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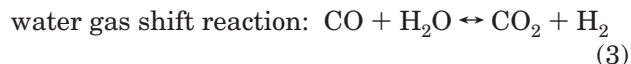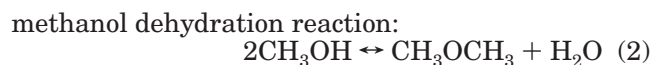# KINETICS, CATALYSIS, AND REACTION ENGINEERING

Effect of Particle Size on the Hybrid Catalyst Activity for Slurry Phase Dimethyl Ether Synthesis

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The hybrid catalyst prepared by physically mixing a commercial methanol synthesis catalyst and a solid acid dehydration catalyst was used for slurry phase dimethyl ether synthesis from syngas. It was found that the addition of dehydration catalyst resulted in a significant synergic effect on the overall syngas conversion. But, the excessive addition of dehydration catalyst could not enhance the synergic effect but instead depressed the whole reaction rate. It was also proven that this phenomenon existed when the methanol catalyst was used for low temperature water gas shift reaction. When the fine powder in hybrid catalyst was sieved away, the special phenomenon disappears and the conversion profile is the same with that in gas phase. It is proved that the presence of the fine and superfine powder could be a primary cause resulting in low catalyst activity. The better activity and stability of the hybrid catalyst can be realized by carefully choosing the catalyst particle size and improving the catalyst strength.

Introduction

The one-step synthesis of dimethyl ether (DME) from synthesis gas (syngas) has received growing attention due to its potential as an alternative clean fuel.[1−4] This process consists of two steps, methanol synthesis followed by methanol dehydration, which employs the hybrid catalyst prepared by physically mixing a commercial methanol catalyst and a solid acid dehydration catalyst. There are three reactions in the dimethyl ether synthesis process, namely

methanol synthesis reaction: $CO + 2H_2 \leftrightarrow CH_3OH$ (1)

methanol dehydration reaction:
$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad (2)$$

water gas shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$ (3)

where reactions 1 and 3 are catalyzed by methanol synthesis catalyst (MSC), and reaction 2 is catalyzed by methanol dehydration catalyst (MDC). Driven from reaction 2, which continuously removes methanol from the reaction system, reaction 1 can proceed more completely. Because water produced in reaction 2 can react with CO in syngas by reaction 3, both reaction 2 and reaction 1 can be promoted directly or indirectly.

These synergic effects of reaction−reaction result in high once-through conversion of syngas and low cost of DME production.[5−6]

The ratio of MSC to MDC is one of the important factors which affect the overall reaction rate. The study on the catalyst ratio has not been conducted in detail up to now. The previous studies investigate the catalyst ratio at limited range.[7−9] This paper reports the experiments conducted in a wider ratio range of the two catalysts and findings on the special phenomenon which have not been noted yet.

Experimental Section

The commercial C301 methanol synthesis catalyst (Cu/ZnO/Al$_2$O$_3$) supplied by Taiyuan Chemical Fertilizer Plant, Shanxi Province, China, and γ-A l$_2$O$_3$ from Shanghai Hengye Chemical Engineering Co., Ltd., were used in all experiments. Before loading, two kinds of catalysts needed to be ground and sieved to a certain particle size, and then, the methanol synthesis catalyst was dried at 110 °C for 3 h and γ-Al$_2$O$_3$ was pretreated by calcination at 500 °C for 4 h.

The experiments of slurry phase dimethyl ether synthesis were carried out with a 250 mL well agitated slurry autoclave reactor. The slurry volume was adjusted to 81 mL after two catalysts were slurred in the paraffin solvent. The catalyst was activated in situ by using 5% H$_2$ diluted with N$_2$ at 260 °C approached at a given programmed temperature rising rate for 16 h. After activation, the synthesis reaction began to proceed by switching reduction gas to syngas, which was measured and controlled by a high-pressure mass flow meter, Brooks 5850E. The analysis of the effluent stream was performed by two on-line gas
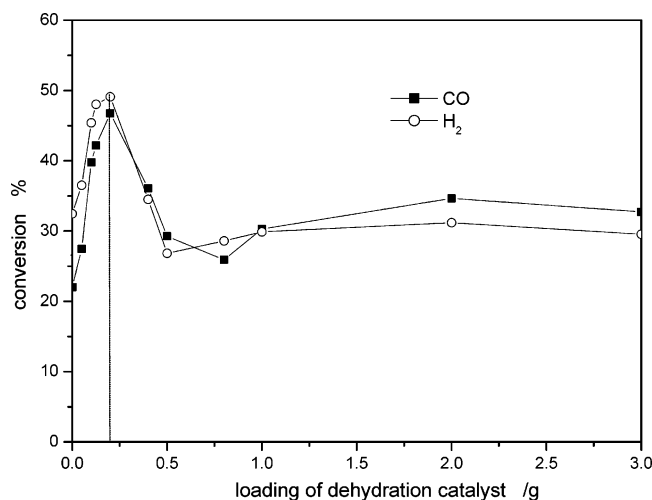
Figure 1. Effect of the loading of methanol dehydration catalyst on CO and H_2 conversion. Conditions: 250 mL CSTR; 5 MPa; 260 °C; 10000 h^{-1} for 4 g of MSC; H_2/CO = 1:1; 1000 rpm.

