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TG STUDY OF THE DISPERSION THRESHOLD OF Mn_2O_3 ON γ-Al_2O_3

J. Liu[1], *H. Xu*[2], *W. Shen*[2], *X. Pan*[2] *and Y. Xiang*[2]

[1]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023
[2]Department of Chemistry, Fudan University, Shanghai 200433, P. R. China

Abstract

Mn_2O_3/γ-Al_2O_3 catalysts were prepared by the impregnation method, and the maximum monolayer dispersion capacity or dispersion threshold value of Mn_2O_3 on the surface of γ-Al_2O_3 was determined to be 13.08% from the decomposition mass loss of supported $Mn(NO_3)_2$ in the monolayer state. This was compared with the values estimated from a close-packed monolayer model and an interaction model. It was confirmed that the high activities and selectivities of the catalysts for benzoic acid hydrogenation to benzaldehyde are due to the monolayer dispersion of the Mn_2O_3 on the surface of γ-Al_2O_3.

Keywords: dispersion threshold value, Mn_2O_3/γ-Al_2O_3 catalyst, TG

Introduction

The fact that high activity and selectivity for a supported catalyst can often be obtained from a monolayer dispersion of an active component on the surface of the support has been confirmed in numerous experiments. Determination and estimation of the maximum monolayer dispersion capacity of the active component, or the threshold value, are therefore important for directing the preparation of the catalyst. In recent years, the application of Mn_2O_3/γ-Al_2O_3 catalysts has gradually been increasing, but few reports are to be found on the determination of the dispersion threshold value of Mn_2O_3/γ-Al_2O_3.

In the present work, the decomposition behaviour of supported $Mn(NO_3)_2$ in air was followed by TG and the dispersion threshold value of Mn_2O_3 on the surface of γ-Al_2O_3 was determined from the decomposition mass loss of supported $Mn(NO_3)_2$ in the monolayer dispersion state. At the same time, a close-packed monolayer model and an interaction model were employed to estimate the dispersion threshold value. It was found that the actual dispersion threshold value is close to the optimal Mn loading, which yields high activity and selectivity for the Mn_2O_3/γ-Al_2O_3 catalysts [1].

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Experimental

Catalysts

All the Mn catalysts were prepared by impregnating γ-Al_2O_3 (surface area: 269 m^2 g^{-1}) with an aqueous solution of $Mn(NO_3)_2$. The loadings of Mn_2O_3 were from 24 to 32%.

Experimental equipment and conditions

Decomposition experiments were performed on the TG unit of a Shimadzu DT-30 thermal analyzer with a sample in range of 5 mg, at a heating rate of 10°C min^{-1} and a chart speed of 1.25 mm min^{-1}, in air atmosphere.

Results and discussion

Decomposition behaviour of supported $Mn(NO_3)_2$ in air

If the loading of salts or oxides is less than the dispersion threshold value, they usually exist in a monolayer dispersion state; if the loading is higher than this value, the crystalline state will appear. In consequence of the differences in decomposition temperature, the amount of supported salts or oxides in both states can be determined from their mass loss in the decomposition process.

TG was first used to follow the decomposition of supported $Mn(NO_3)_2$. Figure 1 shows the TG curves of decomposition of supported $Mn(NO_3)_2$ in air, and the data from these curves are summarized in Table 1.

Table 1 TG results on $Mn(NO_3)_2/\gamma$-Al_2O_3 catalyst decomposition in air

No.	Sample mass/mg	$Mn(NO_3)_2$ loading/%	Desorption of free water (<40°C)/mg	Mass loss between 40 and 450°C		MnO_x/γ-Al_2O_3	
				mg	%	mg	%
1	19.22	43.48	0.1	3.80	19.77	15.32	79.7
2	18.42	46.81	0.15	3.35	18.18	14.93	81.0
3	18.80	50.41	0.20	3.45	18.35	15.15	80.6
4	18.60	53.54	0.10	3.60	19.35	14.90	80.1
5	15.40	56.31	0.07	3.00	19.48	12.33	80.0
6	12.90	57.97	0.18	2.52	19.53	10.20	79.0

It can be seen from Fig. 1 that a set of similar TG curves were obtained in air for the Mn_2O_3/γ-Al_2O_3 catalysts with various loadings. Their reaction temperatures were all in the range 313–723 K. The mass loss in this range corresponds to the desorption of free water and hydroxy radical from the γ-Al_2O_3 and to decomposition of the supported $Mn(NO_3)_2$. If the decomposition of the supported $Mn(NO_3)_2$ can be represented as follows:

$$Mn(NO_3)_2/\gamma\text{-}Al_2O_3 \rightarrow MnO_x/\gamma\text{-}Al_2O_3 + NO_2 + O_2 \quad (1)$$

then the mass loss caused by the decomposition of the supported $Mn(NO_3)_2$ should increase with the $Mn(NO_3)_2$ loading.

