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REVIEW ARTICLE

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Monolayer dispersion thresholds and threshold effect displayed by supported catalysts

Abstract The principle of spontaneous monolayer dispersion holds that active components of many supported catalysts will disperse spontaneously onto the surface of the carrier. The monolayer dispersion threshold of the active component on the surface of the carrier can be measured by X-ray diffraction phase-quantitative extrapolation method, etc. By measuring the monolayer dispersion threshold, beneficial information on the surface structure and dispersion of supported catalysts can be obtained, and the optimal preparative processing conditions of the catalysts can be chosen. The proportion of the active component of many supported catalysts can be optimized while its monolayer dispersion threshold is observed. Mutation values of many physicochemical properties of supported catalysts are related to monolayer dispersion thresholds; the threshold effect on catalysts is apparent, and the proposal regarding the threshold effect provides instruction for the research on catalysts.

Keywords supported catalysts, principle of spontaneous monolayer dispersion, monolayer dispersion threshold, proportion of the active components, threshold effect

The research on many kinds of catalyst systems devoted to by Xie Youchang et al [1,2] and [3] in the 1970 s indicates that the active components of many supported catalysts (e. g. salts and oxides of transition metals) may spontaneously disperse to form a monolayer on the surface of carriers, and that there may exist monolayer thresholds of spontaneous dispersion on the surface of carriers (abbreviation: maximum monolayer dispersion capacity or monolayer dispersion threshold). This quite universal experimental phenomenon may be summed up as the principle of spontaneous monolayer dispersion. Liu Yingjun et al [3–6] and [7] have done massive research on the dispersion of active components on the surface of relevant carriers of many supported catalysts systems, which have provided quantitative experimental bases for the establishment of the principle of spontaneous monolayer dispersion. Several years ago, Wang Chunming et al [8] summarized the work done by domestic and foreign scholars, and comprehensively elaborated on the latest progress in spontaneous monolayer dispersion with very thorough understanding. It can be expected that the principle proposed provides a quantitative investigation method for the development of supported catalysts, drawing much attention from relevant research fields, and has extremely vital significance. Therefore, it is necessary to unify the previous research and our work, to discuss in detail the principle of spontaneous monolayer dispersion involving the monolayer threshold of the spontaneous dispersion on the surface of carriers, and the threshold effects of supported catalysts, etc. in providing instruction for the research on catalysts.

1 Monolayer dispersion threshold

1.1 Measurement of the monolayer dispersion threshold

It is generally believed that due to the monolayer dispersion capacity of the active components of supported catalysts having limitations due to the size of the surface area on the carrier [9], the active components can spontaneously disperse onto specific positions on the surface of the relevant carrier. The number of positions are in proportion to the specific surface area of the relevant carrier, therefore there is a monolayer threshold to spontaneous dispersion on the surface of the carrier. The author once pointed out that [10], as the core content of the principle of spontaneous monolayer dispersion, monolayer dispersion thresholds are important experimental parameters in the research on catalysts, thus accurate measurement of monolayer dispersion thresholds is especially important. For many years, XRD (X-ray diffraction), LRS (Laser Raman spectrum), XPS (X-ray photoelectron spectroscopy), isothermal H_2 reduction method and many other experimental techniques have been

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employed for the measurement of monolayer dispersion thresholds of many supported catalyst systems, and have been mutually confirmed [3,7,9,11] and [12].

The XRD quantitative extrapolation method (also called reference intensity method) is a commonly used method. This method measures the residual amount at crystalline phase after dispersion of the active component on the carrier to get the monolayer dispersion threshold of the catalyst; the specific principle and procedure can be seen in [1] and [3]. Taking the residual amount of the crystalline phase after dispersion of the active component on the surface of the relevant carrier for the Y-coordinate, and the supporting amount of the active component as the X-coordinate, a curve can be obtained. The supporting amount of active component at the point of intersection of extension of the linear part on the curve with X-coordinate is its monolayer dispersion threshold. LRS, the phase-quantitative method, uses the reference intensity method similar to the XRD quantitative extrapolation method; for the specific principle and procedure, refer to [11] and [13]. The XPS peak intensity ratio method can indirectly determine the monolayer dispersion threshold of catalysts through the element content in the quasi-surface, or the mutation value of the physicochemical property of catalysts; the specific principle and procedure can be seen in [5] and [9]. Take the XPS peak intensity ratio corresponding to the inner shell binding energy of the chosen element in the active component and relevant carrier as the Y-coordinate and the supporting amount of active components as the X-coordinate; then two straight lines of different slopes are obtained. The supporting amount of active components at the point of intersection (or turning point) is its monolayer dispersion threshold. The isothermal H_2 reduction method [12] may also indirectly determine the monolayer dispersion threshold. In addition, the gas phase adsorption method is another method estimating monolayer dispersion thresholds of catalysts. For example, the author et al [14] once used the $TiCl_4$ gas phase adsorption method in research on the realization of dispersion of TiO_2 on the surface of γ-Al_2O_3, and the measured quantity of adsorption of $TiCl_4$ on the surface of γ-Al_2O_3 in front of the inflection point of the second mutation of the breakthrough curve. It may correspond to the monolayer dispersion threshold of TiO_2 on the surface of γ-Al_2O_3.

