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On the nature of catalyst promotion by manganese in CO hydrogenation to oxygenates over RhMn / NaY

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CO hydrogenation over Mn promoted Rh/NaY catalysts was studied at 10 bar and 250°C. Significant selectivity to oxygenates, mainly ethanol and ethyl acetate, was obtained after neutralizing the protons that are formed during reduction of Rh ions. Layered bed experiments show that protons act as sites catalyzing secondary reactions. Protons also convert $Mn(OH)_2$ to Mn^{2+} ions; the catalysts with highest selectivity to oxygenates contain MnO particles and Rh clusters. The results suggest chemical interaction of adsorbates on Rh_n clusters with those on MnO.

Keywords: syngas catalysis; catalyst promoters; CO hydrogenation to oxygenates; rhodium / zeolite catalysts

1. Introduction

Rhodium has the ability to catalyze the hydrogenation of carbon monoxide either to hydrocarbons or to oxygen containing products, depending on the *promoter* used. Unpromoted rhodium on an inert support yields mainly methane, but significant amounts of oxygenates are formed over rhodium in contact with oxides or ions of Mn, Fe, Zn, Ti, La, Zr or V [1–8]. Previous research of the interaction between rhodium and promoters led to a tentative model which assumed that interaction of transition metal ions with the oxygen end of carbon monoxide molecules adsorbed on rhodium might be instrumental for the catalyst promoter effect [5,6]. This concept motivated research on zeolite supported Mn promoted Rh catalysts, because zeolites with a cage structure such as Y should provide a better opportunity than amorphous supports to control the relative positions of Rh clusters and Mn ions or Mn oxide particles. The present paper reports on this research.

In related work the oxidation states and carbonyl complexes of Rh inside NaY have been identified. After calcination of ion exchanged Rh/NaY the oxides Rh_2O_3 and RhO_2 and the ions Rh^{3+}, $(RhO)^+$, Rh^{2+}, Rh^+ are detected. They are reduced in flowing H_2 to Rh^0 [9–11]. In the presence of CO the clusters $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ are formed; in the presence of both CO and zeolite protons, the ions $Rh^+(CO)_2$, in at least two coordinations with the zeolite oxygens, and $Rh^+(CO)_3$ have been identified. FTIR data also indicate formation of mixed Rh–Mn carbonyl clusters [10].

2. Experimental

The catalysts used in this work were prepared by ion exchange. The support was zeolite NaY (Linde); manganese, if present, was always introduced first by dropwise addition of 0.16 M solution of $Mn(NO_3)_2 \cdot 4H_2O$ (Aldrich) to a slurry of 5 g/ℓ of NaY in doubly deionized water at room temperature for 24 h. This was followed by increasing the temperature in a flow of pure O_2 from room temperature (RT) to 500°C at 0.5°C/min and holding at 500°C for 6 h. This was done to drive some of the Mn^{2+} ions into the small cages of the zeolite, thus preventing Rh ions, which were subsequently introduced, from occupying them. Rh exchange was done by dropwise addition of a solution of $Rh[(NH_3)_5Cl]Cl_2$ at 85°C for 48 h to a 5 g/ℓ slurry of NaY or Mn-NaY in doubly deionized water. After ion exchange, the samples were calcined in a pure O_2 flow, the temperature was ramped from RT to 200 or 500°C at 0.5°C/min and holding at the final temperature for 2 h. Reduction took place under a 60 ml/min flow of pure H_2 at 0.1 MPa; the temperature was ramped from RT to 200°C at 8°C/min and held at 200°C for 40 min.

In some samples the protons that are formed during the reduction of Rh were neutralized. This was done in two different ways. Some samples were immersed in a stirred NaOH solution at pH = 11 at room temperature for 12 h and then reduced again at 200°C. In other cases, the calcination temperature was limited to 200°C in order to prevent complete decomposition of the ammine ligands of the Rh precursor [12]. During reduction, these ammine groups react with the protons to form ammonium ions.

The pH value is crucial for the state of Mn. At neutral or lower pH, Mn is present as Mn^{2+} ions. At higher pH the hydroxide $Mn(OH)_2$ is formed first; in the presence of air it is rapidly oxidized to MnO_2 [13].

