Photocatalytic Oxidation of Methanol Selectivity in the Preparation of the Application of Methylformate

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ABSTRACT: *In order to improve the application performance of methanol selective photochemical oxidation in the preparation of methyl formate, the catalytic performance of different oxides was analyzed. A series of TiO_2 catalysts supported by gold, silver, and copper were synthesized by the method of metal sol deposition. The catalytic properties of different oxides were analyzed. The most appropriate amount of methanol was selected to explore its application in the preparation of metal formate. The effects of temperature, load, space velocity, and other factors on the catalytic properties were explored through experiments. By comparing the catalytic performance of different oxides, it is found that when the oxides are CH_3OH, the prepared CH_3OH/MoO_3-SnO_2 has a better catalytic effect. Therefore, the catalyst with good dispersion and suitable acid-base position is more favorable for the formation of methyl formate and the conversion of methanol.*

KEYWORDS: *Methanol; Methylformate; Selective photochemical catalysis oxidation; Catalyzer.*

INTRODUCTION

Formic acid methyl acetate is the "basic material" for the production of chemical products such as methylamine[1], formic acid, pesticide, acetic acid, and hexanediol, which play an irreplaceable role in the field of industry and agriculture[2,3]. In recent years, the production capacity of methanol, an important raw material for the production of formic acid and vinegar, is seriously over capacity, so the conversion of methanol to formic acid and vinegar has important practical significance[4,5]. It provides a new direction for chemical production and scientific research, and photocatalytic methanol selective formate as a "green" synthesis route has great research value[6].

In the past few decades, the production mode of formic acid and vinegar is usually deamination with methanol directly or indirectly under high temperature and pressure, which will lead to a large amount of waste of energy, multiple by-products, and low selectivity of formic acid and vinegar[7–10]. At low temperatures, the porous nano Au catalyst selectively oxidizes methyl acetate to methyl formate, which shows a good selectivity of methyl formate, which opens a new way for the production of green methyl formate[8,11]. In recent years, the study of methanol photocatalytic synthesis of formic acid and vinegar has attracted the attention of many researchers,

Table 1: Main chemical reagent.

Reagents	PlaceofOrigin	Level
SnCl4·5H2O	GuoyaoGroupChemicalReagentCo.,Ltd.	Analyticallypure
H40N10O41W12·XH2O	GuoyaoGroupChemicalReagentCo.,Ltd.	Analyticallypure
(NH4)6Mo7O24·4H2O	TianjinNo.4ChemicalReagentFactory	Analyticallypure
NH4VO3	Shenyangreagentno2factory	Analyticallypure
Dimethylether	Daliandategastechnologyco.,ltd.	Standardgas
Oxygen	BeijingYananGasTechnologyCo.,Ltd.	Highpurityoxygen
Nitrogen	HarbinQinghuaIndustrialGasCo.,Ltd.	Highpuritynitrogen
Argongas	HarbinQinghuaIndustrialGasCo.,Ltd.	Highpurityargon

Table 2: Main instruments.

Main instruments	Manufacturers
Shimadzu GC-14C Gas Chromatography	Shimadzu, ltd
GCD-500 Ghighpurity Hydrogen Generator	BeijingJiaweikechuangTechnologyCo., Ltd.
HYG-30 Air Source Generator	ZiboHongrunIndustryandTradeCo., Ltd.
Fixed Bed Flow Reactor	Self-Chambering
CKW1100 Temperature Controller	BeijingDynastySelf-Indulgence
769YP-24B Powder Tablet Press	Tianjin Keqi High-tech Company
Rotameter	ZhejiangYuyao Co., Ltd.
SHB-III Circulating Watery Multipurpose Vacuum Pump	Zhengzhou Changcheng Science, Industry and Trade Co., Ltd.
Electric Heating Constant Temperature Water Bath Pot	Beijing Huabo United Medical Devices Co., Ltd.
Tubular Resistance Furnace	LongkouYuanbang Electric Furnace Manufacturing Co., Ltd.
SX2-5-12 Box Resistance Furnace	Tianjin Zhonghuan Experimental Electric Furnace Co., Ltd
JJ-1 Precision Booster Electric Stirrer	Changzhou Guohua Electric Appliance Co., Ltd
AR1530 Electronic Balance	Ohus Trading (Shanghai Co., Ltd.)
DHG-9070A Type Tune Hot Drum Box	Shanghai Hengke Co., Ltd