For a more convenient discussion, measurement values of the monolayer dispersion thresholds of supported catalyst systems and their calculated values according to the dispersion of a close-packed monolayer model [1,3] are given in Table 1 for comparison. From Table 1, obviously, the monolayer dispersion capacities of the active components on the surfaces of relevant carriers of some supported catalyst systems have definite limitations, where the monolayer dispersion thresholds are mostly equal to or smaller than the calculated values according to the dispersion of the close-packed monolayer model.

1.2 Variations of the monolayer dispersion thresholds are related to interaction of the active component and the relevant carrier

What factors are related to the variation of the monolayer dispersion thresholds? It is generally believed that [1],

Table 1 Monolayer dispersion thresholds of the active component of some catalysts

catalyst systems	specific surface area of carriers	preparation conditions			monolayer dispersion thresholds		close-packed monolayer capacity capacities	references
	$S_{BET}/m^2 \cdot g^{-1}$	method	calcining temperature/°C	time/h	g component/ g carrier	g component/ 100 m^2 carrier	(g component/ 100 m^2 carrier)	
TiO_2/γ-Al_2O_3	211.6	gas-adsorption	550	3	0.168	0.079	0.098	[14]
TiO_2/SiO_2	371.0	gas-adsorption	550	3	0.130	0.035	0.098	[15]
MoO_3/γ-Al_2O_3	178.0	mechanic mixing	400–450	24	0.210	0.118	0.120	[1,3,4,6]
$MoO_3/TiO_2/\gamma$-Al_2O_3	200.0	mechanic mixing	420	24	0.240	0.120	0.120	[13]
MoO_3/TiO_2	60.0	mechanic mixing	400	24	0.073	0.122	0.120	[6]
MoO_3/SiO_2	310.0	mechanic mixing	400–450	24	0.100	0.032	0.120	[6]
$MoO_3/TiO_2/SiO_2$	293.0	impregnation	500	6	0.130	0.044	0.120	[16]
WO_3/γ-Al_2O_3	200.0	impregnation	550	24	0.400	0.200	0.189	[5]
$WO_3/TiO_2/\gamma$-Al_2O_3	200.0	impregnation	500	24	0.360	0.180	0.189	[11]
WO_3/SiO_2	371.0	impregnation	550	24	0.066	0.018	0.189	[9]
$WO_3/TiO_2/SiO_2$	297.0	impregnation	500	24	0.110	0.037	0.189	[11]
NiO/γ-Al_2O_3	236.0	impregnation	450	2	0.265	0.112	0.183	[17]
NiO/η-Al_2O_3	124.0	impregnation	450	2	0.097	0.078	0.183	[17]
NiO/TiO_2	86.0	impregnation	450	3	0.083	0.097	0.180	[7]
MgO/γ-Al_2O_3	236.0	impregnation	400	4	0.182	0.077	0.099	[17]
MgO/η -Al_2O_3	124.0	impregnation	400	4	0.090	0.073	0.099	[17]
CuO/γ-Al_2O_3	205.0	impregnation	400	2	0.082	0.040	0.190	[12]
$CuCl/\gamma$-Al_2O_3	343.3	mechanic mixing	380–400	2	0.330	0.096	0.145	[18]
ZnO/SiO_2	360.0	impregnation	560	4	0.780	0.217	0.197	[19]

regarding certain supported catalyst systems, the spontaneous dispersion of the active components on the surface of relevant carriers should be along the advantageous position of energy and geometry of the surface of the carrier. Different carriers have different positions to satisfy this requirement, therefore the variations of monolayer dispersion thresholds must be determined by the structure properties of the carrier surface and the interaction of the active component and the relevant carrier. Based on this, the preparative processing condition of the catalysts, the choice of promoter etc. also would affect monolayer thresholds of spontaneous dispersions on the surface of carriers.

As an example, the interaction of MoO_3 and some carriers are explained. The experimental results show that [6] as for the catalyst systems with $MoO_3/\gamma\text{-}Al_2O_3$, MoO_3/TiO_2, MoO_3/SiO_2 and MoO_3/MgO etc, obtained by mechanical mixing method and calcined at temperature of 400–450°C, the differences in monolayer dispersion thresholds of actual measurements (see Table 1) mainly lie in the differences in the interaction of MoO_3 with different carriers, and this may also be explained by the differences about the acidity-basicity and structure of the carriers. Basic oxide MgO with acidic oxide MoO_3 easily produce a body-phase reaction to form $MgMoO_4$, not only to reach the stage of monolayer dispersion on the surface of the carrier, but to go beyond it, as there is no monolayer dispersion threshold; however $\gamma\text{-}Al_2O_3$ and TiO_2 are amphoteric oxides, which have more difficulty in producing a body-phase reaction with MoO_3; MoO_3 on the surface of $\gamma\text{-}Al_2O_3$ or TiO_2 may present as the dispersion of a close-packed monolayer under the appropriate temperature. The acidic oxide SiO_2 (silica gel) with MoO_3 also has difficulty in forming the body-phase compound, and monolayer dispersion of MoO_3 on the surface of silica gel is restricted to some special positions only. To form the surface compound, its monolayer dispersion threshold must obviously be lower than the calculated value according to the dispersion of the close-packed monolayer model. In the structure of $\gamma\text{-}Al_2O_3$ and TiO_2, positive and negative ions (atom) pack quite closely, and the surface free energy is also higher [11], thus it is advantageous for MoO_3 to distribute on the surface in a dispersion of a close-packed monolayer. However, the silicon-oxygen tetrahedral skeleton structure in silica gel is quite spacious, and the surface free energy is also lower [11] and wherein it is very hard to form an O^{2-} close-packed monolayer on the surface of silica gel, therefore, the mutual combination of silica gel and MoO_3 is restricted to some positions only.