The catalyst samples were tested at 1 MPa and 250°C in a stainless steel flow reactor with automatic control over the reaction conditions. The H_2/CO ratio was 1 in all cases. Conversion of CO to organic products was kept low, under 3%. Product analysis was done using an HP 5890 gas chromatograph with a 50 m cross-linked methyl silicone capillary column and an FID detector.

3. Results and discussion

The following notation will be used: RhMn/NaY(T_c)-N, where T_c is the calcination temperature in °C, and -N, if present, denotes a catalyst neutralized by immersion in NaOH solution. In all Mn promoted catalysts, the Mn was present in valency Mn^{2+} during steady state operation. No Mn^0 was ever observed from TPR or XPS or EXAFS measurements; Mn^{4+} was formed when Mn containing catalysts were washed with NaOH and exposed to oxygen, as evident from the color change from white to brown. In such samples, the MnO_2 formed is reduced by H_2 or syngas to MnO. The following catalytic test results are reported:

(a) Catalysts: Rh/NaY(500) and Rh/NaY(500)-N. These unpromoted samples yield only hydrocarbons. The absence of protons after neutralization with NaOH does not change the product distribution. On a C atom basis, the selectivity to CH_4 at steady state is about 45%.

(b) Catalysts: RhMn/NaY(500) and RhMn/NaY(500)-N. The non-neutralized sample yields only hydrocarbons. No promoting effect of Mn is observed with this sample. In contrast, significant amounts of oxygenates are formed over the neutralized catalyst, mainly ethanol and ethyl acetate. The latter is probably a secondary product from the reaction between ethanol and acetic acid. In addition, hydrocarbons are formed. The performance of these samples is shown in figs. 1a and 1b. The yields of each oxygenate product for the sample RhMn/NaY(500)-N are shown in fig. 2. The results suggest that protons, formed during metal reduction:

$$Rh^{3+} + \tfrac{3}{2}H_2 \rightarrow Rh^0 + 3H^+ \qquad (1)$$

play a crucial, though negative, role in the selectivity of these catalysts. Two causes can be visualized for the strong effect of acid sites on catalyst performance:

(1) Brønsted acid sites in zeolite Y catalyze secondary reactions of primary formed oxygenates to other products, e.g. hydrocarbons.

(2) Protons affect the hydrolysis equilibrium:

$$Mn(OH)_2 + 2H^+ \rightleftharpoons Mn^{2+} + 2H_2O\,. \qquad (2)$$

Neutralized catalysts will contain the manganese as a hydroxide, which is subsequently transformed into MnO; the non-neutralized catalyst, however, contains free Mn^{2+} ions. It is conceivable that the catalyst promoter action of MnO may differ from that of Mn^{2+}.

(c) To determine the role of acid protons on the product distribution, two samples were prepared in which the Mn was exposed to a pH = 11 *prior* to the Rh exchange. One of them was treated again to pH = 11 *after reduction* of the Rh to neutralize the protons formed by (1). The non-neutralized sample, RhMn*/NaY(500), did not yield oxygenates. In contrast, the neutralized sample, RhMn*/NaY(500)-N, was very active towards oxygenate formation. The product distributions for these catalysts appear in figs. 3a and 3b. These results suggest that a positive effect of the NaOH immersion on catalyst performance is indeed due to neutralization of Brønsted sites that are generated during metal reduction.

