Effect of Added V_2O_5 on the Durability of $NiO–Fe_2O_3–Na_2O$ Catalyst in Vapour Phase Oxidation of Benzoic Acid to Phenol

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Addition of V_2O_5 to $NiO–Fe_2O_3–Na_2O$ catalyst is effective for preventing catalyst deactivation which is caused by the accumulation of sodium benzoate on the catalyst surface.

Recently, we have reported that $NiO–Fe_2O_3–Na_2O$ catalysts prepared by a precipitation method exhibit extremely high catalytic performance in terms of phenol selectivity, benzoic acid conversion and space time yield of phenol in the vapour-phase oxidation of benzoic acid.[1–5] On the other hand, it is the durability of the catalyst which is of the utmost concern from an industrial point of view. Apparent deactivations of conventional CuO catalysts were reported even if used in the vapour phase.[13–15] Although a number of research studies have been performed,[6–20] no effective additives have been suggested for the improvement of catalyst durability. In this work, the durability of $NiO–Fe_2O_3–Na_2O$ catalyst was investigated together with the effect and the role of V_2O_5 added to the catalyst. Precipitation of the $NiO–Fe_2O_3–Na_2O$ catalyst, experimental apparatus and procedures, and analytical methods have been described in previous papers.[1–5] The $NiO–Fe_2O_3–Na_2O–V_2O_5$ catalyst was prepared by impregnating the $NiO–Fe_2O_3–Na_2O$ mixture with an aqueous solution of ammonium metavanadate and then calcining in air at 500 °C for 3 h.

Fig. 1 shows the catalytic activity of $NiO–Fe_2O_3–Na_2O$ catalyst as a function of reaction time. Although >80% selectivity towards phenol was initially observed, an apparent deactivation of the catalyst was observed even under high steam concentrations. Rapid decrease both in conversion and in phenol selectivity was exhibited during the initial 20 h, while selectivity to benzene and $CO + CO_2$ increased steeply with time on stream. After 50 h, the catalyst maintained an almost constant activity, however the resulting performance was very poor in terms of commercial production of phenol.

The most striking aspect of the present results is that the addition of V_2O_5 to $NiO–Fe_2O_3–Na_2O$ is surprisingly effective for the enhancement of catalyst durability as shown in Fig. 2. Stable catalyst activity was obtained and no catalyst deactivation was observed over 100 h, and furthermore, phenol selectivity rose to >90% with almost 100% benzoic acid conversion. According to thermogravimetric analyses and infrared spectra of the unmodified catalyst after 100 h of experimental use, it was revealed that a fairly large amount of sodium benzoate had adhered on the $NiO–Fe_2O_3–Na_2O$ catalyst which probably would cause its deactivation, while little accumulation of sodium benzoate was observed on the V_2O_5–promoted catalyst. In the $NiO–Fe_2O_3–Na_2O$ catalyst system, the decomposition of accumulated sodium benzoate to benzene and CO_2 would be liable to occur, leading to increases in benzene and $CO + CO_2$ selectivities. Moreover, the deposition of sodium benzoate on the catalyst surface is believed to lead to coverage of the active sites so decreasing benzoic acid conversion.

Fig. 3 depicts the proposed reaction mechanism over $NiO–Fe_2O_3–Na_2O$ catalyst. Initially, benzoic acid would be adsorbed on the base component, namely Na_2O on the surface of the catalyst, and is converted to sodium benzoate. It is then transformed to benzoyl salicylic acid which is an intermediate for phenol formation.[17–20] The active species on the $NiO–Fe_2O_3–Na_2O$ catalyst is considered to be NiO dispersed on $NiFe_2O_4$ which has an inverse spinel structure.[3,5]

It is considered that catalysis by NiO is inherently correlated with a redox mechanism. The catalysis cycle of the present reaction consists of (*i*) the formation of nickel benzoate from sodium benzoate and NiO, (*ii*) the decomposition of nickel benzoate to give benzoyl salicylic acid and reduced nickel, and (*iii*) the oxidation of the reduced nickel by oxygen in the vapour phase to regenerate NiO. Of these steps the oxidation of reduced nickel is rate-determining. It is believed that

