Mesoporous SBA-15 supported Pd-Zn catalysts for hydrogen production from methanol

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Introduction

Hydrogen is a potentially very attractive source of energy since its combustion produces only water and energy. The conventional methods of hydrogen production are based on gasoline or natural gas reforming. Among the different feed stocks available, alcohols are very promising candidates because these are easily decomposed in the presence of oxygen/water and generate hydrogen rich mixture at a relatively lower temperature. Methanol is an attractive feed stock for producing hydrogen because if its large abundance and high atomic ratio of H/C. Copper based catalysts have been widely used for hydrogen production from methanol by partial oxidation (PO) as well as steam reforming (SR) reactions. But other metals such as Pd has also been used [1,2]. Various supports such as activated carbon, SiO_2, Al_2O_3, and carbon nanotubes [3] have been reported for Cu and Pd catalysts. The high activity of Pd-Zn catalysts in hydrogen production was ascribed to the presence of PdZn (1:1) alloy in the catalyst. Selection of support to Pd catalysts plays an important role in controlling the dispersion, particle size and alloy formation. It is also well known that supporting an active metal phase on an ordered mesoporous material with a narrow pore distribution can favorably influence the performances of the resulting catalytic system. Hence, in this study, we investigated the activity of Pd-Zn catalysts finely dispersed over mesoporous SBA-15 for PO and SR reactions of methanol with an aim to produce CO free hydrogen. Mesoporous SBA-15 is a promising new support material for catalysts because of its large surface area (>800 m^2/g) and uniform hexagonal channels and a very narrow pore-size distribution.

Materials and Methods

Mesoporous SBA-15 was synthesized by hydrothermal method using Pluronic P123 as template and tetraethyl orthosilicate as Si source. The calcined support was characterized by XRD, N_2 adsorption, and TEM. The calcined SBA-15 was loaded with varying amount of Pd and Zn in the ratio of 2:3 by co-impregnation method. The prepared catalysts were characterized by XRD, TPR, H_2 chemisorption, and DRIFT of CO adsorption. The partial oxidation with air and steam reforming reactions of methanol were carried out at different temperatures (240, 260, 280 and 300°C) over reduced catalysts in a fixed bed reactor with O_2/CH_3OH ratio of 0.3. The effects of reaction temperature and methanol to oxygen ratio on the selectivity of hydrogen are studied in detail.

Results and Discussion

The hexagonal structure and crystallinity of the synthesized SBA-15 were confirmed by XRD (Figure 1a) and the morphology was analyzed by TEM (Figure 1b). The BET surface area values of the catalysts are found to be low compared to that of pure SBA-15 (818m^2/g) support. The XRD patterns of the Pd-Zn/SBA-15 show the existence of PdZn alloy in the catalysts and the particle size increases with increasing Pd-Zn loading. The TPR profiles of Pd-Zn/SBA-15 catalysts show a negative peak around 100°C indicating the release of hydrogen from the decomposition of palladium hydride. A broad peak at higher temperature is observed for all the catalysts may be due to the reduction of ZnO species. The total chemisorbed H_2 uptake is found to increase with Pd content. The DRIFT spectra of CO adsorbed on Pd-Zn/SBA-15 catalysts show bands around ~2072cm^{-1} and in the range of 2000-1950cm^{-1}, indicating linearly adsorbed and bridge-bonded CO on Pd(100) and Pd(111) plane, respectively. The methanol conversion on PO and SR reactions increases with increasing temperature over all the catalysts. Also, the methanol conversion rate is proportional to the total chemisorbed H_2 uptake indicating that the rate determining step is catalyzed by Pd. The hydrogen selectivity is found to increase with temperature up to 280°C and beyond that no significant increase is noted.

Table 1. Physico-chemical characteristics and PO activity of PdZn/SBA-15 catalysts

No	Metal content (wt%)		BET surface area (m^2/g)	Total H_2 uptake	CH_3OH conversion (mol.%)	H_2 Selectivity (%)
	Pd	Zn				
1	0.5	0.75	768	8	34.7	49.2
2	1.5	2.25	683	13.7	57	54
3	3.0	4.5	596	26	68.4	59
4	4.5	6.75	524	34	73	78.4
5	5.5	8.25	507	38.2	78	77.3

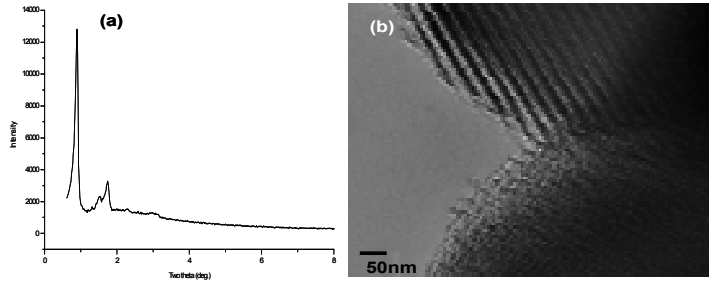

Figure 1. XRD pattern (a) and TEM image (b) of SBA-15

Significance

Because of the mesoporous nature of SBA-15, the Pd-Zn particles are well dispersed and Pd-Zn alloy is formed, resulting enhanced activity and selectivity in hydrogen production from methanol by partial oxidation and steam reforming reactions.

References

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