Further, compared with the supported catalysts systems of $NiO/\gamma\text{-}Al_2O_3$, $NiO/\eta\text{-}Al_2O_3$, $MgO/\gamma\text{-}Al_2O_3$ and $MgO/\eta\text{-}Al_2O_3$ etc. obtained by using the impregnation method and at calcining temperatures of 400–450°C [17], the monolayer dispersion thresholds from actual measurements (see Table 1) are different, the reason lying in the differences in interaction of the different active components NiO or MgO with the carriers $\gamma\text{-}Al_2O_3$ or $\eta\text{-}Al_2O_3$ of different structural patterns. Regarding the $\gamma\text{-}Al_2O_3$ and $\eta\text{-}Al_2O_3$, of different raw materials, their surface structures and properties are different and the interaction with MgO, or NiO of various structures and properties are different, thus their monolayer thresholds of spontaneous dispersion on the surface of carriers can also have differences.

2 Example of application of monolayer dispersion thresholds

2.1 To get useful information about surface structure and dispersion of catalysts

Compare the measured value of the monolayer dispersion threshold with its calculated value according to the dispersion of a close-packed monolayer model. We gain beneficial information about the surface structure and dispersion of supported catalysts. Generally speaking, if the measured monolayer dispersion threshold approaches or equals its calculated value according to the dispersion of a close-packed monolayer model (e.g. in Table 1, $MoO_3/\gamma\text{-}Al_2O_3$ and MoO_3/TiO_2 systems etc), then we may consider that the dispersion of the active components on the surface of the relevant carrier goes according to the conditions of the close-packed monolayer model, and the surface monolayer coverage rate may approach to or reach 100%; if the measured monolayer dispersion threshold is smaller than its calculated value according to the dispersion of a close-packed monolayer model (majority of catalysts systems show such, see Table 1), then we may think that the spontaneous dispersion of the active components on the surface of the relevant carrier goes according to the way of the quasi-monolayer (or the sub-monolayer, monolayer), and its surface monolayer coverage rate is usually smaller, with lower dispersion. The existing surface monolayer dispersion phase may be examined. For example, the author et al [13], worked on $MoO_3/(TiO_2/\gamma\text{-}Al_2O_3)$ serial samples (by using the mechanical mixing method, calcined under 500°C for 24 h, S_{BET} $(TiO_2/\gamma\text{-}Al_2O_3) = 200$ m^2/g), and the LRS method measurement indicated that the LRS spectrogram of the samples in the MoO_3 supporting amount was lower than its calculated value according to the dispersion of the close-packed monolayer model (0.24 g MoO_3/g $(TiO_2/\gamma\text{-}Al_2O_3)$ or 0.12 g MoO_3/100 m^2 $(TiO_2/\gamma\text{-}Al_2O_3)$, also for threshold). Fig. 1 shows the Raman characteristic peaks of the monolayer dispersion phase of MoO_3 with the wave numbers 898 cm^{-1} and 958 cm^{-1}, the former belonging to the expansion and contraction vibration of Mo=O bond of separate tetrahedron coordinate MoO_4^{2-}, and the latter belonging to the expansion and contraction vibration of the Mo=O bond of a polymolybdic acid radical terminal grouping of the octahedron coordinate. With the increase in the supporting amount of MoO_3, the quantity of the octahedron coordinate Mo (O) species increases relatively more than that of the tetrahedron coordinate Mo (T) species until up to the calculated value according to the dispersion of a close-packed monolayer model. Also, the research on the preparation of complex carrier $TiO_2/\gamma\text{-}Al_2O_3$ by gas phase adsorption method [20], using the technology of LRS, XPS etc, confirmed the monolayer dispersion state of TiO_2 on the surface of $\gamma\text{-}Al_2O_3$, and the Raman characteristic peak of the monolayer dispersion state of TiO_2 on the surface of $\gamma\text{-}Al_2O_3$ appeared in its LRS spectrogram with wave number 878 cm^{-1}.