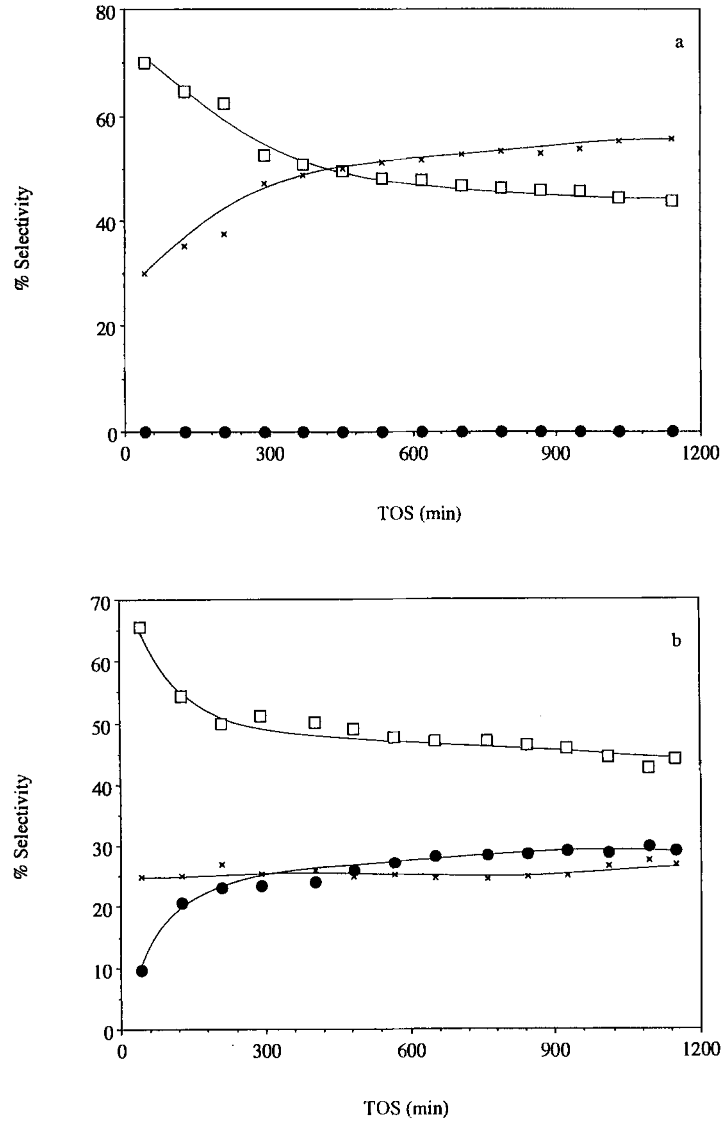

Fig. 1. Selectivity on a C atom basis of catalysts RhMn/NaY(500) (a) and RhMn/NaY(500)-N (b) towards different products plotted versus time on stream (TOS). (□) CH_4; (×) higher hydrocarbons; (●) oxygenates.

(d) Catalytic tests were carried out with layered beds of RhMn* /NaY(500)-N and zeolite HY [14]. With the RhMn* /NaY(500)-N upstream and the HY layer downstream, no oxygenates were detected in the effluent. In contrast, a high yield was found with HY upstream and RhMn* /NaY(500)-N downstream. We conclude that protons catalyze secondary reactions of oxygenates to hydrocarbons and/or carbonaceous deposits.

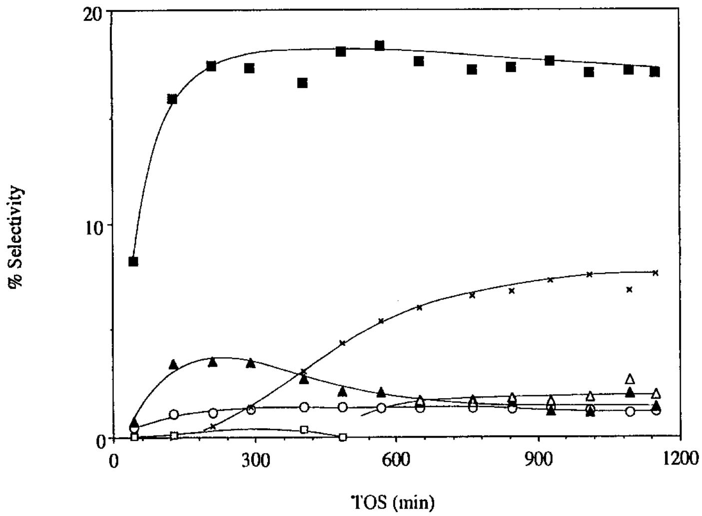

Fig. 2. Selectivity towards different oxygenate products of catalyst RhMn/NaY(500)-N plotted versus TOS. (□) dimethylether; (○) methanol; (■) ethanol; (▲) diethylether; (△) methyl acetate; (×) ethyl acetate.