chromatograms equipped with TCD and FID. The sampling was done at 2 h after the beginning of the reaction.

Results and Discussion

As the general understanding, to eliminate the possible inner diffusion control and improve the efficiency of the catalyst utilization, the catalyst particle in slurry phase reaction should be made as small as possible.[10] Therefore, the catalyst particles less than 200 mesh (0.076 mm) were used for slurry phase dimethyl ether synthesis reaction. The loadings of methanol synthesis catalyst were fixed at 4 g, and the loadings of methanol dehydration catalyst were 0, 0.05, 0.1, 0.125, 0.2, 0.4, 0.5, 0.8, 1.0, 2.0, and 3.0 g in turn. The GHSV of the feedstock based on methanol synthesis catalyst maintained 10000 h^{-1}. The ratio of CO to hydrogen in syngas is 1.0. The reaction conditions except the loading of MDC were the same in the experiments. The results of experiments are illustrated in Figures 1, 2, and 3.

The conversion profiles of CO and H_2 are shown in Figure 1. Because the high temperature is unfavorable for the exothermic methanol synthesis on thermodynamics, the conversion is not high in slurry phase methanol synthesis (the loading of dehydration catalyst is zero). When a small amount of dehydration catalyst is added into the system, CO conversion increases significantly due to the synergic effect between methanol synthesis reaction and methanol dehydration reaction. The conversions of CO and H_2 reach their maxima at 0.2 g of dehydration catalyst, where the weight ratio of MSC to MDC is 20:1. It is worthy to note that the conversions of CO and H_2 decrease rapidly when the loadings of the dehydration catalyst are larger than 0.2 g, and then rise gradually after the depressive trend becomes inconspicuous. This result cannot be explained by the general concept.[8]

Unlike the conversions of CO and H_2, the profiles of oxygenate selectivity with loading of dehydration catalyst follow an ordinary rule (see Figure 2). In the methanol synthesis process, the methanol selectivity nears 90%. When the loading of dehydration catalyst is less than 0.2 g, the curve of dimethyl ether selectivity has a leap and CO_2 selectivity increases obviously. And when methanol loading of the dehydration catalyst
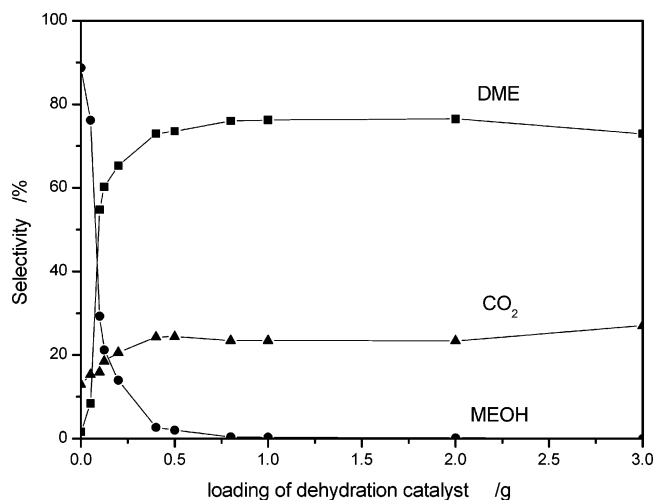

