Zeolite-stabilized Rhodium Sub-Nano Cluster Catalyst for Low-Temperature Oxidation of Methane to Syngas

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The emergence of economical technology for extracting unconventional natural gas and shale-gas has promoted methane to be an ideal feedstock for commodity chemicals and fuels.[1] Syngas is a crucial intermediate which is a bridge to achieve the conversion of methane to high value-added chemicals. However, efficient production of syngas under mild conditions is still a grand challenge.

Here, for the first time, we demonstrate that mordenite zeolite-supported Rh sub-nano clusters via ion-exchange method (Rh/MOR-IE) with a loading of 0.25wt.% catalyze the partial oxidation of methane to syngas at substantially lower temperature 450–600 °C. This catalyst is more active, durable, and selective than conventional catalysts. It gave 84% conversion of methane at 600 °C with 91% selectivity for CO and a H_2/CO ratio of 2.0. Such a high performance was obtained only at above 700 °C in previous reports. Moreover, no deactivation was observed for at least 50 h, reaching a turnover number of 2,600,000. A detailed characterization was carried out for connection of the superior catalytic performances with the catalyst properties.

HAADF-STEM showed particles of Rh species as bright dots, which was confirmed by EDX in the selected areas (008 and 003) for Rh/MOR-IE (Fig. 1a) and Rh/MOR-IM as a contrast catalyst by impregnation method (Fig. 1b), where the average particle size was 0.6 nm and 2.9 nm, respectively. Fig. 2 shows TPR profiles of different samples. Rh/MOR-IE and Rh/MOR-IM showed two main peaks of H_2 consumption at around 50 and 450 °C. The former peak can be assigned to the reduction of surface or bulk rhodium oxide as observed for other typical Rh catalysts at <150 °C.[2] In contrast, the latter one appeared at a much higher temperature, which indicated strong interaction between Rh species and support. The area ratio of the two peaks at 450 °C to 50 °C was 4.0 for Rh/MOR-IE, which was 4 times larger than that for Rh/MOR-IM (1.0). Moreover, Rh/MOR-IE had an additional shoulder peak at 600 °C, clearly showing that Rh species strongly interacted with the MOR support on the catalyst. This sub-nano sized Rh and metal-support interaction contribute to the low temperature activity and the good durability. With regard to reaction mechanism, kinetic studies and X-ray photoelectron spectroscopy revealed that a combustion-reforming mechanism occurs on the Rh^0 sub-nano clusters. Based on the results, we propose the reaction scheme shown in Fig. 3.

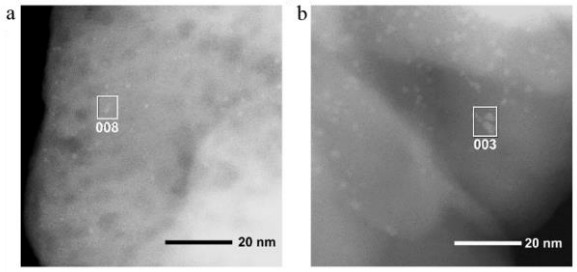

Fig. 1 HAADF-STEM images of Rh/MOR-IE (a) and Rh/MOR-IM (b).

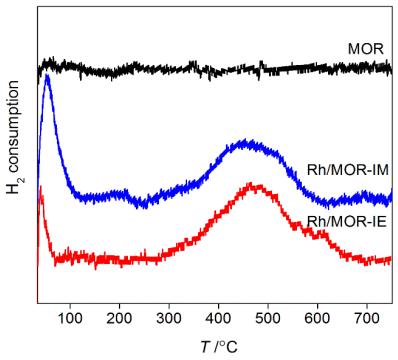

Fig. 2 TPR profiles of different samples.

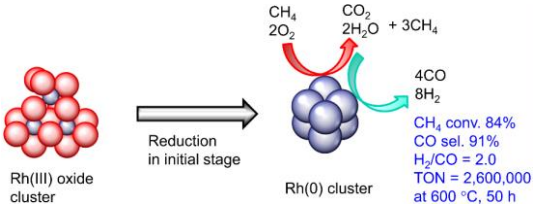

Fig. 3 Scheme of the selective oxidation of methane to syngas reaction over Rh/MOR-IE.

References

[1] Q. Wang, X. Chen, A. N. Jha and H. Rogers, Renewable Sustainable Energy Rev., 30 (2014) 1
[2] H. C. Yao, S. Japar and M. Shelef, J. Catal., 50 (1977) 407.