If the measured monolayer dispersion threshold surpasses its calculated value according to the dispersion of a close-packed monolayer model, one may gain information by analyzing the reason from its structure, properties etc. For example, results from the measurement of LRS in the above $MoO_3/(TiO_2/\gamma\text{-}Al_2O_3)$ system has indicated that [13], when the supporting amount of MoO_3 is 0.24–0.33 g MoO_3/g ($TiO_2/\gamma\text{-}Al_2O_3$), its newly increased MoO_3 exists as the species in the form of a cluster polymolybdic acid salt with high dispersion and which easily dissolves in aqueous ammonia, with wave numbers 1,004 cm^{-1} being the Raman characteristic peak of this species (see Fig. 1), so that the dispersion capacity surpasses its calculated value according to the dispersion of a close-packed monolayer model, to reach 0.33 g MoO_3/g ($TiO_2/\gamma\text{-}Al_2O_3$) (to be equal to 0.165 g MoO_3/100 m^2 ($TiO_2/\gamma\text{-}Al_2O_3$)).

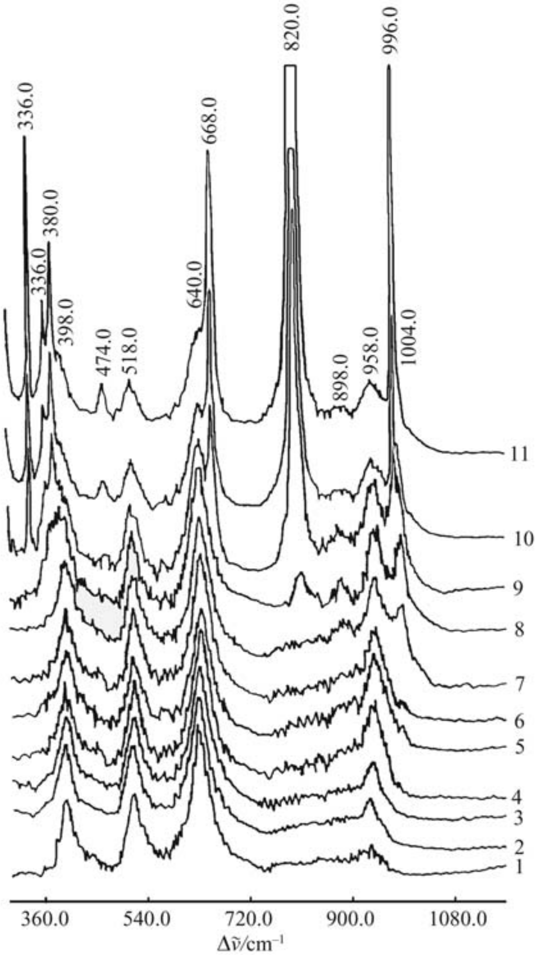

Fig. 1 Laser Raman spectra of $MoO_3/TiO_2/\gamma\text{-}Al_2O_3$
1: 0.02; 2: 0.07; 3: 0.11; 4: 0.16; 5: 0.21; 6: 0.26; 7: 0.32; 8: 0.38; 9: 0.48; 10: 0.58; 11: 0.68 g MoO_3/g($TiO_2/\gamma\text{-}Al_2O_3$)

2.2 Choosing the best preparative processing condition of the catalysts

The influence of the preparative processing condition of supported catalysts (including preparation method, calcining temperature, type and additional order of promoters etc) on the dispersion and the surface structure of active components on the surface of the relevant carrier is remarkable, and the measuring of monolayer dispersion thresholds may often provide the basis for the choice of the optimal preparative processing conditions of the catalysts. Examples are as follows:

2.2.1 Selection of preparation method

First take the $TiO_2/\gamma\text{-}Al_2O_3$ system as an example. The experiment indicated that [21], grafting method can possibly cause TiO_2 to evenly disperse on the surface of $\gamma\text{-}Al_2O_3$, but the supported TiO_2 amount from an only one-time grafting operation could not reach half of the calculated value (0.098 g TiO_2/100 m^2 $\gamma\text{-}Al_2O_3$) according to the dispersion of a close-packed monolayer model. This is possibly related to $\gamma\text{-}Al_2O_3$ adsorbing $TiCl_4$ under a rather high temperature of 120°C, and the increase in the number of grafts can enhance the supporting amount of TiO_2, but it will cause uneven dispersion of TiO_2 on the surface of $\gamma\text{-}Al_2O_3$; the impregnation method can cause TiO_2 to disperse relatively evenly on the surface of $\gamma\text{-}Al_2O_3$. The precipitation method obtains poor dispersity of TiO_2, and TiO_2 only gathers in one part of the surface of $\gamma\text{-}Al_2O_3$. This is possibly concerned with some factors like nucleation between the latter settling deposition and the species precipitating early. However, the author et al [14] used the $TiCl_4$ gas phase adsorption method and proved that it can be a more ideal preparation method with high dispersity, and its monolayer dispersion threshold for TiO_2 on the surface of $\gamma\text{-}Al_2O_3$ may reach 0.079 g TiO_2/100 m^2 $\gamma\text{-}Al_2O_3$, whose surface monolayer coverage rate can reach as high as 81%. Obviously, the preparation method has a tremendous influence on the dispersion of TiO_2 on the surface of $\gamma\text{-}Al_2O_3$.