(e) An alternative way of neutralizing protons makes use of the finding [12] that calcination of the ion-exchanged catalyst precursor below 300°C leaves a considerable fraction of the ammine ligands of the $Rh[(NH_3)_5(H_2O)]^{2+}$ ions inside the zeolite intact. During reduction these NH_3 groups are released from the metallic Rh being formed and react with the protons to give ammonium ions, thus providing a method to neutralize Brønsted sites without affecting the state of the Mn. Use of this was made in two catalysts. The first one, RhMn/NaY(200) was never exposed to a pH higher than 6, thus ensuring that Mn would remain as Mn^{2+} ions inside the zeolite. Accordingly, the color of this catalyst is white after the Mn exchange. No oxygenates were formed over it. The second sample, RhMn*/NaY(200), was exposed to a NaOH solution with pH = 11 after the Mn exchange, but *before* the Rh exchange. Its color changed quickly from white to brown, indicating that MnO_2 was present in the zeolite before reduction. Over this catalyst oxygenates were obtained, again mainly ethanol and ethyl acetate, in addition to hydrocarbons. Fig. 4 shows the selectivity towards oxygenates obtained with these two catalysts.

Since the protons formed in reaction (1) were neutralized in both samples and as NaOH immersion *before* Rh ion exchange has no effect on the protons present *after* reduction, we conclude that the only difference between these samples is the state of the manganese, which is present as Mn^{2+} ions in the first, but as MnO in the second one. In other words, MnO is an active promoter towards the formation of oxygenates, whereas Mn^{2+} ions, though presumably in close contact with Rh clusters, lack this propensity.

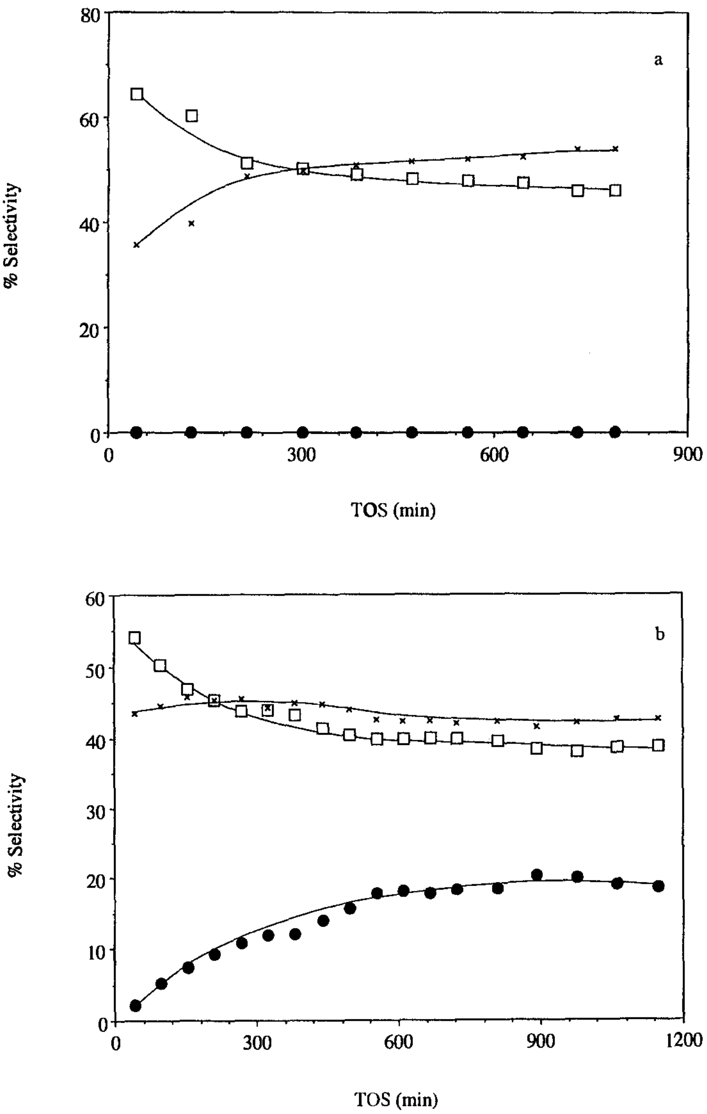

Fig. 3. Selectivity of catalysts RhMn*/NaY(500) (a) and RhMn*/NaY(500)-N (b) towards different products plotted versus TOS. (□) CH_4; (×) higher hydrocarbons; (●) oxygenates.

The results suggest that oxygenates are formed by chemical interaction of adsorbates on Rh clusters with those on MnO, implying that the model mentioned in the Introduction needs modification. A similar idea is suggested by the report that unsupported ruthenium carbido clusters convert syngas to methane, but the same clusters, when in physical contact with an oxide surface, convert syngas to oxygenates [15].