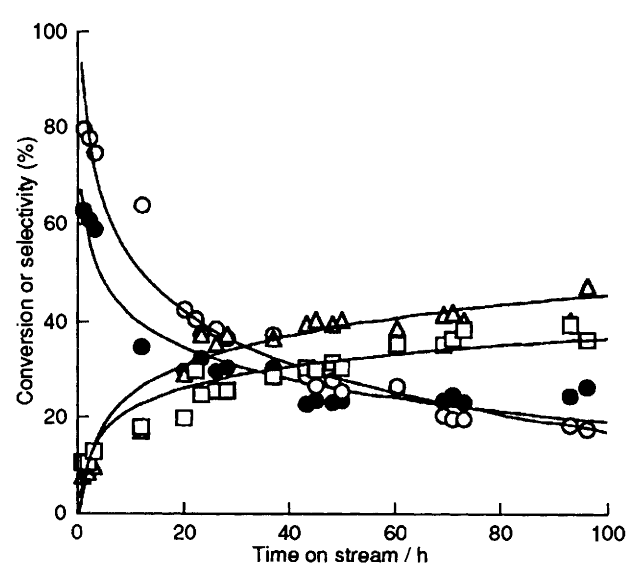

Fig. 1 Change in activity of $NiO–Fe_2O_3–Na_2O$ catalyst with reaction time Catalyst: 47.5 mass% NiO–51.5 mass% Fe_2O_5–1.0 mass% Na_2O, 420 °C. Benzoic acid : air : steam = 1 : 5 : 40 (mol ratio). Space velocity = 3400 h^{-1}. Conversion (●), phenol (○), benzene (△), CO_x selectivity (□), CO_x generated by phenol formation is excluded.

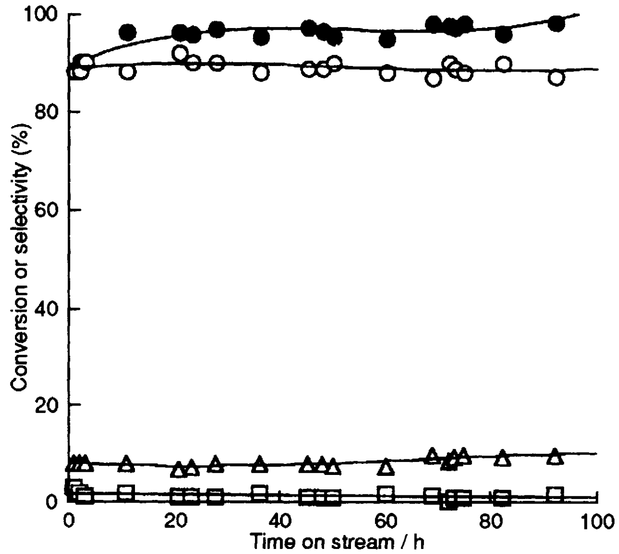

Fig. 2 Change in activity of V_2O_5-promoted catalyst with reaction time. Catalyst: 46.1 mass% NiO–49.9 mass% Fe_2O_3–1.0 mass% Na_2O–3.0 mass% V_2O_5, 400 °C. Benzoic acid : air : steam = 1 : 5.5 : 21 (molar ratio). Space velocity = 1500 h^{-1}. Conversion (●), phenol (○), benzene (△), CO_x selectivity (□), CO_x generated by phenol formation is excluded.

