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In-situ regeneration mechanisms of hybrid catalysts in the one-step synthesis of dimethyl ether from syngas

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One-step synthesis of dimethyl ether (DME) from H_2/CO has been studied in a fixed bed reactor over hybrid catalyst $CuOZnOAl_2O_3/\gamma\text{-}Al_2O_3$-HZSM-5. The physicochemical properties of fresh and used catalysts were also studied by means of H_2-TPR, XRD and N_2O chemisorptions. The results showed that for deactivated catalysts by sintering, redox cycle was an effective method for *in-situ* regeneration. There were two different regeneration mechanisms according to various atmospheres: (i) For O_2-syngas cycle, sintered Cu particles were re-dispersed and initial activity was restored mostly. The process was reversible, which was called reversible regeneration; (ii) for N_2O (CO_2)-syngas cycle, Cu particles could not be re-dispersed and catalytic activity was restored a little due to the regulation of surface state. On the other hand, this process could depress the deactivation velocity and was irreversible, which was called irreversible regeneration.

KEY WORDS: dimethyl ether; sintering deactivation; regeneration; reversible regeneration; irreversible regeneration.

1. Introduction

Dimethyl ether (DME), as a clean alternative fuel for diesel engines, has attracted much attention due to its better combustion performance: lower NO_x emission, lesser smoke and engine noise. DME has properties similar to those of propane and butane, the principal constituents of LPG, so it can be distributed, stored and used as a LPG substitute. As fuel processors and fuel cells are introduced to the public, dimethyl ether can be further exploited as a non-toxic, non-corrosive, environmentally benign hydrogen carrier produced from domestic resources. In addition, DME is also being used as an aerosol propellant to replace chlorofluoro carbons, which are found to destroy the ozone layer of the atmosphere [1].

In the one-step process of DME synthesis, the equilibrium constraints of methanol formation are avoided by continuous removal of methanol to DME. So direct synthesis of DME from synthesis gas in a single reactor with hybrid catalysts has attracted many researchers and industrial attention at the present time [2–6]. In these studies, different problems associated with Cu-based catalyst deactivation, such as Cu particle sintering and coke deposition, are approached [7–9]. In the LPMeOH process, Lee and Sardesai [10] found that sintering velocity of Cu particles was dependent on reaction conditions. The rate of thermal aging and the crystal growth pattern of methanol synthesis catalyst slowed down, when it was used in a co-production mode along with γ-alumina. Meanwhile, according to Aguayo *et al.* [8], during one-step DME synthesis over $CuOZnOAl_2O_3/\gamma\text{-}Al_2O_3$, water in the system can depress the deactivation by coke deposition effectively. In the previous research of our group [9], physicochemical properties of fresh and deactivated catalysts, such as surface area, dispersion, adsorption volume and acidity, were compared. Then it was suggested that sintering of Cu crystalline should be the main reason for deactivation of one-step DME synthesis catalysts.

Lee *et al.* [11] found that a method of redox cycle of Cu-based catalysts could regenerate the catalytic activity from sintering deactivation in 1990s. Therefore, the regeneration of sintered Cu-based catalysts is of great commercial importance for industrial process, and the deactivation and regeneration of Cu-based DME synthesis catalysts deserve intensive investigation. Despite this fact, data with respect to the regeneration of sintered catalysts are sparsely published in the literature. In this research, details in regeneration methods and conditions of sintered Cu-based catalysts for DME synthesis were investigated. Meanwhile, different regeneration mechanisms were contrasted and discussed elaborately.

2. Experimental

Catalysts used in this paper were prepared in a co-precipitation sedimentations method as follows: an aqueous solution of Cu, Zn and Al nitrate and a solution of Na_2CO_3 were co-precipitated under vigorous stirring. The mole ratio of Cu/Zn/Al was 6/3/1. After

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coprecipitation, the slurry was filtered, washed and added to HZSM5 and γ-Al_2O_3, and then it was stirred, filtered, dried and calcined.