because this reaction is carried out at room temperature and has a high yield of formic acid and vinegar[12,13]. As early as 1985, it has been reported that methanol is oxidized with MoO_3/TiO_2 and TiO_2 as photocatalysts[14]. Methyl formate vinegar is one of many products. In 2010, this reaction was studied on anatase-type TiO_2, but TiO_2 showed a very low MF production rate and produced many by-products at room temperature. Under the irradiation of an ultraviolet lamp, TiO_2 was used as the support to support Au, Ag, Au-Ag alloy, and Cu nanoparticles as photocatalysts[15], and methanol was used to synthesize formic acid and vinegar under the reaction temperature of 25℃~ 45℃ in gas phase. It was found that CuO/TiO_2 was reduced to Cu/TiO_2 under light, and the production rate of formic acid methyl acetate reached 56.4mmol/L, which is the most active catalyst in the world[16].

In this research, a methanol selective photocatalyst was prepared and the catalytic properties of different oxides were analyzed. The catalysts were characterized by XRD, NH_3-TPD, CO_2-tpd, and Raman methods. Finally, the effects of CH_3OH content, reaction conditions, loading, air velocity, and different reaction time on the catalytic performance of CH_3OH / MoO_3-SnO_2 were studied.

EXPERIMENTAL SECTION
Reagents and instruments
Reagent preparation
The chemical reagents used in this experiment are shown in Table 1.

Instrument preparation
The main instruments used in the experiment are shown in Table 2.

Table 3: Reagent content for preparation of Au/TiO$_2$.

Catalysts	1% Au/TiO$_2$	3% Au/TiO$_2$	5% Au/TiO$_2$	7% Au/TiO$_2$
HAuC$_{14}$(mL)	2.500	7.500	12.50	17.5
P25(g)	0.2000	0.2000	0.2000	0.2000
H$_2$O(mL)	25	75	125	175
NaBH$_4$(g)	0.0057	0.0171	0.0285	0.0399
Au/Ti(%)	1	3	5	7

Table 4: Reagent content for the preparation of Ag/TiO$_2$.

Catalysts	1% Au/TiO$_2$	3% Au/TiO$_2$	5% Au/TiO$_2$	7% Au/TiO$_2$
AgNO$_3$(mL)	2.500	7.500	12.50	17.50
P25(g)	0.2000	0.2000	0.2000	0.2000
H$_2$O(mL)	25	75	125	175
NaBH$_4$(g)	0.0057	0.0171	0.0285	0.0399
Ag/Ti(%)	1	3	5	7

Table 5: Reagent content for the preparation of Cu/TiO$_2$.

Catalysts	1% Au/TiO$_2$	3% Au/TiO$_2$	5% Au/TiO$_2$	7% Au/TiO$_2$
Cu(NO$_3$)$_2$(mL)	2.500	7.500	12.50	17.50
P25(g)	0.2000	0.2000	0.2000	0.2000
H$_2$O(mL)	25	75	125	175
NaBH$_4$(g)	0.0029	0.0057	0.0142	0.0199
Cu/Ti(%)	1	3	5	7

Application of selective photocatalytic oxidation of methanol

Preparation of methanol selective photocatalyst

In this experiment, a series of TiO$_2$ catalysts supported by gold, silver, and copper were synthesized by the method of metal sol deposition. The method of metal sol deposition is using metal alkoxide as a precursor, the material is obtained by hydrolysis polycondensation, aging, and drying. The specific method is as follows: dissolve 0.2g of P25 in a certain amount of deionized water in a 500mL volumetric flask, ultrasonic dispersion for about 25min, take it out and stir it in an ice bath for about 30min. Add a certain amount of metal ion solution (HAuCl$_4$, AgNO$_3$, Cu(NO$_3$)$_2$) into the above solution drop by drop, and continue to stir for 30min. After mixing, add a certain proportion of NaBH$_4$ (different metals corresponding to different proportions), mix in an ice bath for 3h, and continue to mix at room temperature. After mixing, the mother liquor is centrifuged and washed many times. After drying at 60℃ for a period of time, the catalyst Au/TiO$_2$, Ag/TiO$_2$, and Cu/TiO$_2$ were prepared by taking it out and grinding. Table 3, Table 4, and Table 5 respectively show the reagent content used to prepare Au/TiO$_2$, Ag/TiO$_2$, and Cu/TiO$_2$ catalysts with different loading.

