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NOTE

Role of Vanadium Promoter in Rh-V/SiO_2 Catalysts for the Synthesis of C_2-Oxygenates from Syngas

Previous studies by this and other research groups have reported that the vanadium component of Rh–V/SiO_2 catalysts exhibits important promoting effects on the activity and selectivity for the synthesis of C_2-oxygenates from syngas (1–7). However, the promoting effects of vanadium have not been well understood yet. IR spectroscopy has been extensively used to characterize the catalysts for the synthesis of C_2-oxygenates, but the question concerning the promoting effects has remained open (3, 5, 6, 8). In this work, IR spectra of adsorbed CO were recorded to probe the influence of the Rh active component modified by the vanadium promoter, and of adsorbed hydrogen on the activation behavior of adsorbed CO. Additional experiments including reaction evaluation, TEM, CO uptakes, TPR, and H_2-TPD were also conducted with the intent to gain insight into the role of vanadium promoters in Rh–V/SiO_2 catalysts.

The catalysts were prepared by coimpregnating silica supports (BET area: 200 m^2/g, Haiyang Chemicals Plant, China) with aqueous solutions containing the required amounts of $RhCl_3 \cdot xH_2O$ (Beijing Institute of Chemical Engineering, China) and vanadyl chloride (prepared in this laboratory (5)). The rhodium loading for all catalysts was 2 wt%, and V/Rh atomic ratios of the catalysts were in the range of 0.5 to 8.0. Catalysts were dried at 120°C overnight before use. CO/Rh atomic ratios was found to be ca. 0.3 with CO chemisorption. The average size of rhodium particles measured by TEM, for catalysts reduced at 300°C in flowing hydrogen, was ca. 30–40 Å. The results of syngas reaction (H_2/CO = 2, vol., P = 0.1 MPa, T = 190°C, GHSV = 1200 ml/$g_{cat} \cdot$ h) after reduction at 300°C in flowing hydrogen for 3 h were similar to previous ones of 4 wt% Rh–V/SiO_2 catalysts ($VOCl_2 \cdot xH_2O$ as vanadium promoter) (5). The selectivity toward C_2 oxygenates can reach over 75%, based on carbon efficiency. The rate of formation of C_2 oxygenates (or overall activity) on Rh–V/SiO_2 catalyst, was an order of magnitude higher than that on Rh/SiO_2 catalysts.

Temperature-programmed reduction (TPR) of various catalysts was performed in H_2 + Ar flow (H_2/Ar = 5 : 95, 15 ml/min) with a heating rate of 16°C/min. The effluent was analyzed by a thermal conductivity detector. The TPR profiles in Fig. 1 show that the SiO_2-supported vanadium was hardly reduced by hydrogen at the temperature range of 50–500°C (Fig. 1a). However, the rhodium-containing samples started to be reduced at a temperature of ca. 60°C, and gave a peak at ca. 150°C (Fig. 1b). The addition of vanadium led to a remarkable increase of H_2 consumption (Fig. 1c). The results clearly indicate that the vanadium promoter in the Rh–V/SiO_2 catalysts can be easily reduced by hydrogen only in the presence of rhodium.

Temperature-programmed desorption (TPD) of adsorbed hydrogen on the catalysts was carried out in the same way as in TPR. Argon was employed as the carrier gas and its flow rate was 22 ml/min. The heating rate was 32°C/min. The catalysts were reduced with hydrogen at 300°C for 3 h and then cooled in H_2 flow to room temperature. The TPD spectrum of the Rh/SiO_2 catalyst shown in Fig. 2a exhibits three peaks at ca. 100, 400, and 500°C respectively. The TPD peak at 100°C remained unchanged by the addition of vanadium (Fig. 2b–2d). However, the other two peaks changed very much for Rh–V/SiO_2 with varying V/Rh ratio. For Rh–V/SiO_2(V/Rh = 0.5) sample, the positions of TPD peaks at around 400 and 500°C are still similar to those for Rh/SiO_2 (Fig. 3a), but the amount of consumed H_2 increased significantly. With increasing V/Rh ratio (Fig. 2c–2d), the two high-temperature peaks incorporated into one peak at 280°C and showed a tendency toward lower temperature with higher V/Rh ratio. The first peak appears to be associated with hydrogen desorption from rhodium surface, and the second and third peaks can be assigned to the hydrogen desorbed from vanadium with lower valence or spilled over. These results revealed that the vanadium promoter seemed to play a role of hydrogen storage, and the area of high-temperature peak can be regarded as a measurement of the hydrogen storing capacity. The shift of the second peak towards lower temperature at the ratio of V/Rh > 2 could be attributed to the higher hydrogen mobility with more vanadium in Rh–V/SiO_2 catalysts.