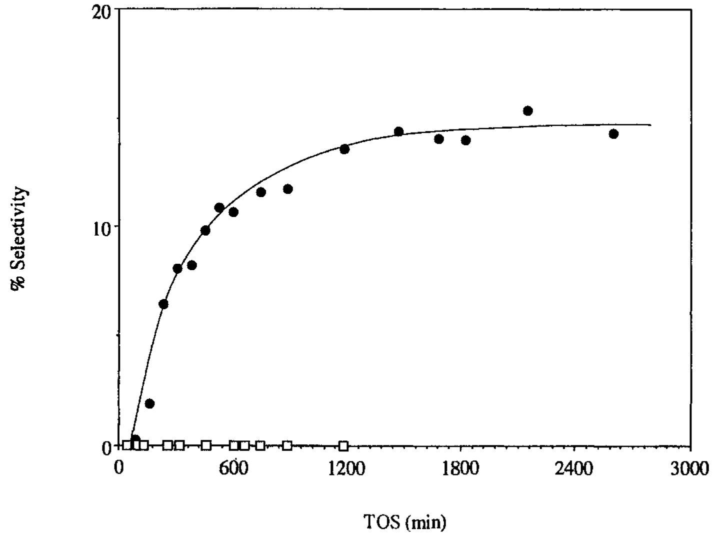

Fig. 4. Effect of NaOH immersion after Mn ion exchange *but prior* to Rh exchange. Selectivity of catalysts RhMn/NaY(200) (□) and RhMn*/NaY(200) (●) towards oxygenates plotted versus TOS.

4. Conclusions

(1) In the absence of a promoter, rhodium clusters in NaY cavities do not catalyze formation of oxygenates under the conditions of syngas conversion used in this work.

(2) Manganese is able to promote Rh/NaY catalysts towards formation of oxygenates, especially ethanol and acetic acid; this propensity is strong for MnO but apparently lacking for free Mn^{2+} ions.

(3) Protons in Y zeolites catalyze secondary reactions of the oxygenates that are formed as primary products of CO hydrogenation, transforming them to hydrocarbons and/or catalyst deposits. Oxygenates are, therefore, only obtained with essentially proton-free catalysts.

Acknowledgement

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References

[1] T.P. Wilson, P.H. Kasai and P.C. Ellgen, J. Catal. 69 (1981) 193.

[2] M. Ichikawa, Bull. Chem. Soc. Japan 51 (1978) 2268.

[3] M. Ichikawa, CHEMTECH (1982) 674.

[4] M. Ichikawa, T. Fukushima and K. Shikakura, in: *Proc. 8th Int. Congr. on Catalysis*, July 1984, Vol. II (Verlag Chemie, Weinheim, 1984) p. 69.

[5] W.M.H. Sachtler, in: *Proc. 8th Int. Congr. on Catalysis*, July 1984, Vol. I (Verlag Chemie, Weinheim, 1984) p. 151.

[6] W.M.H. Sachtler, D.F. Shriver, W.B. Hollenberg and A.F. Lang, J. Catal. 92 (1985) 429.

[7] F.G.A. van den Berg, J.H.E. Glezer and W.M.H. Sachtler, J. Catal. 93 (1985) 340.

[8] J. Kowalski, G. van der Lee and V. Ponec, Appl. Catal. 19 (1985) 423.

[9] D.C. Tomczak, V.L. Zholobenko, H. Treviño, G.-D. Lei and W.M.H. Sachtler, in: *Proc. 10th Int. Congr. on Zeolites*, Garmisch-Partenkirchen, 17–22 July 1994, in press.

[10] T. Beutel, H. Knözinger, H. Treviño, Z.C. Zhang, W.M.H. Sachtler, C. Dossi, R. Psaro and R. Ugo, J. Chem. Soc. Faraday Trans., submitted.

[11] V. Schünemann and W.M.H. Sachtler, Catal. Lett. submitted.

[12] T.T.T. Wong, Z. Zhang and W.M.H. Sachtler, Catal. Lett. 4 (1990) 365.

[13] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th Ed. (Wiley, New York, 1988) p. 699.

[14] H. Treviño and W.M.H. Sachtler, Chem. Eng. & Tech., submitted.

[15] Y. Izumi, T. Chihara, H. Yamazaki and Y. Iwasawa, J. Am. Chem. Soc. 115 (1993) 6462.