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New Rh-ZnO/Carbon Nanotubes Catalyst for Methanol Synthesis

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Abstract: A new catalyst for methanol synthesis, ZnO-promoted rhodium supported on carbon nanotubes, was developed. It was found that the Rh-ZnO/CNTs catalyst had high activity of 411.4 mg CH₃OH/g/cat/h and selectivity of 96.7 % for methanol at 1 MPa and 523 K. The activity of this catalyst is much higher than that of NC 207 catalyst at the same reaction conditions. It was suggested that the multi-walled structure CNTs favored both the couple transfer of the proton and electron over the surface of the catalyst and the uptake of hydrogen which was favorable to methanol synthesis.

Keywords: Rh-based catalyst, methanol synthesis, carbon nanotubes.

The production and recovery of the catalyst for methanol synthesis, Cu-ZnO-Al₂O₃, have heavily polluted our environment. Looking for a new highly effective but no pollutant catalyst becomes an urgent task. In this paper, a new catalyst for methanol synthesis, Rh-based catalyst supported on carbon nanotubes which is a good for uptake of hydrogen¹, is reported.

Experimental

The Rh-based catalyst supported on CNTs, Rh-ZnO/CNTs, was prepared by impregnation. The CNTs used here were prepared by catalytic decomposition of methane and pretreated in 6 mol/L HCl first and then refluxed in 12 mol/L HNO₃ for 3.5 h². After pretreatment, the CNTs were doped into the solution of RhCl₃ and promoter, followed by drying in infrared heater, heating in air at 383 K overnight and subsequently calcining in air at 623 K for 4 h.

Catalytic activity was determined in kinetic system composed of gas chromatograph with a thermal detector and a fixed bed flowing reactor made by stainless tubes of 8 mm inner diameter. The catalyst of 0.5 g was packed into reactor, followed by heating the sample in a flow of purified hydrogen from room temperature to 573 K and maintained this temperature for 4 h and then dropping down the requirement temperature of reactions.

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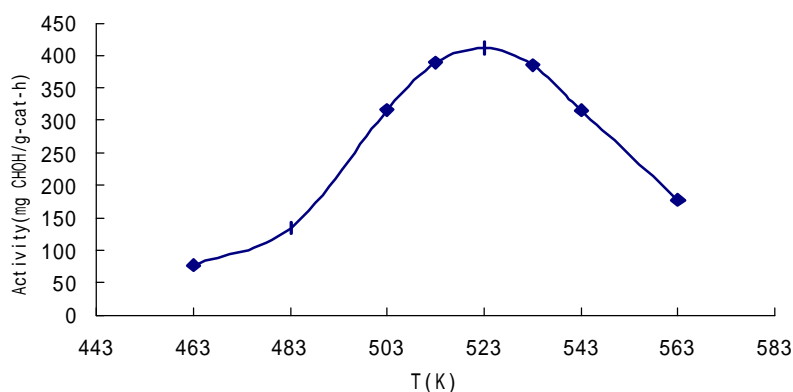
The syngas ($\text{H}_2/\text{CO}/\text{CO}_2 = 6/3/1$, V/V) was introduced to replace hydrogen.

The micrograph of pure carbon nanotubes and catalyst were studied by using transmission electron microscopy (JEM-100CXII, 100 KV) after sonicating the samples in suitable amount of ethanol solvent for 20 minutes and then dispersing a drop of the resulting solution over copper grid.

Results and Discussion

As we can see from **Figure 1**, it is obvious that, under the same space velocity and pressure, the activity of methanol synthesis changed with temperature and displayed the highest activity at 523 K. The highest activity is 411.4 mg $\text{CH}_3\text{OH}/\text{g}/\text{cat}/\text{h}$ at 523 K and the pressure of 1 MPa.

Figure 1 Methanol synthesis activity of Rh-ZnO/CNTs



Reaction conditions: GHSV=3000 h⁻¹, reaction pressure=1 MPa

Table 1 shows that the activity of this catalyst is much higher than that of NC207 catalyst. The curve showed in **Figure 1** was almost symmetric at the point 523 K. The activation energy of methanol synthesis on this catalyst is approximately 68.8 kJ/mol which is lower than that of Cu-ZnO-Al₂O₃ catalyst for methanol synthesis. The latter is 94.98 kJ/mol³.

Table 1 Activity of methanol synthesis over Rh-ZnO/CNTS and Cu-ZnO-Al₂O₃ catalyst at same reaction conditions (mg MeOH/g-cat.-h)

Catalyst	Reaction temperature (K)				
	483	503	523	543	563
CuO-ZnO-Al ₂ O ₃	187.3	203.5	213.6	184.2	163.7
Rh-ZnO/CNTS	133.8	316.1	411.6	315.7	177.6

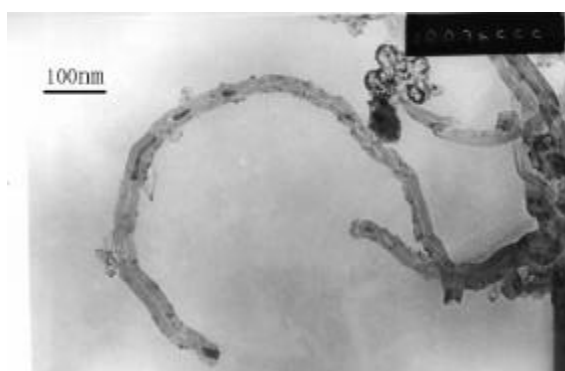
We can see from **Figure 2**, that the tip of carbon nanotubes are opened and inner wall of carbon nanotubes is very clean. Thus it can provide expedite channels for adsorption and desorption of feedgas and product, furthermore purified carbon nanotubes has high surface area ($160 \text{ m}^2/\text{g}$), it is appropriate support for this kind of catalyst.

Figure 2 TEM photograph of pure carbon nanotubes



Figure 3 showed that rhodium and zinc oxide are loaded on support very well, it is important for this action. We think that higher catalytic activity may due to the special properties of the support, that has excellent behavior of transferring proton and electron⁴ and storing hydrogen⁵. Therefore, when carbon nanotubes were used as a support, activation proton produced from syngas over promoter of the catalyst could be stored in CNTs. So concentrated proton around activation center favores greatly hydrogenation of CO to methanol.

Figure 3 TEM photograph of Rh-ZnO/CNTS



For the catalyst Rh-ZnO/CNTs, the yield of CH_3OH was 133.8, 316.1, 389.2, 411.4, 385.7, 315.5, 177.6 mg $\text{CH}_3\text{OH}/\text{g-cat-h}$ at 483 K, 503 K, 523 K, 533 K, 543 K and 563 K, respectively. The optimal reaction temperature is 523 K, and it was found that the catalyst was active even at 463 K.

When we change other supports such as SiO₂ and Al₂O₃, the main product of this reaction is ethanol instead of methanol at the same reaction condition. The result indicated that inner diameter of carbon nanotubes play important roles in this reaction. More research will be investigated in future.

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