Figure 2. Effect of the loading of methanol dehydration catalyst on product selectivity. Conditions: 250 mL CSTR; 5 MPa; 260 °C; 10000 h^{-1} for 4 g of MSC; H_2/CO = 1:1; 1000 rpm.
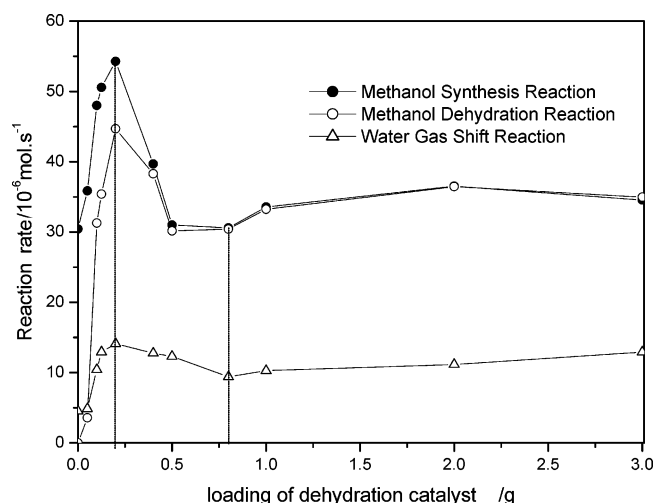

Figure 3. Effect of the loading of methanol dehydration catalyst on the rates of three reactions. Conditions: 250 mL CSTR; 5 MPa; 260 °C; 10000 h^{-1} for 4 g of MSC; H_2/CO = 1:1; 1000 rpm.

exceeds 0.5 g, the ascending trend becomes gentle. Under the condition that the dehydration catalyst loading is larger than 1 g, the product selectivity does not change with the increase of the dehydration catalyst and the selectivity of methanol almost nears to zero.

The changes of three reaction rates, CO hydrogenation to methanol, methanol dehydration, and water gas shift reaction, with the dehydration catalyst loading are given in Figure 3. As can be seen, the rate of methanol synthesis reaction is very low in the slurry phase methanol synthesis, and a small amount of CO_2 is formed during reaction. After a small amount of dehydration catalyst is added, the rates of three reactions increase significantly. When the loading of dehydration catalyst arrives at 0.2 g, the rates reach their maxima. With the rightward move of the loading of dehydration catalyst, the rates of methanol synthesis reaction and methanol dehydration reaction reduce abruptly. The two rate curves of methanol synthesis reaction and methanol dehydration reaction start to overlap when the loading of dehydration catalyst is lager than 0.5 g. It indicates that methanol produced from methanol synthesis reaction is almost entirely converted to dimethyl ether. The lack of methanol synthesis catalyst relative
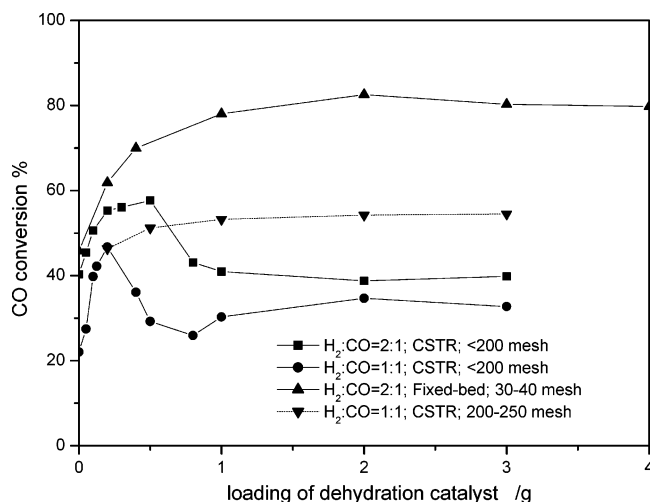
Figure 4. The collective comparison of H_2/CO ratios and particle size of catalyst at different loadings of dehydration catalyst in gas and slurry phase. Conditions: 250 mL CSTR; 5 MPa; 260 °C; 10000 h^{-1} for 4 g of MSC; H_2/CO =1:1 or 2:1; 1000 rpm. Fixed bed: 5 MPa; 260 °C; 10000 h^{-1} for 4 g of MSC; H_2/CO =2:1.

Figure 5. The sketch map of the collision process between MSC-(S) and MDC(D) in slurry phase dimethyl ether synthesis: (a) <200 mesh, (b) 200−250 mesh.

to dehydration catalyst becomes a bottleneck of overall reaction rate.

In the experiments of adding dehydration catalyst, there exist the maxima of conversions and the reaction rates of three reactions at the experimental range. In other words, the excessive dehydration catalyst reduces apparently the activity of methanol synthesis catalyst. What leads to the decrease of the activity of methanol synthesis catalyst in the presence of the excessive dehydration catalyst? How does the ratio of H_2 to CO affect the phenomenon? Is there also this phenomenon in gas-phase synthesis process? To solve these puzzles, the corresponding contrastive experiments were designed as follows.

