehmite $AlO(OH)$ with the solution of K_2CO_3 and then calcining at 773 K for 3 h). The result of XRD quantitative phase analysis shows that the dispersion threshold of K_2CO_3 on the surface of $\gamma-Al_2O_3$ is about 0.39 g $K_2CO_3/g \gamma-Al_2O_3$. So several samples with K_2CO_3 loading near its dispersion threshold are selected and washed with distilled water to get pure $\gamma-Al_2O_3$ support. The BET surface areas of the resultant $\gamma-Al_2O_3$ increases to 356—374 m^2/g , while the surface area of the obtained by calcining pure $AlO(OH)$ at the same condition is only 266 m^2/g . Such $\gamma-Al_2O_3$ with very high surface area can be impregnated again with other active components to prepare catalysts with very high surface areas. It should be emphasized that for the systems in which active components are likely to react with $AlO(OH)$ in the course of impregnation or heat treatment, this method is especially valuable to obtain the catalyst with large surface area.

Discussion

Universality of this novel method

Many oxides and salts can disperse onto the surfaces of supports as monolayers. If a layer of active component is dispersed on the surface of ZrO_2 , TiO_2 or $\gamma-Al_2O_3$ support to segregate the particles of the support from each other when the particles are still very small (for example at the state of hydrous oxide or only calcined at a low temperature), the surface diffusion will be suppressed, and therefore the crystallite growth and inter-crystallite sintering will be greatly hindered. As results, the thermostability of the support will be improved and catalysts with large surface areas will be obtained. All the results of so many above-mentioned TiO_2 and $\gamma-Al_2O_3$ -supported catalysts and ZrO_2 -supported catalysts reported previously prove that this way is universal and effective to increase the surface areas of the catalysts. One of the authors has also proved this point by her work on SnO_2 -supported systems as gas sensors.²³

Differences among ZrO_2 , TiO_2 and $\gamma-Al_2O_3$ supported systems

Although this method is effective to increase the surface areas of ZrO_2 , TiO_2 and $\gamma-Al_2O_3$ supported catalysts, the extent of increase is quite different. For the samples calcined at 773—873 K, the surface areas of MoO_3/ZrO_2 ¹⁸ and WO_3/ZrO_2 ¹⁸ increase 4 times compared with that of pure ZrO_2 , while the surface areas of MoO_3/TiO_2 and WO_3/TiO_2 are only 75% and 52% higher than that of pure ZrO_2 , respectively. The surface areas of $\gamma-Al_2O_3$ -supported catalysts can only get an increase of 20—50%. That is to say, the effectiveness of this method is $ZrO_2 > TiO_2 > \gamma-Al_2O_3$. We think that this difference mainly depends on the intrinsic thermostability of the support: the lower the thermostability of the support, the more effective the method, *i. e.* the more remarkable the increase in the surface area. In addition, during the heat-treatment of pure ZrO_2 , meta-stable tetragonal phase $ZrO_2(t)$ which can exist only when the particles are very small will turn into more stable monoclinic phase $ZrO_2(m)$, in the meantime of crystallite growth and inter-crystallite sintering. As a result of the phase transformation, the surface area will decrease drastically. This is the special phenomenon for ZrO_2 , so it is most effective to disperse a layer of active component onto the surface of $Zr(OH)_4$ or $ZrO_2(t)$ in advance. However, there is no such phase transformation for TiO_2 and $\gamma-Al_2O_3$ in the temperature range investigated in this paper.

Problem this preparation method might cause and its solution

Since hydrous oxide is more active compared to the calcined oxide, the bulk reaction between the active component and the support may occur for some systems, and the state of the active component in the sample and its catalytic property may be changed. In order to avoid the negative interaction between the active component and the support, an alternative way is suggested. That is, at first impregnating the hydrous oxide with an active component such as K_2CO_3 that can be easily removed to prepare sample with high surface area; secondly, removing the active component to get pure oxide support; at last impregnating the resultant oxide support with high surface area with the solution of the required active component or its precursor

to obtain catalyst wanted.

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