Catalysis Letters Vol. 83, No. 1–2, October 2002 (©2002)

Effects of ZnO contained in supported Cu-based catalysts on their activities for several reactions

Masahiro Saito[a]*, Jingang Wu[a], Kazumi Tomoda[b], Isao Takahara[c], and Kazuhisa Murata[c]

[a] *Japan Science and Technology Corporation (JST), 16-1 Onogawa, Tsukuba-shi, Ibaraki-ken 305-8569, Japan*
[b] *New Energy and Industrial Technology Development Organization (NEDO), 16-1 Onogawa, Tsukuba-shi, Ibaraki-ken 305-8569, Japan*
[c] *Research Institute for Green Technology, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba-shi, Ibaraki-ken 305-8569, Japan*

Received 15 February 2002; accepted 23 May 2002

The specific activity of Cu-based catalyst supported on Al_2O_3, ZrO_2 or SiO_2 for methanol synthesis and reverse water–gas shift reactions was improved by the addition of ZnO to the catalyst. On the other hand, the specific activity of the supported Cu-based catalyst for methanol steam reforming and water–gas shift reactions was not improved by the addition of ZnO to the catalyst.

KEY WORDS: Cu-based catalyst; methanol synthesis; methanol steam reforming; water–gas shift; reverse water–gas shift; effect of ZnO.

1. Introduction

Cu-based catalysts, especially Cu/ZnO-based catalysts, have been used for many important reactions in chemical industries such as methanol synthesis, water–gas shift reaction, methanol steam reforming and so on [1–27].

In the present study, the effects of ZnO contained in Cu-based catalysts supported on different supports on their activities for methanol synthesis, methanol steam reforming, water–gas shift reaction and reverse water–gas shift reaction were investigated for obtaining some useful information for developing high-performance catalysts for those reactions.

2. Experimental

The supports used in the present study were Al_2O_3, ZrO_2 and SiO_2. The Cu-based catalysts supported on Al_2O_3 or ZrO_2 were prepared by a coprecipitation method using Na_2CO_3 as a precipitant, as described in detail elsewhere [6]. The Cu-based catalysts supported on SiO_2 were prepared by an impregnation method using copper nitrate and zinc nitrate. SiO_2 used for a support was Cariact Q-3 supplied by Fuji-Silysia Chemical Ltd. The precursor of the catalyst was dried overnight at 393 K, calcined at 623 K for 2 h, and then the powder calcined was pelletized, crushed and screened to a size between 250 and 600 μm before use for the reaction. The compositions of the catalysts used are given in the footnotes to table 1.

The activities of the catalysts prepared for methanol synthesis, methanol steam reforming, water–gas shift and reverse water–gas shift were examined using a fixed-bed down-flow reactor. The catalyst loaded in the reactor was reduced in a stream of a gas mixture of H_2 (10%) and He (90%) at 573 K for 2 h before starting the reaction. The conditions for each reaction are given in the footnotes to table 1. The amount of the catalyst used for the reaction was adjusted in order to obtain almost the same Cu surface area of the post-reaction catalysts.

The Cu surface area of the post-reaction catalyst was measured with N_2O/He (2.4% N_2O) gas by reactive frontal chromatography after re-reducing the post-reaction catalyst with H_2 at 523 K, as previously reported [3,6]. The post-reaction catalyst was transferred from the reaction tube to a small glass bottle at room temperature in air, and then the sample in the bottle was placed in a sample tube for Cu surface-area measurement. Since a part of the surface of Cu in the post-reaction catalyst was oxidized with air while it was moved from the reaction tube to the sample tube, the post-reaction catalyst in the sample tube was re-reduced with H_2 at 523 K before measuring its Cu surface area. The present procedure gave a reproducible Cu surface area of the catalyst sample.

3. Results and discussion

Table 1 shows the Cu surface area of the post-reaction catalyst and the specific activity of the catalyst for

---

* To whom correspondence should be addressed.
E-mail: m-saito@aist.go.jp

1011-372X/02/1000-0001/0

Table 1
Surface areas, Cu surface areas and specific activities of various Cu-based catalysts for several reactions.