Also, the author et al [22], in their research on the supported catalyst $NiO/\gamma\text{-}Al_2O_3$ for reforming of CH_4 with CO_2 to syngas, found that $NiO/\gamma\text{-}Al_2O_3$ samples, prepared by the impregnation method or the co-precipitation method and both calcined under 400°C for 10 hours, have an experimental monolayer dispersion threshold of NiO

0.112 g NiO/100 m^2 γ-Al_2O_3 and 0.103 g NiO/100 m^2 γ-Al_2O_3, respectively. It is possible that samples prepared through the co-precipitation method have partly active components contained in the body-phase of the carrier, resulting in its imperfect dispersion on the surface. Therefore, it is advised that the impregnation method should be used more often to prepare reforming catalysts of high dispersity and high activity.

2.2.2 Selection of calcining temperature

The experiment on the MoO_3/SiO_2 catalyst system indicated that [6] a series of MoO_3/SiO_2 samples prepared through the mechanic mixing method and calcining for 24 h under 300°C (much lower than the MoO_3 melting point, 795°C), cannot offer the curve needed to get the threshold by the XRD quantitative extrapolation method. This is possible because when the calcining temperature is lower, the thermal dispersion of MoO_3 is insufficient to overcome the binding force of its crystal interior and for proliferation in the surface of the silica gel to form the corresponding surface compound; as calcined under 400–500°C for 24 h, MoO_3 disperses only on the surface of the silica gel and achieves balance, and the experimental monolayer thresholds of the spontaneous dispersion on the surface of the carriers are all 0.032 g MoO_3/100 m^2 SiO_2; as calcined under 700°C for 24 h, sublimated MoO_3, MoO_3 and the silica gel are not easy to carry on the body-phase reaction. In addition, in the research on nickel catalyst for methanation we also found [17] that for a NiO/γ-Al_2O_3 sample prepared by the impregnation method with calcining temperature above 630°C, the measured maximum monolayer dispersion capacity increased as compared with what was originally gotten for an appropriate calcining temperature of 450°C; the diffraction peak of the nickel aluminum spinel ($NiAl_2O_4$) appeared in the XRD pattern, and it indicated that there occurs a body-phase reaction. Similarly, for an MgO/η-Al_2O_3 sample prepared by the impregnation method and calcined for various times under 450°C or 570°C separately, compared with calcination at the appropriate temperature of 400°C for 4 h, its maximum monolayer dispersion capacity increased along with enhancement of the calcining temperature and lengthening of the calcining time, which indicated that MgO and η-Al_2O_3 had body-phase reactions to some degree.

Obviously, when the calcining temperature of sample is somewhat low, the active components on the surface of the relevant carrier do not easily proliferate and achieve balance. When the calcining temperature is somewhat high, it can frequently cause body-phase diffusion and body-phase reaction or other changes. The form of existence or the surface concentration of the active components on the surface of the relevant carrier will have changes. The choice of the appropriate calcining temperature lower than melting point of the active component, and the control of calcining time would result in an ideal dispersion and monolayer threshold of spontaneous dispersion of the active components on the surface of the carrier. This is quite significant for the preparation of supported catalysts with excellent catalytic property.

2.2.3 Selection of type and additional order of promoters

Research on the effects of TiO_2-modified γ-Al_2O_3 on the catalytic performance of MoO_3/γ-Al_2O_3 and CoO-MoO_3/γ-Al_2O_3 catalysts has found that [13] and [23], TiO_2-modified γ-Al_2O_3 would benefit the weakening or adjusting of the strong interaction of MoO_3 and γ-Al_2O_3, and it would also benefit the formation of an octahedron coordinate Mo(O) species; it also would suppress the formation of the $Al_2(MoO_4)_3$ phase, obviously improve the surface structure of the supported Mo catalyst, and enhance its property of H_2 reduction. The activities of the MoO_3/(TiO_2/γ-Al_2O_3) catalyst for thiophene hydrodesulfurization (HDS) and cyclohexene hydrogenation are obviously higher than the MoO_3/γ-Al_2O_3 catalyst without TiO_2-modified. Addition of a CoO promoter in the appropriate amount promotes dispersion of MoO_3 on the surface of the carrier, obviously increases its monolayer dispersion capacity, and enhances HDS activities of the Mo catalyst. Similarly, research on the $MoO_3/(TiO_2/SiO_2)$ catalyst showed that [15] and [16], the TiO_2-modified silica gel may strengthen interaction of MoO_3 and the carrier, and promote dispersion of MoO_3 on the surface of TiO_2/SiO_2; its monolayer dispersion threshold is enhanced from 0.032 g MoO_3/100 m^2 SiO_2 to 0.044 g MoO_3/100 m^2 (TiO_2/SiO_2), and the increasing scope reaches 37%. The TiO_2 existence is also advantageous to the depth reduction of MoO_3, and the HDS and hydrogenation activities of $MoO_3/(TiO_2/SiO_2)$ catalyst are also higher than that of the MoO_3/SiO_2 catalyst. Obviously, in the Mo catalysts of the hydrogenation refinery, the addition of the promoter in the appropriate amount may improve the surface condition of the Mo catalyst, adjust the monolayer dispersion threshold of MoO_3, and obviously enhance the catalytic performance of supported catalysts.