FT-IR studies were performed with a multipurpose IR

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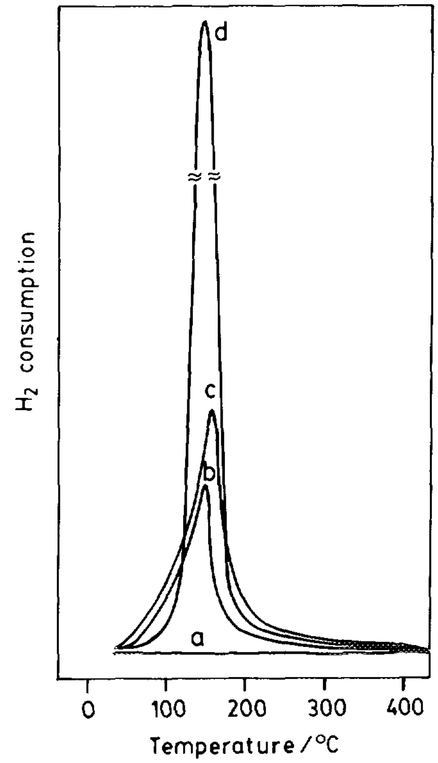

FIG. 1. TPR Profiles of various catalysts: a. V/SiO$_2$ (V = 4 wt%); b. Rh/SiO$_2$ (Rh = 2 wt%); c. Rh–V/SiO$_2$ (V/Rh = 2); d. Rh–V/SiO$_2$ (V/Rh = 8).

cell. The catalyst wafers for all experiments were first reduced *in situ* with flowing hydrogen at 300°C for 3 h. The IR spectra of adsorbed CO were recorded by a Perkin-Elmer 1800 FT-IR spectrometer. The catalyst samples for CO adsorption were treated with two procedures after the reduction: (i) by evacuating the samples at 300°C for 1 h, then cooling to room temperature and introducing CO (50 Torr); (ii) by cooling the samples in hydrogen to room temperature, and then pumping out the gaseous hydrogen and admitting CO. The band positions of adsorbed CO for all catalysts which had been evacuated to release H_2 at 300°C after reduction were nearly identical, irrespective of vanadium content (Fig. 3a$_1$,b$_1$). The IR bands at 2096 and 2030 cm^{-1} were attributed to adsorbed twin CO and those located at 2065 and 1850 cm^{-1} were attributed to linearly and bridged adsorbed CO, respectively. Coadsorption of carbon monoxide with hydrogen at room temperature did not appreciably change the positions and intensities of these bands of adsorbed CO.

The IR measurement for the CO adsorbed on Rh/SiO$_2$ and Rh–V/SiO$_2$ catalysts treated following procedure (ii) showed a significant difference. No band shift for the Rh/SiO$_2$ catalyst (Fig. 3a) was observed. But the promoted Rh–V/SiO$_2$ catalyst exhibited red shifts of 40–70 cm^{-1} for bridged CO and about 10 cm^{-1} for linear CO (Fig. 3b$_2$). Comparing spectrum b$_2$ with b$_1$, both b$_1$ and b$_2$ were produced from the same Rh–V/SiO$_2$ catalyst which experienced the same reducing treatment. They also had similar band intensities. The only difference was that the catalyst for spectrum b$_2$ kept the adsorbed hydrogen after high temperature reduction. Therefore, it seems reasonable to assume that this hydrogen, in addition to lower valence vanadium and rhodium, took part in the activation of adsorbed CO. In the case of catalysts cooled in H_2 to r.t., no bands of twin-adsorbed CO were detected; this can be explained by the production of the twin bands from adsorbed CO on Rh$^+$ sites and by activated hydrogen keeping rhodium in the Rh^0 state.

In the published literature, Tinet *et al.* (9) and Bond *et al.* (10) have also reported that hydrogen can react with V_2O_5 to form $H_{2x} \cdot V_2O_5$ compounds (x = 0.2–1.7), which can play the role of hydrogen storage. Gonzalez-Elipe *et al.* (11), on the basis of the results of hydrogen adsorption, TPD, PMR, and XPS/Ar$^+$ etching investigations, have concluded that the hydrogen adsorbed at 300°C on the reduced M/TiO$_2$ (M = Ni, Pt, Rh) was incorporated by spillover into the oxygen vacancies (TiV$_0$) in the reduced TiO$_2$ support, and gave rise to the hydride-like species (Ti–H). The role of hydrogen as a major reactant in the

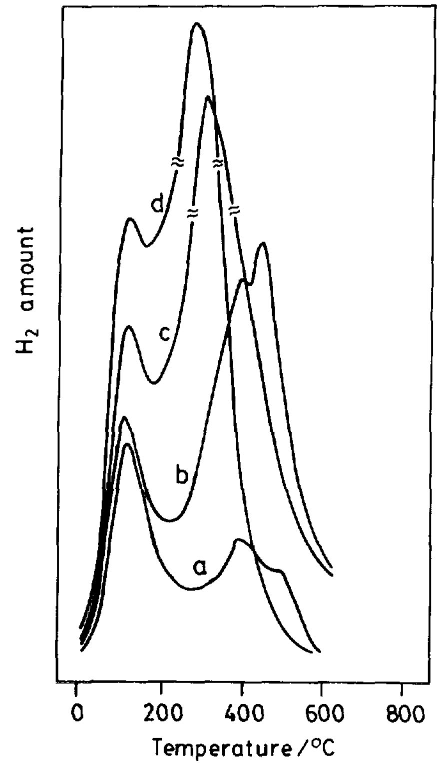

FIG. 2. TPD Profiles of adsorbed H_2 on catalysts: a. Rh/SiO$_2$ (Rh = 2 wt%); b. Rh–V/SiO$_2$ (V/Rh = 0.5); c. Rh–V/SiO$_2$ (V/Rh = 2); d. Rh–V/SiO$_2$ (V/Rh = 4).