Reaction	Catalyst	Surface area [k] (m^2/ml-cat)	Cu surface area [l] (m^2/ml-cat)	Specific activity (μmol/m^2-Cu·min)
Methanol synthesis [a]	Cu/Al_2O_3 [e]	59	6.6	7.4 [m]
	$Cu/ZnO/Al_2O_3$ [f]	53	14.0	20.2 [m]
	Cu/ZrO_2 [g]	53	5.0	13.8 [m]
	$Cu/ZnO/ZrO_2$ [h]	52	12.7	20.8 [m]
	Cu/SiO_2 [i]	263	12.9	2.5 [m]
	$Cu/ZnO/SiO_2$ [j]	231	11.5	6.7 [m]
Methanol steam reforming [b]	Cu/Al_2O_3 [e]	51	4.3	116 [n]
	$Cu/ZnO/Al_2O_3$ [f]	51	7.5	125 [n]
	Cu/ZrO_2 [g]	44	6.0	127 [n]
	$Cu/ZnO/ZrO_2$ [h]	50	11.3	122 [n]
	Cu/SiO_2 [i]	252	14.2	67 [n]
	$Cu/ZnO/SiO_2$ [j]	228	10.7	66 [n]
Water–gas shift [c]	Cu/Al_2O_3 [e]	47	4.2	110 [o]
	$Cu/ZnO/Al_2O_3$ [f]	45	9.5	114 [o]
	Cu/ZrO_2 [g]	45	5.7	128 [o]
	$Cu/ZnO/ZrO_2$ [h]	45	11.5	119 [o]
	Cu/SiO_2 [i]	271	11.9	24 [o]
	$Cu/ZnO/SiO_2$ [j]	226	11.4	13 [o]
Reverse water–gas shift [d]	Cu/Al_2O_3 [e]	53	5.5	10.3 [p]
	$Cu/ZnO/Al_2O_3$ [f]	50	10.1	27.9 [p]
	Cu/ZrO_2 [g]	47	5.1	16.6 [p]
	$Cu/ZnO/ZrO_2$ [h]	45	12.0	25.3 [p]
	Cu/SiO_2 [i]	264	14.1	5.5 [p]
	$Cu/ZnO/SiO_2$ [j]	242	11.3	9.6 [p]

Note: Numbers in parentheses are percentages.

[a] Reaction conditions: 523 K, 5 MPa, feed gas = $CO(3)/CO_2(22)/H_2(75)$.

[b] Reaction conditions: 483 K, 0.6 MPa, feed gas = $CH_3OH(17)/H_2O(25)/He(58)$ for Cu-based catalysts supported on Al_2O_3 and on ZrO_2, but 503 K for Cu-based catalysts supported on SiO_2.

[c] Reaction conditions: 503 K, 0.15 MPa, feed gas = $CO(6)/CO_2(11)/H_2(45)/H_2O(38)$ for Cu-based catalysts supported on Al_2O_3 and on ZrO_2; 523 K for Cu-based catalysts supported on SiO_2.

[d] Reaction conditions: 523 K, 0.15 MPa, feed gas = $CO_2(25)/H_2(75)$.

[e] $Cu(50)/Al_2O_3(50)$ prepared by a coprecipitation method.

[f] $Cu(50)/ZnO(30)/Al_2O_3(20)$ prepared by a coprecipitation method.

[g] $Cu(40)/ZrO_2(60)$ prepared by a coprecipitation method.

[h] $Cu(40)/ZnO(10)/ZrO_2(50)$ prepared by a coprecipitation method.

[i] $Cu(20)/SiO_2(80)$ prepared by an impregnation method.

[j] $Cu(20)/ZnO(5)/SiO_2(75)$ prepared by an impregnation method.

[k] The surface area of the catalyst used for the reaction.

[l] Cu surface area of the catalyst used for the reaction.

[m] Rate of methanol produced per unit Cu surface area.

[n] Rate of $(CO_2 + CO)$ produced per unit Cu surface area.

[o] Rate of CO converted per unit Cu surface area.

[p] Rate of CO produced per unit Cu surface area.

each reaction, i.e., the rate of the reaction per unit Cu surface area of the post-reaction catalyst. In addition, figure 1 shows the relative specific activity of the catalyst containing ZnO, which is defined as the ratio of the specific activity of the catalyst containing ZnO relative to that of the catalyst without ZnO.