Catalytic performance of different oxides

CH3OH/MoO$_3$-SnO$_2$, V$_2$O$_5$/MoO$_3$-SnO$_2$, and Al$_2$O$_3$/MoO$_3$-SnO$_2$ were used as catalysts. The selected conditions are as follows: the molar ratio of methanol to oxygen is 1, the reaction temperature is 150℃, the volume airspeed is 600km/h, and the loading amount of catalyst is 3mL. Under the same conditions for the three catalysts, the methanol conversion rate and the selectivity of methyl formate for the reaction of methanol and oxygen are obtained, as shown in Table 6.

Table 6: Effect of different oxides on catalytic reaction.

Catalyzer	CH_3OH/MoO_3-SnO_2	V_2O_5/MoO_3-SnO_2	Al_2O_3/MoO_3-SnO_2
ConversionofDimethylether(%)	92.2	81.3	83.7
MFselectivity(%)	57.1	0.2	59.9
DMMselectivity(%)	18.3	60.3	1.9
Dimethyletherselectivity(%)	3.2	0.7	1.0
Formaldehydeselectivity(%)	21.3	38.8	37.1

MF: Methyl formate ; DMM : Dipropyleneglycol dimethyl ether

It can be seen from the data in Table 6 that when the catalyst is CH_3OH / MoO_3-SnO_2, the conversion of methanol and the selectivity of methyl formate are very high. When the catalyst is Al_2O_3 / MoO_3-SnO_2, the conversion of methanol and the selectivity of methyl formate are also very high, which shows that methylaluminum has a high application value. When the catalyst is V_2O_5/MoO_3-SnO_2, and the conversion of alcohol and the selectivity of methyl formate are significantly lower than the other two catalysts. When CH_3OH/MoO_3-SnO_2 was used, the selectivity of formaldehyde was significantly lower than the other two catalysts. Therefore, CH_3OH/MoO_3-SnO_2 in the three catalysts has a certain research value. It is necessary to find the most suitable CH_3OH for the oxidation reaction. Therefore, CH_3OH / MoO_3-SnO_2 was characterized as follows to explore the application of metal formate preparation.

Characterization of methanol selective oxidant
XRD of different catalysts

Fig. 1 is the X-ray diffraction pattern of CH_3OH series catalysts with different contents. As we all know, the width of the X-ray diffraction peak reflects the crystallinity of the sample. Figure 1 is the XRD pattern between $2\theta = 5\sim70°$.

It can be seen from Figure 1 that in the catalyst with different CH_3OH content, the characteristic diffraction peaks of MoO_3 appear at $2\theta = 38°$, but the peaks are wide (the characteristic wide diffraction peaks of MoO3 appear at $2\theta = 38°$). At $2\theta = 34°$, $62°$, and $66°$ $67°$, the (101) and (211) diffraction peaks of SnO_2 crystals with tetragonal rutile structure appear (JCPDSNo.41-1445). At $2\theta = 25.2°$ and $52°$, there are suspected TiO_2 diffraction peaks[17]. From the spectrum, we can see that the peak width of the diffraction peak is larger, which shows that SnO_2 is highly dispersed in the catalyst system. When the dosage is 3.5%, the catalyst has the highest activity. When the content of
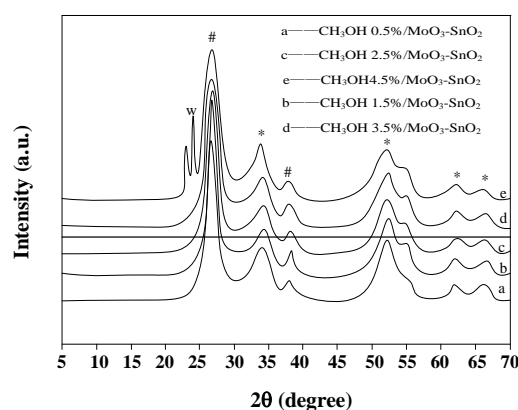

Fig. 1: XRD spectrum of catalysts

CH_3OH increased to 4.5%, there was an obvious diffraction peak of CH_3OH crystal phase at $2\theta = 23\sim24°$, which indicated that the higher the content of CH_3OH is, the stronger the diffraction peak of the crystal phase is. This may be due to too much CH_3OH, which leads to agglomeration on the surface of the catalyst and hinders the dispersion of tungsten species in the catalyst system, and results in a decrease in catalyst activity. This is consistent with the data obtained from the experimental results. It can be seen that the high dispersion of CH_3OH in the catalyst system is the main reason for the high activity of the catalyst.