The DME synthesis reaction was carried out in a conventional fixed-bed flow reactor. The catalyst (1 ml, 20–40 mesh) was packed in a stainless-steel tube. The catalyst was re-reduced *in situ* with H_2 under atmospheric pressure at 220 °C. Reaction conditions: 220 °C, 3 MPa, 2000 h^{-1}. In the regeneration experiments, oxidants (5%O_2–He, 5%CO_2–He, 5%N_2O–He) are used to transform metallic Cu to oxidative state at different temperatures for 2 h, then the feed gas , $H_2/CO(2/1)$, are re-introduced to catalyst bed for the same time to complete this cycle.

X-ray diffraction (XRD) data of catalysts were collected on a Rigaku Dmax-B diffractometer (CuKa radiation, 40 kV, 100 mA). The crystallite sizes of metallic Cu were evaluated from the full width at half maximum of the Cu (1 1 1) peaks by using the Scherrer equation.

Copper surface areas were determined by N_2O chemisorptions. According to the reaction: $N_2O(g) + 2CuO \rightarrow (Cu\text{–}O\text{–}Cu) + N_2(g)$. The products were analyzed on-line by a TCD detector. The copper surface area was calculated assuming a value of 1.46×10^{19} Cu atoms/m^2.

Temperature-programmed reduction experiments were performed on a self-made system which equipped with a TCD detector. Catalyst (30 mg) was charged in a U-typed quartz cell, reduced in H_2 at 220 °C for 2 h, then oxidized under 5%O_2–He, 5%CO_2–He, 5%N_2O–He, respectively. The oxidized samples were pretreated in Argon for 1h, then reduced in a 5% H_2/Ar stream (40 ml/min) with a ramp of 10 °C/min.

3. Results and discussion

3.1. *Effect of pretreatments on catalysts regeneration*

Over hybrid catalysts $CuOZnOAl_2O_3/\gamma$-Al_2O_3HZSM5, the decrease and regeneration of catalytic activity for DME synthesis are listed in table 1. From the table we can find that the decrease of CO conversion was significant, while the turnover frequency (TOF) and DME selectivity were rather stable during the time on stream of 48 h. So it is suggested that the deactivation of catalysts was more likely due to the sintering of Cu particle, rather than dehydration components. Likewise, it is found that redox cycle of deactivated catalysts can also restore their activity, but the regeneration methods should be divided into two groups. (1) For O_2-syngas regeneration, sintered Cu particles can be re-dispersed, at the same time the initial activity and metallic Cu surface area will be resumed mostly. During the regeneration process, the TOF value kept constant about 4×10^{-3}; (2) For N_2O or CO_2-syngas regeneration, sintered Cu particles were not re-dispersed and catalytic activity was renewed a little. The increase of TOF means that there might be changes of the nature of active sites after regeneration.

Figure 1 depicts the H_2-TPR results of active catalysts (reduced state) oxidized by various atmospheres. In the range of temperature, only Cu species were reduced and consumed H_2. It can be seen from the figure that the TPR results correlated well with the two regeneration groups mentioned above. At 230 °C, O_2 can oxidize metallic Cu to Cu^{2+}, whether on surface or in bulk. Its TPR pattern was a sharp peak centered at 530 K with a weak shoulder of low temperature, just like that of fresh catalyst. High reduction velocity showed its good dispersion [12]. The result of N_2O-oxidation was rather similar to that of CO_2-oxidation and both were patterns of a broad peak centered at about 650 K. Differences of reduction temperature, reduction velocity as well as H_2 consumption indicate that O_2 oxidation varied basically from that of N_2O or CO_2.

3.2. *Effect of temperature on catalysts regeneration*

Figure 2 shows the effect of regeneration temperature on catalytic activity. It is clearly seen that the plots of N_2O and CO_2 were so similar and quite different from that of O_2. Oxygen is such a strong oxidant that it can transform all of Cu species in the catalysts thoroughly into Cu^{2+} at 190 °C. So the initial activity was regenerated mostly at this temperature and did not change even up to 250 °C. But for the relatively weak oxidants, such as N_2O and CO_2, their oxidations were more complex. As the temperature increased from 170 °C to 230 °C, the degree of oxidation was enhanced and the regeneration of activity got improved. Just at 230 °C, oxidation of catalysts came to a balance, but their states were not as much as Cu^{2+} by oxygen oxidation, which was deduced from TPR patterns.