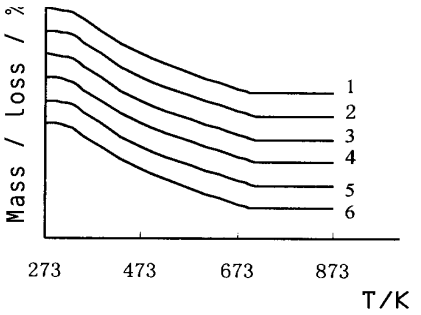

Fig. 1 Decomposition TG curves of $Mn(NO_3)_2/\gamma\text{-}Al_2O_3$ catalyst in air

However, to our surprise, the decomposition mass loss % obtained was nearly constant. Accordingly it is reasonable to attribute it to the decomposition of supported $Mn(NO_3)_2$ in a monolayer dispersion state, because the threshold value is usually a constant and does not change with the loading when the loading is higher than the dispersion threshold value. The colour of $Mn(NO_3)_2/\gamma\text{-}Al_2O_3$ changes to dull when it is dried in air, suggesting that the supported $Mn(NO_3)_2$ in the crystalline state already decomposes in consequence of its instability; Mn_2O_3 is left as product.

Calculation of the total Mn_2O_3 on γ-Al_2O_3

As discussed above, if only supported $Mn(NO_3)_2$ in a monolayer dispersion state is loaded onto the surface of $\gamma\text{-}Al_2O_3$, then according to Eq. (1) the dispersion threshold value of MnO_x on $\gamma\text{-}Al_2O_3$ can be calculated from the mass loss in the decomposition process. For this purpose, it is first necessary to know the composition of $Mn(NO_3)_2$ because the mass loss in the decomposition process is related to x.

Table 2 Calculation results on the total Mn_2O_3

No.	Sample mass/ mg	$Mn(NO_3)_2$ loading/ mg	$Mn_2O_3/\gamma\text{-}Al_2O_3$/ mg	Total Mn_2O_3	
				mg	%
1	19.22	8.53	15.32	3.68	24.02
2	18.43	8.62	14.93	3.80	25.45
3	18.80	9.47	15.15	4.18	27.59
4	18.60	9.95	14.90	4.38	29.39
5	15.40	8.67	12.33	3.82	30.98
6	12.90	7.48	10.20	3.30	32.35

It has been reported that, when supported $Mn(NO_3)_2$ is calcined at 723 K, its decomposition product is Mn_2O_3 [2], so Eq. (1) can be re-written as follows:

$$2Mn(NO_3)_2/\gamma\text{-}Al_2O_3 \rightarrow Mn_2O_3/\gamma\text{-}Al_2O_3 + 2NO_2 + 1/2O_2 \quad (2)$$

The total Mn_2O_3 calculated via Eq. (2) from the loading of $Mn(NO_3)_2$ is listed in Table 2.

These results show that the Mn_2O_3 loading on the catalysts approximately ranges from 24 to 32%.

Determination of the dispersion threshold value from TG data

In view of the analysis mentioned above, the dispersion threshold value of Mn_2O_3 on γ-Al_2O_3 can be determined from the mass loss supported $Mn(NO_3)_2$ in a monolayer dispersion state in the decomposition process. The decomposition mass loss can be obtained by deducting the mass loss of dehydration, including the free water and hydroxy radical on γ-Al_2O_3, from the mass loss in the interval 313–723 K. The calculated dispersion threshold values are listed in Table 3. In addition, it can be obtained by the graphical method. Figure 2 depicts a plot of the crystalline Mn_2O_3% *vs.* the total Mn_2O_3%.

Table 3 Calculated results on the dispersion threshold value of Mn_2O_3 on γ-Al_2O_3

No.	Sample mass/ mg	Dehydration of γ-Al_2O_3/ mg	Mass loss at 313–723 K/ mg	Mass loss of $Mn(NO_3)_2$ in monolayer state/mg	Monolayer Mn_2O_3/%	Crystalline Mn_2O_3/%
1	19.22	1.30	3.80	2.50	12.85	11.19
2	18.42	1.17	3.35	2.18	11.52	13.94
3	18.80	1.11	3.45	2.34	12.14	15.45
4	18.60	1.03	3.60	2.57	13.55	15.90
5	15.40	0.80	3.00	2.20	14.03	16.93
6	12.90	0.65	2.52	1.87	14.41	17.54

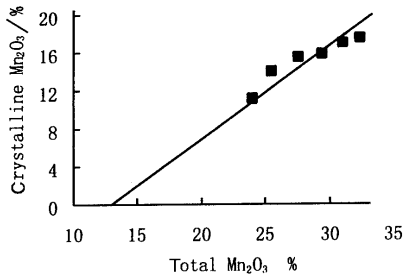

Fig. 2 Relationship between crystalline Mn_2O_3% and total Mn_2O_3%

From Table 3 it can be seen that the dispersion threshold values calculated from the mass loss of decomposition of supported $Mn(NO_3)_2$ in a monolayer dispersion state are 11.5–14.4%, with an average value of 13.08%. The error may be mainly due to the fact that the amount of catalyst prepared was very small (support Al_2O_3 only 0.5 g).