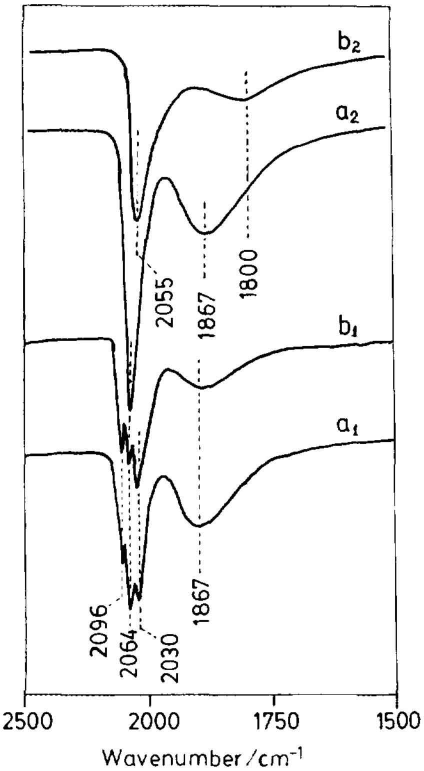

FIG. 3. IR Spectra of adsorbed CO on a. Rh/SiO_2 (Rh = 2 wt%), b. Rh–V/SiO_2 (V/Rh = 2) catalysts: a_1, b_1—outgassed by evacuation at 300°C after H_2 reduction; a_2, b_2—cooled to room temperature in H_2 after reduction at 300°C.

synthesis gas reaction seems to be an essential factor in the study of the promoting role of reducible metals for the synthesis of C_2 oxygenates on Rh/SiO_2 catalysts. In previous infrared investigations (3, 5, 12), very little information was obtained on how the reducible metals play an important part in the formation of C_2 oxygenates; this appeared to be due to disregard of the role of hydrogen. In this paper, the results of IR studies showed that the appreciable red shifts of CO bands only appeared on the Rh–V/SiO_2 catalyst cooled in H_2 to room temperature after reduction by hydrogen at 300°C and exposure to gaseous CO (Fig. 3b_2). In contrast, no shifts of adsorbed CO bands were observed either on Rh/SiO_2 catalyst or on Rh–V/SiO_2 catalyst outgassed at 300°C after reduction. The results suggest that the coexistence of rhodium, lower valence vanadium, and activated hydrogen is an essential condition to cause shifts of the bands of adsorbed CO.

Therefore the high activity and selectivity of vanadium-promoted rhodium catalysts in the synthesis of C_2-oxygenates may be attributed to the combined effects of rhodium, lower valence vanadium, and activated hydrogen.

REFERENCES

1. Ichikawa, M., Shikakura, K., and Kawai, M., *in* "Heterogeneous Catalysis related to Energy Problems," Proceedings of China–USA–Japan Symposium in Dalian, China, 1982, A08J.
2. Lee, G. van der, and Ponec, V., *Catal. Rev.* **29,** 183 (1987).
3. Kip, B. J., Smeets, P. A. T., Grondelle, J. van, and Prins, R., *Appl. Catal.* **33**(1), 157 (1987).
4. Lee, G. van der, Schuller, B., Post, H., Favre, T. L. F., and Ponec, V., *J. Catal.* **98,** 522 (1986).
5. Luo, H. Y., Bastein, A. G. T. M., Mulder, A. A. J. P., and Ponec, V., *Appl. Catal.* **38,** 241 (1988).
6. Bastein, A. G. T. M., Boogert, W. J. van den, Lee, G. van der, Luo, H. Y., and Ponec, V., *Appl. Catal.* **29,** 243 (1987).
7. Lee, G. van der, Bastein, A. G. T. M., Boogert, W. J. van den, Schuller, B., Luo, H., and Ponec, V., *Faraday Sympos. Chem. Soc.* **21,** paper 12 (1986).
8. Arakawa, H., Hanaoka, T., Takeuchi, K., Matsuzaki, T., and Sugi, Y., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), P. Guz. Chem. Institute of Canada, Ottawa, 1988.
9. Tinet, D., Legay, M. H., Gatineau, L., and Fripiat, J. J., *J. Phys. Chem.* **90,** 948 (1986).
10. Bond, G. C., Shermon, P. A., and Wright, C. J., *Mater. Res. Bull.* **19,** 701 (1984).
11. Gonzalez-Elipe, A. R., Munuera, G., Soria, J., Conesa, J. C., and Sanz, J., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), p. 602. Chem. Institute of Canada, Ottawa, 1988.
12. Bastein, A. G. T. M., Ph.D. thesis, Leiden University, 1988.

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