NH₃-TPDof different catalysts

In the NH3-TPD spectrum, the NH3 desorption peaks are is usually located between divided into low 180 and 400°C temperature ranges. (<180℃) and high-temperature range (>400℃) according to the temperature position of the desorption peak. In order to study the relationship between the surface acidity and the addition of CH_3OH, we characterized the catalysts by NH_3-TPD and CO_2-TPD. Fig. 2 shows the NH_3-TPD spectrum of the catalyst with different CH_3OH content.
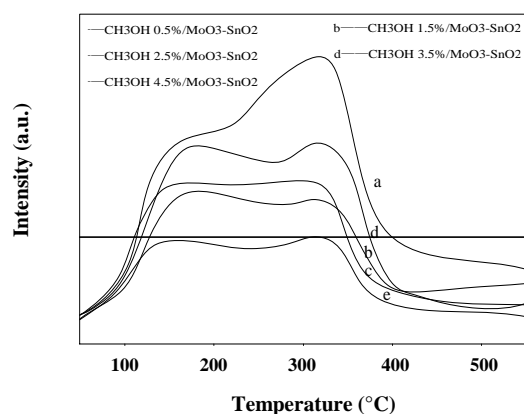
Fig. 2: NH3-TPD spectrum of catalysts.

Fig. 3: CO2-TPD spectrum of catalysts.

From the figure, we can see that there are two NH_3 desorption peaks in the acid center of all catalysts, which indicates that there are two acid center active sites, i.e. weak acid active site near 160℃ and a medium-strong acid active site near 320℃ (The acid content is 0.628mmol/g) [18]. When the CH_3OH content is different, the catalyst shows different acidic sites. When the content of CH_3OH is 0.5%, the catalyst shows the most strong acid sites. With the increase of CH_3OH content, the peak area of weak acid sites decreased gradually, which indicated that with the increase of CH_3OH content, the number of weak acid sites decreased, and the active center of medium-strong acid decreased with the increase of CH_3OH. This shows that CH_3OH affects the amount of acid on the catalyst surface. With the increase of CH_3OH content, the dispersion of CH_3OH metal particles on the catalyst surface changed. Although the amount of acid on the catalyst surface can be detected by NH_3 molecules with a small molecular volume, for the selective photocatalytic oxidation of methanol, because the molecular diameter of the involved raw materials and products is large, which limits the molecular dynamic diffusion, not all the acid centers can become effective active sites. Therefore, when the loading of CH_3OH reaches 3.5%, the dispersion degree of catalyst surface and the degree of interaction with MoO_3-SnO_2 just become the most suitable condition for catalyst activity.

CO₂-TPD of different catalysts

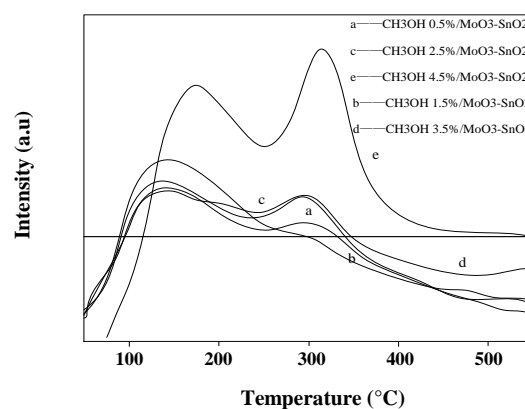Fig.3 shows the CO_2-TPD spectrum of the catalyst with different content CH_3OH.

It can be seen from the figure that there are almost two desorption peaks of CO_2 in the alkali center of all catalysts, which shows that there are two alkali center active sites of the catalyst, i.e. weak alkali active site near 150℃ and medium-strong alkali active site near 310℃. When the CH_3OH content is different, the catalyst shows different basic sites. When the content of CH_3OH is 4.5%, the catalyst shows the weakest base sites and medium-strong base sites. With the change of CH_3OH content, the peak displacement of weak base sites gradually moves in the direction of low temperature, while the peak position of medium-strong base sites hardly changes. However, when the content of CH_3OH is 1.5%, there is almost no strong alkaline site on the surface of the catalyst, which may be due to the interaction between CH_3OH and the catalyst, resulting in almost complete adsorption of CO_2 at low temperatures. According to the experimental data, when the content of CH_3OH is 3.5%, it has the most suitable acidity and basicity for methanol oxidation. In the catalytic oxidation of methanol, used the catalyst used should have both acidic and alkaline active sites with (The acid content is 0.628 and mmol/g, The amount of alkali is 0.678 mmol/g contents. The characterization shows that the acidity and basicity of the catalyst system are suitable for the catalytic oxidation of methanol.