The specific activities of the catalysts containing ZnO for methanol synthesis were found to be higher than those of the catalysts without ZnO. This promoting effect found in the present study is consistent with the findings in previous studies on methanol synthesis from CO_2/H_2 over Cu surface modified with Zn [7,9], which suggested that ZnO added to a Cu-based catalyst could produce active sites which have higher specific activities for methanol synthesis. However, the present results are not consistent with the results in the previous study on methanol synthesis from a feed-gas mixture containing around 10% of CO and of CO_2 over various Cu-based catalysts [2], which reported that their specific activities were almost the same. Since the present study employed a feed-gas mixture containing 3% of CO and 22% of CO_2 for methanol synthesis, the inconsistency might be due to the difference in CO concentration or in the ratio of CO/CO_2 in the feed-gas mixture. Therefore, the present finding suggests that both increasing the Cu surface area of the catalyst and adding ZnO to a Cu-based catalyst should be important for developing a high-performance catalyst for methanol synthesis

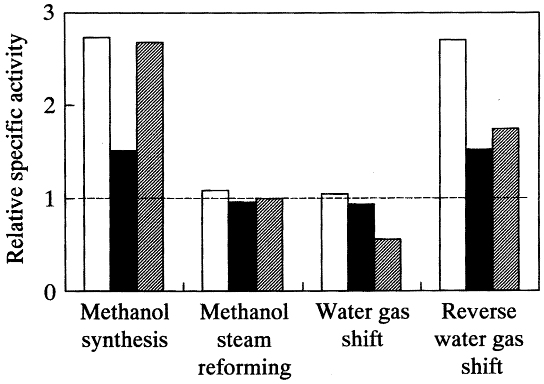

Figure 1. The specific activities of Cu-based catalysts containing ZnO relative to that of the catalysts without ZnO for several reactions: (☐) Al_2O_3-supported Cu catalyst; (■) ZrO_2-supported Cu catalyst; (▨) SiO_2-supported Cu catalyst.

from a feed-gas mixture with a low CO concentration or with a low CO/CO_2 ratio.

The specific activities of the catalysts containing ZnO for methanol steam reforming were found to be about the same as those of the catalysts without ZnO. This finding indicates that ZnO added to the catalysts could hardly exert any promoting effects on their activities, and suggests that it should be more important to increase the Cu surface area of a Cu-based catalyst for developing a high-performance Cu-based catalyst for methanol steam reforming.

The specific activities of the catalysts supported on Al_2O_3 and ZrO_2 containing ZnO for water–gas shift were found to be about the same as those of the catalysts without ZnO, whereas the specific activity of the catalyst supported on SiO_2 containing ZnO was less than that of the catalyst without ZnO. These findings indicate that ZnO added to the catalysts could exert no promoting effects on their activities for water–gas shift, and suggest that it should be more important to increase the Cu surface area of a Cu-based catalyst for developing a high-performance Cu-based catalyst for water–gas shift.

The specific activities of the catalysts containing ZnO for reverse water–gas shift were found to be higher than those of the catalysts without ZnO. This promoting effect found in the present study is not consistent with the findings in the previous studies [7,9], which reported that the specific activity of the Cu surface for reverse water–gas shift was not affected by Zn deposited on the Cu surface. The present finding suggests that ZnO particles adjacent to Cu particles could play some role in promoting the activity of the catalyst for reverse water–gas shift, and also that both increasing the Cu surface area of the catalyst and adding ZnO to a Cu-based catalyst should be important for developing a high-performance catalyst for reverse water–gas shift.

The present findings described above apparently indicate that ZnO works as a promoter for reactions carried out under reducing conditions, whereas ZnO does not work as a promoter for reactions run under oxidizing conditions in the presence of a large quantity of water. This might suggest that water could be adsorbed on ZnO to suppress some promoting actions of ZnO.

The specific activities of the catalysts supported on Al_2O_3 and ZrO_2 were about the same as for the reactions tested in the present study, whereas the specific activities of the catalyst supported on SiO_2 for the reaction were much lower than those of the catalysts supported on Al_2O_3 and ZrO_2. Although no reasonable explanation for the finding could be given, it is suggested that SiO_2 should not be employed as a support for Cu-based catalysts for the reactions tested in the present study.

The Cu surface area of the catalyst containing ZnO was much larger than that of the catalyst without ZnO when preparing the catalysts by a coprecipitation method, whereas the Cu surface area of the catalyst containing ZnO was smaller than that of the catalyst without ZnO when the catalyst was prepared by an impregnation method. This finding suggests that the addition of Zn nitrate to an aqueous solution of Cu nitrate could improve the dispersion of Cu in the catalyst during the preparation of the catalyst by a coprecipitation method, as previously reported [4].