Table 1
Comparison between fresh, used and regenerated catalysts

	Fresh catalyst	Catalyst after 48 h	O_2 regenerated	N_2O regenerated	CO_2 regenerated
S_{Cu} (m^2/g)	38	27.2	36.9	26.9	25.8
D_{Cu} (nm)	6.3	9.0	6.9	9.2	9.6
Conv.co (%)	66.9	49.5	65.1	53.5	54.1
Sel. $_{DME}$(%)	68.5	65.2	66.1	66.2	65.3
TOF(10^{-3} s^{-1})	4.08	3.99	3.93	4.75	4.68

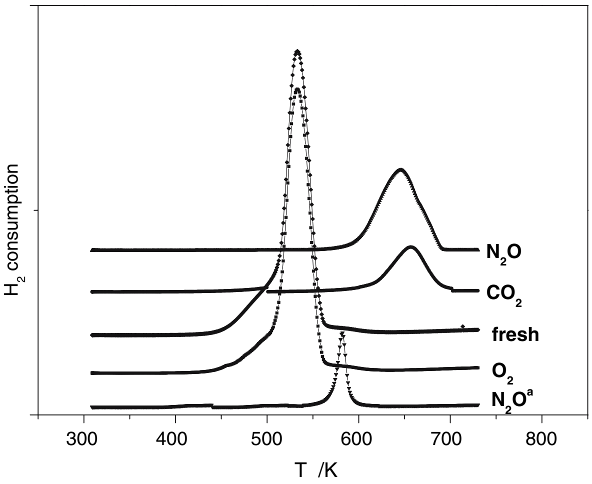

Figure 1. TPR patterns of catalysts oxidized in different atmospheres (a) N_2O oxidation at 55 °C.

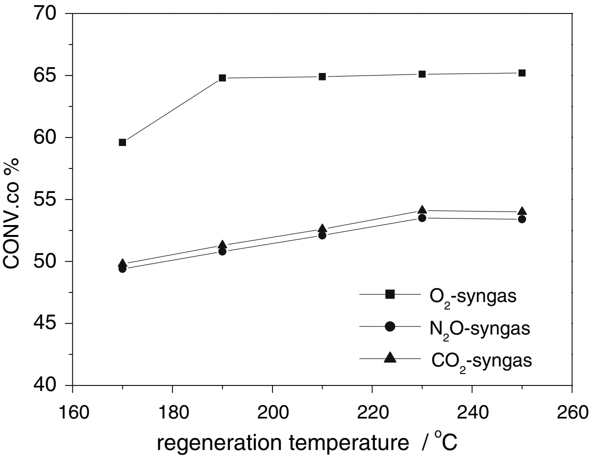

Figure 2. Effect of temperature on catalysts regeneration.

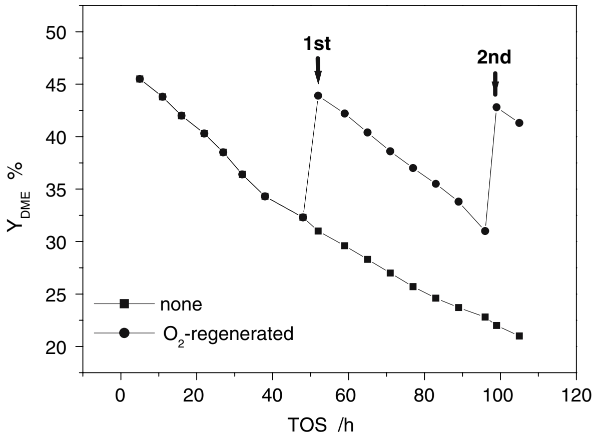

Figure 3. Effect of O_2-regeneration on activity.

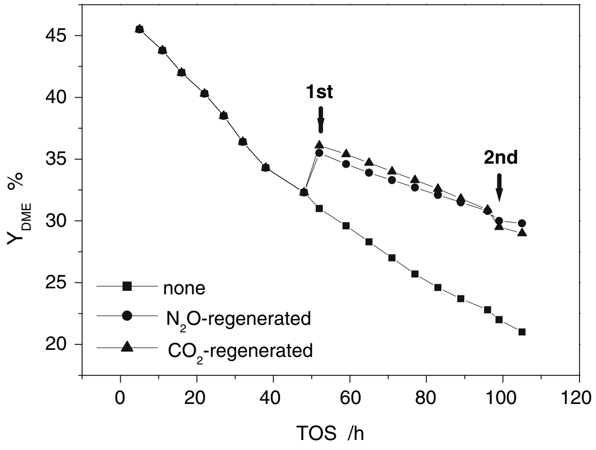

Figure 4. Effect of N_2O,CO_2-regeneration on activity.