Raman of different catalysts

Raman spectrum is a kind of molecular vibration spectrum, which can provide information on adsorbed species on the surface of catalyst at the molecular level. Fig. 4 is the Raman spectrum of CH_3OH series catalysts with different contents added.
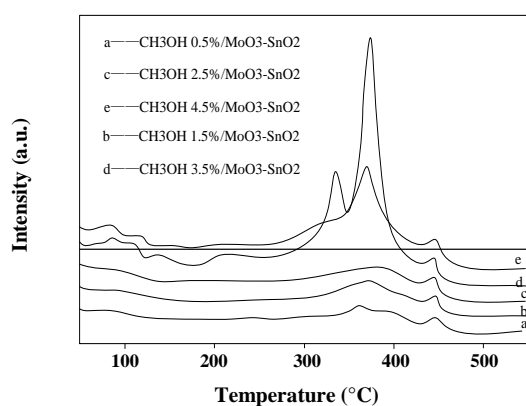
Fig. 4: Ramam spectrum of catalysts.

It can be seen from the figure that the strength increases with the increase of CH_3OH content. However, when the CH_3OH content is 3.5%, the strength at the peak height is higher than that at the CH_3OH content of 4.5%, indicating that MoO_3 content is the highest. Because the properties of MoO_3 crystal are mainly determined by the Tensile vibration of Mo = 0 at 993 cm^{-1}, it shows that MoO_3 crystal exists in the catalyst system. With the increase in temperature, the strength of CH_3O with the content of 0.5%, 1.5%, and 2.5% had no significant increase or decrease. However, the strength of CH_3OH with 3.5% and 4.5% contents increased obviously from 300℃ to 400℃, which may be due to the interaction between CH_3OH and MoO_3. In this spectrum, there is no characteristic Raman peak of SnO_2, which may be because SnO_2 does not enter the metal oxide lattice, so there is no stretching vibration peak of Sn = 0, but only exists on the catalyst surface. This is consistent with XRD results. In this spectrum, the characteristic Raman peak of CH_3OH was not detected. This is because CH_3OH crystal is highly dispersed in the system, which is consistent with the conclusion of high catalyst activity in this chapter.

RESULTS AND DISCUSSION
Effect of CH_3OH content on the catalytic performance of CH_3OH / MoO_3-SnO_2

Fig. 7 shows the effect of CH3OH content on the catalytic performance of CH3OH / MoO3-SnO2.

It can be seen from Table 7 that when the content of CH_3OH is 3.5%, the selectivity of methyl formate is the highest, reaching 57.08%, and the selectivity of by-product methanol and formaldehyde is relatively low. The results show that methanol is beneficial to the reaction of oxygen and the formation of methyl formate at low temperatures. At this time, the conversion of methanol is also very high. With the increase in temperature, the conversion of methanol remained stable, but the selectivity of methyl formate decreased significantly. The conversion of methanol and the selectivity of methyl formate increased first and then decreased with the increase of the amount of dressing. As the experimental airspeed continues to increase from 600 km/h, the selectivity of the metal format increases first and then decreases with the increase of airspeed. The results show that CH_3OH/MoO_3-SnO_2 catalyst has the best catalytic performance for the reaction of methanol and oxygen when the molar ratio of methanol to oxygen is 1, the reaction temperature is 150℃, catalyst loading is 3mL and the volume of airspeed is 600km/h. This is the best reaction condition for the reaction of methanol and oxygen.
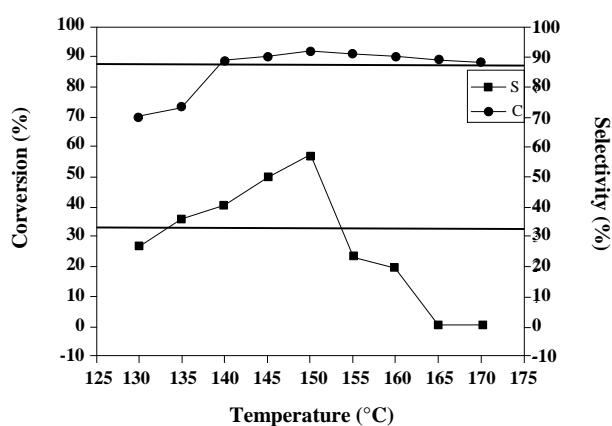
Effect of reaction conditions on the catalytic performance of CH_3OH/MoO_3-SnO_2
Effect of temperature