From Fig. 2, it can also be seen that the plot of crystalline Mn_2O_3% *vs.* the total Mn_2O_3% is a straight line and that the value corresponding to the intersection point of the straight line with the abscissa is 13%, i.e. the dispersion threshold value. The value is very close to the average value.

Estimation of the dispersion threshold value from the close-packed monolayer model [3–5]

The close-packed monolayer model is illustrated in Fig. 3.

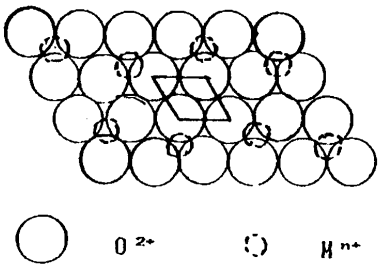

Fig. 3 Close-packed monolayer model

The area of the rhombus shown in Fig. 3 is a minimum 2-dimensional unit for the model. According to this model, the area occupied by one salt or oxide molecule is approximately equal to that occupied by three O^{2-} ions in close-packed monolayer. The area occupied by one O^{2-} ion is just equal to the rhombus area which can be calculated from the radius of the O^{2-} ion ($1.40 \cdot 10^{-20}$ m^2) to be $6.79 \cdot 10^{-20}$ m^2.

Thus, the dispersion threshold value of Mn_2O_3 on γ-Al_2O_3, *Tv* may be calculated via the following equation:

$$Tv = \frac{SM}{abN} \text{ g/g support} \tag{3}$$

where S – the specific surface area of γ-Al_2O_3 (m^2 g^{-1}), a – the area occupied by one O^{2-} ion in close-packed monolayer ($6.79 \cdot 10^{-20}$ m^2), b – the number of O^{2-} ions occupied Mn_2O_3 on γ-Al_2O_3 (3); M – the molecular mass of Mn_2O_3 (157.86); N – the Avogadro constant ($6.02 \cdot 10^{23}$).

The dispersion threshold value of Mn_2O_3 on γ-Al_2O_3 is estimated from Eq. (3) to be 0.346 g/g Al_2O_3 or 0.128 g/100 m^{-2}.

According to the interaction model, the area occupied by one salt or oxide molecule relates not only to the number of vacant sites on the support, but also to the co-

ordination environment of the metal ion. The number of vacant sites varies with the support. For example, the number of vacant sites on γ-Al_2O_3 is 20.5 nm^{-2}, but that on CeO_2 is 7.4 nm^{-2} [6]. Moreover, the usage ratio of the vacant sites is also related to the radius of the cation M^+ interacting. In this case, the dispersion threshold value of Mn_2O_3 on γ-Al_2O_3 can be calculated via the following equation, with n (M^+nm^{-2}) estimated via the model.

$$T = n\frac{M}{N}10^{18} \quad g\ m^{-2} \tag{4}$$

where n – the number of cations M^+ occupied per nm^2, M – the molecular mass of Mn_2O_3 (157.86), N – the Avogadro constant ($6.02 \cdot 10^{23}$), n for MO type oxides is estimated to be 9.8 nm^{-2} , while for those of MO_3 type it is 4.9 nm^{-2}. However, only n for La_2O_3 has been estimated to be 9.8 nm^{-2} for those of M_2O_3 type. If n for Mn_2O_3 is close to that for La_2O_3, then the dispersion threshold value of Mn_2O_3 on γ-Al_2O_3, estimated via Eq. (4), is 0.257 g/100 m^2. The estimated threshold values are compared with the experimental values in Table 4.

Table 4 Comparison of estimated threshold value with experimental value

Closed-packed monolayer model		Interaction model		Experimental g/100 m^2
g/100 m^2	Mn_2O_3 %	M^+ nm^{-2}	g/100 m^2	
0.128	25.72	9.8	0.257	0.056

It can be seen from Table 4 that the experimental value is close to the value of 0.051 100 m^{-2} determined by Xie Yuchang [7] for Fe_2O_3 on γ-Al_2O_3, but obviously less than the estimated value. This is very probably due to the screening effect of Mn_2O_3 on nearby vacant sites. Obviously, if the salt or oxide conforms to a close-packed monolayer, then the estimated threshold value will be in agreement with the experimental value, and if the number of cations occupied per nm^2 is accurately given, the correct threshold value can be obtained. If not, the threshold value has to be experimentally determined.

Conclusions

Recent results showed that when the Mn loading on the catalyst is about 10%, the conversion of benzoic acid is more than 98% and the selectivity for benzaldehyde is 96%. The maximum monolayer dispersion capacity, i.e. the threshold value of Mn_2O_3 on γ-Al_2O_3 was determined by the TG method to be 13.0 (Mn_2O_3%) or 9% (Mn%). This implies that the high activity and selectivity of the Mn_2O_3/γ-Al_2O_3 catalyst is due to a monolayer dispersion of Mn_2O_3 on γ-Al_2O_3. The threshold value estimated via the close-packed model and the interaction model are both higher than the experimental value. This suggests that both models have limitations for estimating the threshold value of M_2O_3 type oxides on γ-Al_2O_3.

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