The research on nickel catalysts for methanation prepared through the impregnation method also found that [17], the addition of promoter MgO or La_2O_3 at the appropriate amount can promote dispersion of NiO on the surface of the carrier of modified γ-Al_2O_3 or η-Al_2O_3 and increase its monolayer dispersion threshold. If MgO and La_2O_3 are first loaded by impregnation on the surface of γ-Al_2O_3 then on NiO, the influence of impregnation order of MgO and La_2O_3 on the dispersion of NiO is observed. Table 2 lists the monolayer dispersion threshold of NiO on the surface of a 0.010 g MgO/0.045 g La_2O_3/g γ-Al_2O_3 carrier by way of different impregnation methods, and compares them with the monolayer dispersion threshold of NiO on the surface of γ-Al_2O_3. The

Table 2 Effect of impregnation order on the monolayer dispersion threshold of NiO

	NiO/γ-Al_2O_3	impregnation order of promoter		
		MgO (before La_2O_3)	La_2O_3 (before MgO)	co-impregnation
S_{BET}(carrier)/(m^2/gcarrier)	236	206	170	158
monolayer dispersion threshold/(g NiO/g carrier)	0.265	0.246	0.270	0.275
monolayer dispersion threshold/(gNiO/100 m^2 carrier)	0.112	0.113	0.151	0.165

result indicated that, as the promoters MgO and La_2O_3 at the appropriate amount were added in different orders of impregnation, the monolayer dispersion threshold of NiO computed according the surface area of the modified carrier increased to various degrees, and the method of co-impregnation by magnesium and lanthanum compounds increased the most. This possibility may be due to the dispersion of NiO, MgO and La_2O_3 on the surface of γ-Al_2O_3, and interactions among them are different when different impregnation methods are used. In addition, the promoters MgO or La_2O_3, added at the appropriate amounts, can also suppress growth of Ni crystals of the reduction state, and comparatively enhance the specific activity and the thermostability of the catalyst.

Obviously, the selection of the type and the additional order of promoters connected with the monolayer dispersion threshold can be instructive for the preparation of new highly effective supported catalysts.

2.3 The monolayer dispersion threshold may be an important parameter for optimizing the proportion of catalyst

From the research on the $MoO_3/(TiO_2/SiO_2)$ catalyst for hydrogenation refinery, the author et al encouragingly found that [16] when the supporting amount of MoO_3 was lower than the monolayer dispersion threshold of MoO_3 on the surface of TiO_2/SiO_2 (0.044 g MoO_3/100 $m^2(TiO_2/SiO_2)$), HDS and hydrogenation activities of the supported catalyst of Mo all increased linearly with the increase in the supporting amount of MoO_3. However, when the supporting amount of MoO_3 was higher than the monolayer dispersion threshold, HDS and the hydrogenation activities of the catalyst nearly stays invariable. This is possible due to the active species mainly being concerned with the monolayer dispersion phase of MoO_3, but generally speaking, the octahedral coordination Mo(O) species are the advanced species of the active phase. Under this experimental condition, the monolayer dispersion threshold of the $MoO_3/(TiO_2/SiO_2)$ catalyst is far lower than calculated value according to the dispersion of a close-packed monolayer model (0.120 g MoO_3/100 $m^2(TiO_2/SiO_2)$); MoO_3 on the surface of TiO_2/SiO_2 presents dispersion of a non-close-packed monolayer. The experiment indicated that the monolayer dispersion threshold of MoO_3 on the surface of TiO_2/SiO_2 was closely connected with HDS and the hydrogenation activities of catalyst. This important result brings us beneficial enlightenment: the monolayer thresholds of the spontaneous dispersion on the surface of carriers may be taken as important parameters for optimizing the proportion of the supported catalyst, and especially have practical significance in the optimization of the proportion of the catalyst with dispersion of a non-close-packed monolayer of the active components on the surface of carrier.

Similarly, in another research on the $MoO_3/(TiO_2/\gamma$-$Al_2O_3)$ catalyst for hydrogenation refinery we also found that [23], only when the supporting amount of MoO_3 was chosen at the mass fraction (ω_{MoO3}) of 0.18 (which is equal to 0.12 g MoO_3/100 m^2 (TiO_2/γ-Al_2O_3)), the supported Mo catalyst can show high HDS and HYD hydrogenation activities. Under the experimental condition, the supporting amount of MoO_3 with high activity was equal to its calculated value according to the dispersion of a close-packed monolayer model (0.12 g MoO_3/100 $m^2(TiO_2/\gamma$-$Al_2O_3)$), that is, the monolayer dispersion threshold of MoO_3. The high activity at the threshold is possibly concerned with the active species mainly MoO_3 of the monolayer dispersion phase; the Mo(O) species at threshold can reach the maximum. The research also indicated that [3], in industrial catalysts of Mo systems for hydrogenation refinery, the supporting amount (ω_{MoO3}) of MoO_3 on the surface of γ-Al_2O_3 generally is chosen as 0.15–0.20, and in this situation the supporting amount of MoO_3 is equal to or slightly lower than the calculated value according to the dispersion of a close-packed monolayer model. This is reasonable to fully display the function of $MoO_{3.}$ It means, for a catalyst with the dispersion of a close-packed monolayer, the monolayer threshold of the spontaneous dispersion on the surface of the carrier may also be taken as an important parameter for optimizing the proportion of the supported catalyst.