When the molar ratio of methanol to oxygen is 1, the loading amount of catalyst is 3mL, and the volume air speed is 600h^{-1}, the performance of the catalyst in the reaction of methanol and oxygen is investigated at different temperatures (130℃-170℃). The conversion of methanol in the reaction and the selectivity of the product change with the temperature. According to the results of previous experiments, Cox COx will be produced when the temperature of methanol and oxygen is high. It affects the selectivity of the main product, so the reaction of methanol and oxygen starts at a low temperature. When the reaction temperature rises from 130℃ to 150℃, the conversion of methanol increases rapidly, which is due to the molecular fracture of methanol and the decomposition of CH_3OCH_2*, H, CH_3O*, and CH_3*. When the temperature rises to 150℃, the groups gather, methanol is oxidized to formaldehyde, and formaldehyde continues to form methyl formate. As the reaction temperature continues to rise, when the temperature is higher than 150℃, the conversion of methanol begins to decline, but the decline is not very large. The selectivity of methyl formate decreased rapidly, and the selectivity of by-products formaldehyde and methanol began to increase. This may be due to the fact that the dimerization between

Table 7: Effect of CH₃OH content on the catalytic performance of CH₃OH / MoO₃-SnO₂ .

Catalyzer	Twomethylethertransfer Conversionrate(%)	MFselectivity (%)	DMMselection (%)	Methanolselection (%)	Formaldehydeselection (%)
CH₃OH/MoO₃-SnO₂(0.5%)	89.4	4.8	10.5	5.5	79.3
CH₃OH/MoO₃-SnO₂(1.5%)	91.3	38.8	1.3	0.6	59.3
CH₃OH/MoO3-SnO₂(2.5%)	92.1	48.6	3.5	1.5	46.45
CH₃OH/MoO₃-SnO₂(3.5%)	92.2	57.1	18.3	3.2	21.3
CH₃OH/MoO₃-SnO₂(4.5%)	93.6	23.5	1.5	1.9	73.1

Fig. 5: Effect of reaction temperature on the catalytic performance of the catalyst.

groups no longer occur after the temperature rise but exist in the form of intermediate products. Therefore, the conversion of methanol and the selectivity of methyl formate are the highest at 150℃. The effect of reaction temperature on the catalytic performance of the catalyst is shown in Fig. 5.

It can be seen from Fig. 5 that the selectivity of the metal format first increases with the increase of temperature, reaches the maximum value at 150℃, and then decreases with the increase of temperature. However, the selectivity of by-products methanol and formaldehyde was first increased and then decreased with the increase of temperature. The results show that the reaction of methanol and oxygen is easier to synthesize methyl formate at a lower temperature, while the reaction is easier to synthesize by-products such as methanol and methylal at a higher temperature. According to the experimental results, when the temperature is 150℃, the conversion of methanol and the selectivity of methyl formate are the highest, so 150℃ is the most suitable temperature for the reaction of methanol and oxygen.

Effect of loading amount on the catalytic performance of CH₃OH/MoO3-SnO₂

The conversion rate of methanol and the selectivity of the product vary with the amount of loading when he molar ratio of methanol to oxygen is 1, the reaction temperature is 150℃, and the volume air speed is 600h⁻¹. It can be seen from the figure that with the increase in the filling volume, the conversion rate of methanol starts to rise. This is because the increase of catalyst volume increases the surface area of the catalyst and the contact area of feed gas methanol and oxygen with the catalyst so that the conversion rate of methanol increases. It can also be seen from the figure that when the catalyst loading is more than 3mL, the conversion of methanol begins to decline. When the load increases, the selectivity of the catalyst increases, reaches the maximum when the load is 3mL, and then decreases, indicating that as the load increases, the hydrogenation capacity of the catalyst gradually increases. When the load reaches a certain level When the degree is higher, it will promote the formation of deep hydrogenation products, thereby reducing the selectivity of methyl formate [19]. According to the above results, the conversion of methanol and the selectivity of methyl formate are the highest when the loading amount is 3mL, so 3mL is the best catalyst volume. The effect of loading capacity on catalytic performance is shown in Fig. 6.