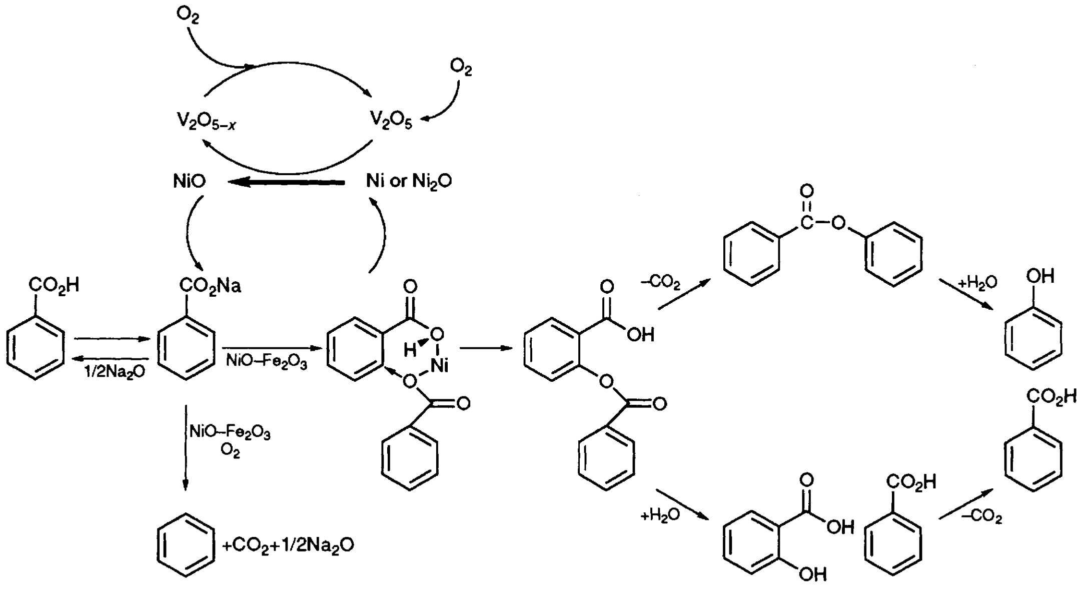

Fig. 3 Proposed reaction mechanism over Ni–Fe–Na catalyst and role of V_2O_5

adding V_2O_5 to the catalyst accelerates this process with V_2O_5 acting as an oxidising agent.

In conclusion, V_2O_5 was found to be remarkably effective for the enhancement of the durability of $NiO–Fe_2O_3–Na_2O$ catalyst. The promotional effect of V_2O_5 added is presumably attributed to an acceleration of the redox cycle of the nickel component which prevents the accumulation of sodium benzoate on the catalyst surface.

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References

1 J. Miki and M. Asanuma, *Jpn. Kokai Tokkyo Koho*, 4-5250, 1992.
2 *Jpn. Kokai Tokkyo Koho*, 4-330944, 1992.
3 J. Miki, M. Asanuma, Y. Tachibana and T. Shikada, *J. Chem. Soc., Chem. Commun.*, 1994, 691.
4 J. Miki, M. Asanuma, Y. Tachibana and T. Shikada, *J. Chem. Soc., Chem. Commun.*, 1994, 1685.
5 J. Miki, M. Asanuma, Y. Tachibana and T. Shikada, *Appl. Catal.*, **115**, 1994, L1.
6 W. W. Kaeding, R. O. Lindblom and R. G. Temple, *US Pat.*, 2 727 926, 1955.
7 R. D. Barnard, Walnut Creek and R. H. Meyer, *US Pat.*, 2 852 567, 1958.
8 C. T. Lam and D. M. Shannon, *US Pat.*, 4 567 157, 1986.
9 D. F. Pontz, *US Pat.*, 3 288 865, 1966.
10 R. E. Woodward, *US Pat.*, 3 356 744, 1967.
11 D. N. Glew and J. E. Ollerenshaw, *US Pat.*, 3 803 247, 1974.
12 A. P. Gelbein and A. M. Khansari, *US Pat.*, 4 277 630, 1981.
13 P. C. van Geern and A. J. J. M. Tenuissen, *US Pat.*, 4 383 127, 1983.
14 Y. Inoue, *Jpn. Kokoku Tokkyo Koho*, 64-934, 1989.
15 T. Maki and T. Masuyama, *Jpn. Kokoku Tokkyo Koho*, 2-10812, 1990.
16 T. Maki and T. Masuyama, *Jpn. Kokoku Tokkyo Koho*, 2-10813, 1990.
17 A. P. Gelbein and A. S. Nislick, *Hydrocarbon Process*, 1978, **57**, 125.
18 M. Stolcova, M. Hronec, J. Ilavsky and M. Kabesova, *J. Catal.*, 1986, **101**, 153.
19 M. Stolcova, M. Hronec and J. Ilavsky, *J. Catal.*, 1989, **119**, 83.
20 M. Hronec, M. Stolcova, Z. Cvengrosova and J. Kizlink, *Appl. Catal.*, 1991, **69**, 201.