3.3. *Effect of regeneration on catalytic stability*

The effects of various regeneration atmospheres on catalytic stability are shown in figure 3 and figure 4. From figure 3, one can clearly see the achievement after O_2-syngas regeneration. The second redox cycle at the 96th hours during the time on stream showed that the oxygen-syngas regeneration was a reversible process and the activity can be restored repeatedly by O_2-syngas redox cycle. So oxygen regeneration promoted DME production significantly, although this process did not change the deactivation velocity at all.

It can be found from figure 4 that N_2O or CO_2 regeneration was rather different from that of oxygen. The former restored activity by a little but depressed deactivation velocity effectively, which is consistent with the fact that the TOF value increased after N_2O or CO_2 regeneration. Meanwhile, we find that the second N_2O or CO_2 redox cycle at the 96th hours did not change the catalytic activity again. Consequently, we call this process irreversible regeneration. Despite the fact, N_2O or CO_2 regeneration also promoted DME production.

3.4. *Comparison of two regeneration mechanisms*

Lee and Sardesai [10] found that in the LPMeOH process, deactivated catalysts restored their activity through a redox cycle. According to Andreasen *et al.* [13], in gas-phased methanol synthesis over Cu, Zn solid solution oxide catalyst, the shape and size of Cu crystalline have undergone a reversible change during a redox cycle. These results were coincident with our reversible regeneration mechanism of oxygen, in which sintered Cu particles were re-dispersed, and the initial catalytic activity and active surface area were restored leaving constant TOF. Moreover, this process can be realized repeatedly, which is called reversible regeneration. However, an apparently different regeneration mechanism occurred by N_2O or CO_2 oxidation.

The TPR patterns showed that reduction plot of N_2O or CO_2-oxidized catalysts were not like that of fresh catalyst, but so like that of pure CuO [12]. Nevertheless, the fact does not rationalize the restoration of activity and depression of deactivation velocity after regeneration. In addition, N_2O or CO_2 is not such a strong oxidant like oxygen that can transform all of Cu, surface or bulk, into Cu^{2+} species. As is well known, N_2O can oxidize surface Cu atoms to Cu_2O at 55 °C. Reduction temperature of surface Cu_2O was much close to that of N_2O or CO_2-oxidized catalysts. Therefore, from area, shape and location of reduction peaks, it is concluded that at 230 °C, N_2O or CO_2 oxidized Cu^0 to Cu^+–Cu^{2+} hybrid species. Furthermore, this hybrid species can not be reduced thoroughly to Cu^0 in the conditions of DME synthesis. As a result, the active sites, TOF value as well as deactivation velocity shifted after regeneration. The regeneration method can not be used repeatedly, which is called irreversible regeneration.

These results agree well with that of temperature-programmed reduction experiments obtained by Fierro *et al.* [12] who found that broadened reduction peaks implied several complex species, and that Cu_2O was more difficult to reduce than CuO. Previous research of our group [14] showed that as active sites of methanol synthesis, Cu^0–Cu^+ was more active than Cu^0, and there needed some oxidative atmosphere in the system to complete the cycle. Likewise, Sun *et al.* [15] also found that Cu^0–Cu^+ in methanol synthesis depressed sintering of Cu crystalline significantly.

The further affirmance of the interaction of Cu^+–Cu^{2+} in oxidative state and that of Cu^0–Cu^+ in reductive state is in progress.

4. Conclusions

For deactivated Cu-based catalysts by sintering, redox cycle was an effective method for *in-situ* regeneration. There were two different regeneration mechanisms according to various atmospheres: (i) reversible regeneration: O_2-syngas cycle, sintered Cu particles were re-dispersed and initial activity was restored mostly. The process was reversible; (ii) irreversible regeneration: $N_2O(CO_2)$-syngas cycle, Cu particles could not be re-dispersed and catalytic activity was restored a little due to the regulation of surface state. This process could depress the deactivation velocity and was irreversible.

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