According to the above results, the optimum catalyst volume is 3mL when the reaction temperature is 150℃, the molar ratio of methanol to oxygen is 1, and the volume air speed is 600h⁻¹.

Effect of airspeed on the catalytic performance of CH₃OH/MoO₃-SnO₂

The variation of selectivity with airspeed is shown in the figure. When the airspeed changes, the reaction of
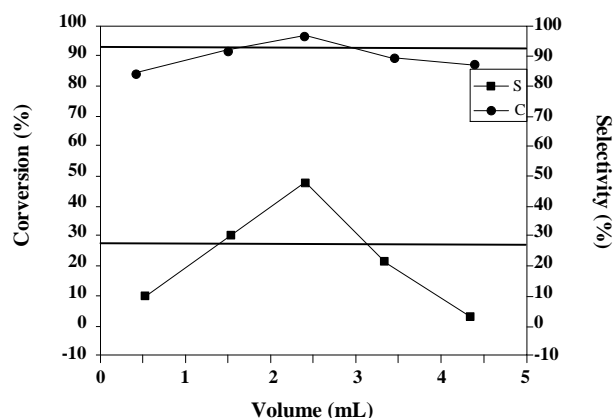
Fig. 6: Effect of loading capacity on Catalytic Performance.

Fig. 7: Effect of airspeed on catalytic performance.

methanol with oxygen is also affected. When the airspeed is $360h^{-1}$, the conversion rate of methanol is low, which may be due to the fact that the airspeed is small, the flow rate of methanol and oxygen is small, and the resistance of outward diffusion is large, so the conversion rate of methanol is low. With the increase of airspeed, the resistance of material diffusion decreases, and the conversion of methanol increases. With the increase in airspeed, the conversion rate of methanol is basically the same. This is because when the amount of catalyst is fixed, the surface area provided by the catalyst is certain, and the number of active centers of the catalyst is certain, so when airspeed continues to increase, the conversion rate of methanol will not continue to increase. The variation of selectivity with airspeed is shown in Fig. 7.

In terms of product selectivity, the selectivity of methylate and methylal first increased and then decreased with the increase of airspeed. When the airspeed was $600h^{-1}$, the total selectivity of methylate and methylal was the highest, about 71.2%. When the airspeed is more than $600h^{-1}$, the selectivity of the target product begins to decline. This may be because there are too many reactants when the airspeed is too large, and a large number of intermediate products are obtained by side reactions, which hinders the formation of the metal format so that the selectivity of the target product decreases. According to the conversion of methanol and the total selectivity of methylate and methylal, $600h^{-1}$ was selected as the best condition of airspeed.

According to the experimental results, in order to make full use of feed gas without waste and achieve optimal conversion efficiency, when the airspeed is $600h^{-1}$, the conversion of methanol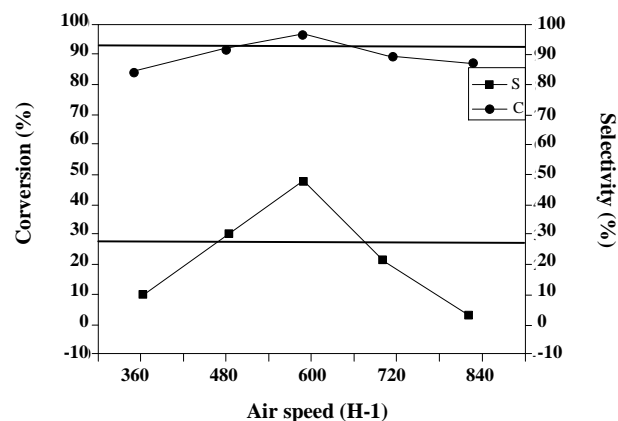 and the selectivity of methyl formate are the highest. Therefore, $600h^{-1}$ was chosen as the optimal volume of airspeed for the catalytic oxidation of methanol and oxygen.