In addition, in the research on the activity of reforming the catalyst NiO/γ-Al_2O_3, we similarly found that [22], in experimental conditions under the reaction temperature of 750°C and GHSV of 2500 h^{-1}, if the chosen supporting amount (ω_{NiO}) of NiO was slightly lower than its monolayer dispersion threshold ($\omega_{NiO} = 0.192$, as equal to 0.112 g NiO/100 $m^2\gamma$-Al_2O_3, down to $\omega_{NiO} = 0.140$, equal to 0.077 g NiO/100 $m^2\gamma$-Al_2O_3), as a result, we can obtain the best start-up activities for reforming the catalyst for CH_4 with CO_2 to syngas. In the above experiment, the monolayer dispersion threshold of NiO is obviously lower than the calculated value according to the dispersion of a close-packed monolayer model (0.183 g NiO/100 m^2 γ-Al_2O_3), i.e. NiO on the surface of γ-Al_2O_3 also presents the dispersion of a non-close-packed monolayer. Considering that NiO on the surface of γ-Al_2O_3 exists in the monolayer dispersion phase form, the monolayer dispersion phase NiO reduces to Ni particles, smaller than that from crystal NiO. The Ni of active components possibly exists in the highly dispersed form; the smaller Ni particles can raise the specific activity of the Ni catalyst, strengthen the thermostability of the catalyst, and decrease carbon deposition. Thus, it can be seen that supported catalysts of Ni systems for methane conversion is similar to the Mo catalyst for hydrogenation refinery, and the proportion of the active components of catalysts can be optimized through their monolayer dispersion thresholds.

3 Threshold effect on catalysts

It is generally believed that, for a crystal compound on the surface of the relevant carrier after spontaneous monolayer dispersion, its physicochemical properties are entirely different from its original ones, and the monolayer threshold of spontaneous dispersion on the surface of the carrier can be regarded as the threshold value between the monolayer dispersion form on the surface and the crystalline state subsequently appearing. Therefore, monolayer dispersion thresholds may be related to the mutation values of many physicochemical properties of the supported catalysts, namely, the existence of threshold effect (or threshold phenomenon) of catalysts. Apparently, the above-mentioned maximum values of the catalytic activity of some supported catalysts and the transition point value of the broken line of the XPS peak intensity ratio etc., all correspond to their monolayer dispersion thresholds, and may be regarded as examples of the threshold effect. In order to further expound on the threshold effect, more examples are given as follows:

3.1 Reduction property

An experiment on H_2 reduction indicated that [12] and [17], the monolayer dispersion state NiO of an NiO/γ-Al_2O_3 catalyst was reduced at 450–530°C, but its crystalline phase NiO was actually reduced at 300–400°C. This is possible because the former is more stable in thermodynamics, and it is hard for the Ni particles from reduction to gather into a Ni crystallite. If we choose the appropriate reduction temperature (e.g. 400°C), causing crystalline phase NiO to be completely reduced but the monolayer dispersion condition not, plotting the reduction amount of NiO (crystalline phase) to the total supported amount of NiO, the reduction amount of crystalline phase NiO of the transition point value of the curve will be 0.25 g NiO/g γ-Al_2O_3 (equal to 0.12 g NiO/100 m^2 γ-Al_2O_3), similar to the experimental measurement value of the monolayer dispersion threshold of NiO (0.112 g NiO/100 m^2 γ-Al_2O_3) [17]. The H_2 reduction experiment of the CuO/γ-Al_2O_3 catalyst similarly indicated that [12], the monolayer dispersion state CuO at reduced temperatures (240–400°C) must be higher than crystalline phase CuO at a reduced temperature (180°C), the transition point value of the curve of reduction amount of crystalline phase CuO measured by the isothermal (180°C) H_2 reduction method and the experiment-measured monolayer dispersion threshold of CuO, both are 0.082 g CuO/g γ-Al_2O_3 (equal to 0.040 g CuO/100 m^2 γ-Al_2O_3). The experimental result from isothermal H_2 reduction method indicated that the threshold effect on supported catalysts is obvious, and this method, as one good method, truly determines the monolayer dispersion threshold.