4. Conclusions

1. The specific activity of a Cu-based catalyst supported on Al_2O_3, ZrO_2 or SiO_2 for methanol synthesis and reverse water–gas shift reactions was improved by the addition of ZnO to the catalyst. This finding suggests that both increasing the Cu surface area of the catalyst and adding ZnO to a Cu-based catalyst should be important for developing a high-performance catalyst for those reactions.
2. The specific activity of the supported Cu-based catalyst for methanol steam reforming and water–gas shift reactions was not improved by the addition of ZnO to the catalyst. This finding suggests that it should be more important to increase the Cu surface area of a Cu-based catalyst for developing a high-performance Cu-based catalyst for those reactions.
3. SiO_2 should not be employed as a support for Cu-based catalysts for the reactions tested in the present study.
4. The Cu surface area of the catalyst containing ZnO was much larger than that of the catalyst without ZnO when preparing the catalysts by a coprecipitation method, whereas the Cu surface area of a catalyst containing ZnO was smaller than that of the catalyst without ZnO when the catalyst was prepared by an impregnation method. This finding suggests that the addition of Zn nitrate to an aqueous solution of Cu nitrate should be important to increase the Cu surface area of a Cu-based catalyst when preparing the catalysts by a coprecipitation method.

Acknowledgments

The present study was supported in part by the Japan Science and Technology Corporation (JST) and the New Energy and Industrial Technology Development Organization (NEDO).

References

[1] K. Klier, Adv. Catal. 31 (1982) 243.

[2] G.C. Chinchen, K.C. Waugh and D.A. Whan, Appl. Catal. 25 (1986) 101.

[3] G.C. Chinchen, C.M. Hay, H.D. Vandervell and K.C. Waugh, J. Catal. 103 (1987) 79.

[4] S. Fujita, A.M. Satriyo, G.-C. Chen and N. Takezawa, Catal. Lett. 34 (1995) 85.

[5] K.M. Vanden Bussche and G.F. Froment, J. Catal. 161 (1996) 1.

[6] M. Saito, T. Fujitani, M. Takeuchi and T. Watanabe, Appl. Catal. A 138 (1996) 311.

[7] T. Fujitani, I. Nakamura, T. Uchijima and J. Nakamura, Surf. Sci. 383 (1997) 285.

[8] M.S. Spencer, Topics Catal. 8 (1999) 259.

[9] Y. Choi, K. Futagami, T. Fujitani and J. Nakamura, Appl. Catal. A 208 (2001) 163.

[10] M. Saito, J. Wu, M. Takeuchi and T. Watanabe, Appl. Catal. A 218 (2001) 235.

[11] S. Velu, K. Suzuki, M. Okazaki, M.P. Kapoor, T. Osaki and F. Ohashi, J. Catal. 194 (2000) 373.

[12] S. Murcia-Mascaros, R.N. Navarro, L. Gomez-Sainero, U. Constantino, M. Nocchetti and J.L.G. Fierro, J. Catal. 198 (2001) 338.

[13] B.A. Peppley, J.C. Amphlett, L.M. Kearns and R.F. Mann, Appl. Catal. A 179 (1999) 21.

[14] B.A. Peppley, J.C. Amphlett, L.M. Kearns and R.F. Mann, Appl. Catal. A 179 (1999) 31.

[15] S.P. Asprey, B.W. Wojciechowski and B.A. Peppley, Appl. Catal. A 179 (1999) 51.

[16] J.P. Breen and J.R.H. Ross, Catal. Today 51 (1999) 521.

[17] P.J. de Wild and M.J.F.M. Verhaak, 60 (2000) 3.

[18] D.S. Newsome, Catal. Rev. Sci. Eng. 21 (1980) 275.

[19] C. Rhodes, G.J. Hutchings and A.M. Ward, Catal. Today 23 (1995) 43.

[20] M.J. Gines, N. Amadeo, M. Laborde and C.R. Apesteguia, Appl. Catal. A 131 (1995) 283.

[21] J.R. Mellor, N.J. Coville, S.H. Durbach and R.G. Copperthwaite, Appl. Catal. A 171 (1998) 273.

[22] J. Wu, M. Saito, J. Catal. 195 (2000) 420.

[23] S. Fujita, M. Usui and N. Takezawa, J. Catal. 134 (1992) 220.

[24] M.J.L. Gines, A.J. Marchi and C.R. Apesteguia, Appl. Catal. A 154 (1997) 155.

[25] E. Tserpe and K. C. Waugh, Stud. Surf. Sci. Catal. 109 (1997) 401.

[26] C.-S. Chen, W.-H. Cheng and S.-S. Lin, Catal. Lett. 68 (2000) 45.

[27] V.Z. Fridman and A.A. Davydov, Chem. Ind. 75 (1998) 495.