The experiments employing H_2 rich syngas (H_2/CO = 2) were conducted in the same reactor. The conversion profile is shown in Figure 4. It is clear that the change of the ratio of H_2 to CO does not influence the trend presented in the 1H_2/1CO syngas except that the location where the maximum appears has a rightward move.

Another contrastive experiment was conducted in the gas phase, using the flow type fixed bed reactor (φ = 13 mm). The particle size of the two catalysts ranged from 30 to 40 mesh (0.66−0.45 mm). The loadings of methanol synthesis catalyst were fixed at 4 g, and the loadings of methanol dehydration catalyst were 0, 0.2, 0.4, 1.0, 2.0, 3.0, and 4.0 g, respectively. The GHSV based on the methanol synthesis catalyst was maintained at 10000 h^{-1}. The quartz sand was used to dilute catalyst for avoiding the possible overheating. The result of the experiments is shown in Figure 4. It is seen that the phenomenon that the excessive dehydration catalyst reduces CO conversion does not appear, which is in good agreement with previously published result in gas-phase reaction.[8]

The above comparisons indicate that the decrease of CO conversion caused by the excessive dehydration catalyst is the particular phenomenon in slurry phase dimethyl ether synthesis and it is independent of the syngas composition. In fact, one of the significant differences between slurry phase reaction and gas phase reaction is the interaction among catalyst particles. Unlike in gas phase reaction where catalyst particles
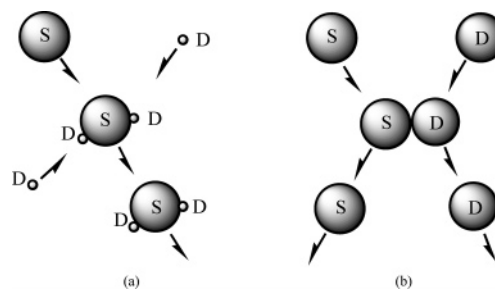
are fixed after they have been packed in, the catalyst particles in the slurry phase reactor are suspended in inert liquid medium. Thus, catalyst particles can move freely and contact each other frequently during their movement. For slurry phase dimethyl ether synthesis employing two different types of catalysts, however, this convenient movement does not always bring a positive effect on the reaction.[11] For all catalyst particles less than a certain size, the fine powder is easy to migrate and adsorb onto the surface of medium-size or large-size particles of the other type of catalyst. When the fine catalyst particles migrate or adsorb on the different type of catalyst particles, the active sites on the later one[12] will be covered partially, and it results in a lower catalyst effectiveness factor (see Figure 5a). For the three reactions revolved in DME synthesis, the methanol synthesis reaction is the limiting step due to its strictest thermodynamic limitation. The coverage of methanol synthesis catalyst must decrease the formation rate of methanol, resulting in the lower overall reaction rate. From Figure 1, it can be found that methanol dehydration catalyst used in this study has relatively high activity and shows the highest synergic effect at a very low weight ratio to methanol synthesis catalyst (1:20). Therefore, the coverage of the dehydration catalyst by the methanol synthesis catalyst does not cause obvious activity decrease of the hybrid catalyst. This might be the reason that the excessive dehydration catalyst decreases the overall reaction rate in slurry phase dimethyl ether synthesis using the hybrid catalyst.

To validate the detrimental effect of the fine powder, the contrastive experiments were performed using the catalyst which does not contain the fine particle less than 250 mesh (0.057 mm). The loadings of MSC were fixed at 4 g, and the loadings of MDC were 0.2, 0.5, 1, 2, and 3 g in turn. The results are depicted in Figure 4 by the short dashed line. It is found from Figure 4 that CO conversion is nearly equal to the result in the experiment using particles less than 200 mesh at 0.2 g of the dehydration catalyst. When the loadings of methanol dehydration catalyst are 0.5, 1, 2, and 3 g, respectively, CO conversions are about 20% higher than the corresponding values in experiments using particles less than 200 mesh. The decrease of CO conversion caused by the excessive dehydration catalyst does not occur in these experiments. It proves that the virtual cause resulting in the decrease of catalyst activity is the presence of the excessive fine powder of the dehydration catalyst.