3.2 Adsorption performance

An adsorption experiment of ethylene on the CuCl/γ-Al_2O_3 catalyst indicated that [18], if we can plot the adsorption quantities of ethylene under room temperature and atmospheric pressure with the supported amounts of CuCl and get the curve of adsorption quantity of ethylene. This curve of adsorption quantity has provided the following facts: that the adsorption quantities of ethylene on the CuCl/γ-Al_2O_3 catalyst first increased linearly with the increase of supported amounts of the CuCl; after reaching the maximum value, it dropped. Its maximum value of curve of adsorption quantity exactly corresponds to the monolayer dispersion threshold of CuCl (0.33 g CuCl/g γ-Al_2O_3 or 0.096 g CuCl/100 m^2 γ-Al_2O_3), and it might adsorb ethylene 6.50 mL/g γ-Al_2O_3 (after threshold, the adsorption quantity of ethylene on the unit surface of γ-Al_2O_3 should be a constant). In addition, the experiment also indicated that [18] the molecular proportion of adsorbed ethylene to post-dispersion CuCl may be as high as 0.19 C_2H_4 molecule/Cu^+, and CuCl dispersion on the surface of γ-Al_2O_3 may form the surface π-complex with C_2H_4. It is easy to see that: adsorption only occurs on the CuCl of monolayer dispersion on the surface of γ-Al_2O_3; the monolayer dispersion capacity at monolayer dispersion threshold is the biggest; and the adsorption quantity of ethylene is also the biggest. The experiment on the CuCl/γ-Al_2O_3 catalyst of adsorbing propylene also produced a similar result [18]. Obviously, extreme points of the curve of adsorption quantity on some supported catalysts correspond to their monolayer dispersion threshold, similarly demonstrating the threshold effect on catalysts.

3.3 Surface acidity

The determination of surface acidity of the ZnO/SiO_2 catalyst indicated that [19] the surface acidity of the ZnO/SiO_2 catalyst and the supported amount of ZnO on the silica gel surface have good correlation, and the maximum value of the surface acidity corresponds to the monolayer dispersion threshold. Namely, when the supported amount of ZnO is lower, the surface acidity will increase along with the increase of the supported amount of ZnO, and this will be possible as a result of the monolayer dispersion amount of ZnO on the surface of the silica gel increasing. When the supported amount of ZnO increases to the monolayer dispersion threshold (0.78 g ZnO/g SiO_2 or 0.217 g ZnO/100 m^2 SiO_2), the monolayer dispersion amount of ZnO on the surface of the silica gel may achieve its maximum; while the surface acidity may also achieve its maximum value, the largest acidic quantity is 0.42 mmol/g SiO_2 (equal to 0.23 mmol/g sample or 2.1×10^{-3} mmol/m^2 sample). When the supported amount of ZnO continues increasing, surpassing the monolayer dispersion threshold, part of the ZnO appears in the crystalline phase form, and the monolayer dispersion amount of ZnO on the surface of the silica gel will have no more change. Also, the surface acidity computed according to the unit surface has no more changes. Catalyst systems, such as $MoO_3/\gamma\text{-}Al_2O_3$ and MoO_3/SiO_2, also show the similar change rule in the surface acidity and the threshold effect [19].

3.4 Pore volumes and specific surface area

The threshold effect on catalysts does not lack examples. The determination of pore volumes (V) and specific surface area (S_{BET}) of the $MoO_3/\gamma\text{-}Al_2O_3$ catalyst indicated that [4], if plotted, the pore volumes (V) or the specific surface areas (S_{BET}), which are in accord separately with per g $\gamma\text{-}Al_2O_3$ and the supported amount of MoO_3, the pore volumes (V) and specific surface area (S_{BET}) of $MoO_3/\gamma\text{-}Al_2O_3$ catalyst both drop with the increase in the supported amount of MoO_3. Afterwards, it basically stays invariable; the transition point value of the pore volumes (V) and the specific surface area (S_{BET}) both become constant with the monolayer dispersion threshold of MoO_3, demonstrating the threshold effect on catalysts.

4 Conclusions

The principle of spontaneous monolayer dispersion holds that active components of many supported catalysts will disperse spontaneously onto the surface of the carrier, and relevantly, there exists a monolayer threshold for spontaneous dispersion on the surface of the carrier. The monolayer dispersion threshold could be measured by XRD phase-quantitative extrapolation method, etc. Its variation is related to the structure, properties and interaction between the active components and the relevant carriers. By measuring the monolayer dispersion thresholds, beneficial information about surface structure and dispersion of supported catalysts could be obtained, and the basis for choosing the best preparative processing conditions of the catalysts (including preparation method, calcining temperature, selection of promoters etc) could be provided. The monolayer dispersion threshold could be regarded as an important parameter to optimize the proportion of catalysts. Mutation values of many physicochemical properties, such as the maximum of the catalytic activity of supported catalysts, the transition point of curve of reduction amount of the crystalline phase, etc. all correspond to their monolayer dispersion thresholds, and the threshold effect on catalysts is obvious. Thus it can be seen that measuring monolayer dispersion thresholds and the proposal of an existing threshold effect on supported catalysts not only lay a foundation for widespread application of the principle of spontaneous monolayer dispersion, but also provide a quantitative investigation method for the development of catalysts. Its significance is profound. Concerning this aspect, the work and the experimental technology are still in development.

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