Effect of different reaction times on the catalytic performance of CH_3OH/MoO_3-SnO_2

The effect of reaction time on the catalytic performance of CH_3OH/MoO_3-SnO_2 under the same conditions (molar ratio of methanol to oxygen is 1, the reaction temperature is 150℃, catalyst dosage is 3ml and volume airspeed is $600h^{-1}$). The conversion of methanol and the selectivity of the product with time are shown in the figure. The conversion rate of methanol did not change much with time, which was about 90%, while the selectivity of methyl formate was lower in 1h. With the increase of time, the selectivity increased gradually and reached the maximum at 3h, which was about 57%. With the increase in time, the selectivity of methyl formate remained basically unchanged. When the reaction went on to the 6th hour, it was found that the selectivity of methyl formate decreased significantly, while when the reaction went on to the 10th hour, the selectivity of methyl formate was only about 39%. This shows that the stability of CH_3OH/MoO_3-SnO_2 for methanol oxidation remains to be improved. The effect of reaction time on catalytic performance is shown in Fig. 8.

The results showed that CH_3OH/MoO_3-SnO_2 had the best catalytic activity for methanol and oxygen in the third hour. At this time, the selectivity of methyl formate is about 57%, but with time going on, the activity of the catalyst decreases, which shows that the stability of the catalyst is not as good as expected, so in the fourth chapter, the catalyst is modified to improve the stability.
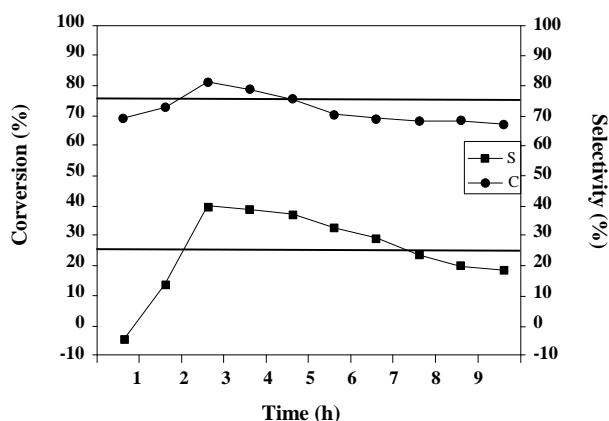
Fig. 8: Effect of reaction time on Catalytic Performance.

In this paper, by comparing the catalytic performance of different oxides, it is found that when the oxide is MoO_3-SnO_2, the prepared CH_3OH/MoO_3-SnO_2 has a better catalytic effect. Therefore, a series of CH_3OHx/MoO_3-SnO_2 (x = 0.5, 1.5, 2.5, 3.5, 4.5wt%) catalysts were prepared, and the most appropriate amount of catalyst was explored. Methanol is oxidized to form methyl formate. When the amount of CH_3OH was 3.5%, the catalyst showed the best activity. The conversion of methanol increased with the increase of CH_3OH, but the selectivity of methyl formate increased first and then decreased with the increase of CH_3OH. This may be because the acidity and basicity of the catalyst are not suitable for the reaction when the content of CH_3OH is too much. When the amount of CH_3OH is 3.5%, the yield of methyl formate is the highest and the activity of the catalyst is the best. At this time, the conversion of methanol is 92.2%, and the selectivity of methyl formate is 57.1%.

CONCLUSIONS

Through the characterization and analysis of methanol selective oxidant, it can be seen that: The high dispersion of CH_3OH in the catalyst system is the main reason for the high activity of the catalyst; When the loading of CH_3OH reaches 3.5%, the dispersion degree of the catalyst surface and the degree of interaction with MoO_3-SnO_2 just becomes the most suitable condition for catalyst activity; The pH value of the catalyst system is suitable for the catalytic oxidation of methanol.

When the content of CH_3OH was 3.5%, CH_3OH dispersed well in the catalyst system. Therefore, the catalyst with a better dispersing degree and suitable acid-base position is more conducive to the formation of methyl formate and the conversion of methanol.

The test results of reaction time show that the stability of the catalyst is not ideal. As the reaction time goes on, the metal oxide surfaces in contact with each other, the surface area and pore structure will be destroyed, and the activity of the catalyst will be reduced. This reduces the active sites needed for methanol dimerization. When the reaction time was more than 6 hours, the selectivity of methyl formate began to decrease obviously, but the conversion of methanol remained stable with the increase in reaction time. After 3 hours of reaction, the conversion of methanol reached 92.2%, and the selectivity of methyl formate reached 57.1%. Therefore, attention should be paid to the stability of the catalyst in future research.

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