It has been well-known that methanol synthesis catalyst and methanol dehydration catalyst are basic catalyst and acidic catalyst, respectively. The adsorption of the fine powder on different catalyst will induce the
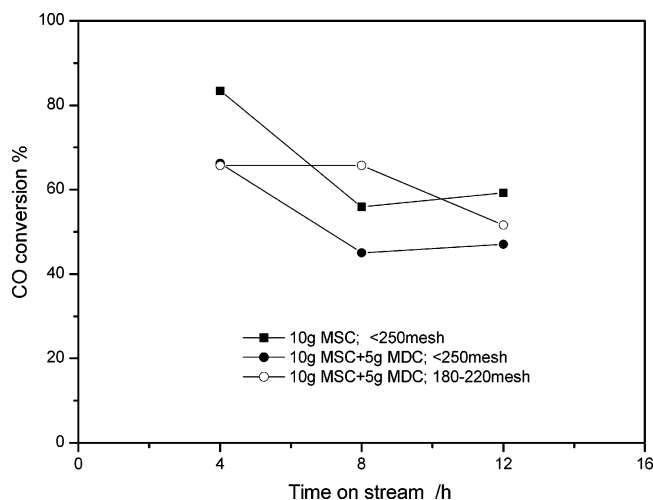
Figure 6. Effect of particle size on water gas shift reaction in a 1 L autoclave reactor. Conditions: 1 L CSTR; 2 MPa; 240 °C; 4380 h^{-1} for 10 g of MSC; CO/H$_2$O = 1:1.25; 1000 rpm.

changes of the acidic or basic properties of the later one. When the fine powder is sieved away, the collision among the bigger particles will be the main interaction or contact for the catalysts. This kind of collision does not result in adsorption or intermigration among particles (see Figure 5b). Thus, the catalyst activity depression caused by coverage of active sites as well the change of surface properties will disappear simultaneously.

On the basis of the above analysis, the effect of the fine powder should exist in a single reaction process, for example, slurry phase water gas shift reaction which can be catalyzed by methanol synthesis catalyst.[13] The experiments were performed in a 1 L well agitated autoclave reactor. The same methanol synthesis catalyst, C301, was employed as the catalyst. γ-Alumina in different particle size was added to verify its influence on the reaction. The 99.99% CO and distilled water, mixed at the molar ratio of 1:1.25, were used as the reactants. The GHSV based on the methanol synthesis catalyst was fixed at 4380 h^{-1}. The activity changes of the methanol synthesis catalyst in 12 h are illustrated in Figure 6. Under the condition that the two catalysts are less than 250 mesh, there is a comparison between 10 g of MSC and 10 g of MSC + 5 g of MDC. It can be seen from Figure 6 that the addition of 5 g of methanol dehydration catalyst decreases methanol synthesis catalyst activity more than 10%. However, when the particle size of two catalysts stands at the range 180 (0.081 mm)−220 mesh (0.065 mm), the activity and stability of the methanol synthesis catalyst have better improvement than when employing catalyst less than 250 mesh. It is clear that the fine powder in the dehydration catalyst depresses water gas shift activity of methanol synthesis catalyst. Because of the comparability between synthesis activity and shift activity of methanol catalyst, it can prove indirectly that physical adsorption of fine powder onto the bigger particles of different type catalyst conceals the intrinsic activity of the hybrid catalyst.

In slurry phase dimethyl ether synthesis, the fine or superfine catalyst particles in the reactor are derived not only from the catalyst grinding process but also from the mechanical abrasion of the hybrid catalyst during reaction. For the former, it can be removed by means of sieving; however, the deactivation caused by mechanical abrasion of the hybrid catalyst is eliminated with

difficulty. Although there is no detailed experimental datum to testify to this influence, it is concluded on the basis of the detrimental effect of fine powder in above experiments that better catalyst strength is favored for the improvement of stability of a hybrid catalyst in slurry phase dimethyl ether synthesis.

It is emphasized here that this work lies merely in putting forward a new method to improve the activity of a hybrid catalyst based on the investigation of the detrimental effect of the fine powder. Aside from the mechanism of interadsorption, some other mechanisms[14−15] including the intermigration of activated species,[11] the formation of new mixed oxides,[16] the crystal growth of hybrid catalyst,[17] and the pore mouth plugging of catalyst[18] could also explain convincingly the detrimental effect of the fine powder. Therefore, great efforts need to be made to explore the real mechanism of quick catalyst deactivation in slurry phase dimethyl ether synthesis.

Conclusion

The fine powder in hybrid catalyst, derived not only from loading process but from mechanical abrasion of catalyst, damages badly the activity of the hybrid catalyst. For avoiding the presence of the fine particles in reactor, it is necessary to keep catalyst particle size at the same or adjacent magnitude. In practical operation, the better activity and stability of hybrid catalyst can be gotten by avoiding the use of fine or superfine powder catalyst and improving catalyst strength.

Acknowledgment

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