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A novel preparation method for zeolite encaged Co clusters

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A method has been devised to prepare reduced Co clusters in zeolite Y. Sodium acetate is impregnated after exchanging Co^{2+} ions into the zeolite. During calcination the acetate is partially or completely oxidized to sodium oxide. This not only stabilizes Co^{2+} ions in supercages, impeding their migration to smaller cages, but it also neutralizes the protons that are formed during the reduction of the Co^{2+} ions with H_2. As a result, the temperature of effective reduction is lowered by up to 350°C, depending on the calcination program. In unmodified zeolites, Co reduction requires a temperature above 750°C, which inevitably induces partial destruction of the zeolite lattice; this novel method permits complete reduction of Co without damaging the zeolite lattice. It is predicted that this novel method should be applicable to other zeolite encaged metals of low reducibility such as Ni.

Keywords: Cobalt/zeolite; Na acetate assisted Co reduction; high dispersion of transition metals; zeolite supported transition metals

1. Introduction

Numerous methods have been attempted for preparing zeolite encaged Co as shape-selective Fischer–Tropsch (FT) catalysts. The three stategies used to introduce Co into zeolite cages or channels were: decomposition of a volatile complex, impregnation and ion exchange. In the first route, $Co_2(CO)_8$ is adsorbed followed by removal of the ligands [1]. Recently, zero-field ferromagnetic nuclear resonance has been used to determine the size and location of Co clusters prepared in this way [2]. A sharp transition from superparamagnetism to ferromagnetism is observed between 4.2 and 1.3 K for a sample treated in H_2 at 200°C. This indicates uniform Co clusters of about 6 Å in the supercages of zeolite Y. A major concern with this method arises when high metal loading is desired. Due to the size of the carbonyl and the strong interaction of the carbonyl ligands with zeolitic cations such as Na^+ and H^+, diffusion from the outer shell to the core of a zeolite crystallite is very slow and long adsorption times are required to obtain homogeneous distribution of Co. Impregnation, though frequently used with amorphous supports, is

not a technique of choice for introducing metals into zeolites, because inhomogeneity of metal distribution usually leads to the formation of large particles upon reduction [3].

Ion exchange, while being a convenient technique, suffers from the unfavorable thermodynamics and kinetics of the reduction equilibrium:

$$Co^{2+} + H_2 \rightleftharpoons Co^0 + 2H^+ \quad (1)$$

with zeolites which stabilize the Co^{2+} ions, e.g. in sodalite cages or hexagonal prisms. It has been reported that reduction of Co^{2+} ions does not start below 750°C, a temperature at which the zeolite framework suffers from destruction [4]. The same problem exists for the preparation of zeolite supported Ni catalysts. It has also been found that the reverse reaction of (1) takes place in bimetal catalysts; in zeolite supported PtCu, PdCu or PdNi catalysts, e.g., the less noble metal is efficiently reoxidized by protons [5–7].

Several attempts have been made to solve this problem. They include: (1) using other reducing agents, e.g. cadmium vapor [8]; (2) lowering the energy of Co^0 or Ni^0 by alloying with a noble metal such as Pd and Pt, facilitating reduction by dissociating H_2 [9–11]; (3) preventing migration of Co^{2+} or Ni^{2+} ions to small zeolite cages, e.g. by hydrolysis of Co^{2+} ions in supercages, and (4) shifting the equilibrium (1) to the right by neutralizing the protons. A combination of methods (3) and (4) was proposed by Suzuki et al. [12], who treated the catalyst precursor with an aqueous NaOH solution at pH > 10.5. They observed a significantly lower reduction temperature, but large particles of Co_3O_4 and CoO are formed during the calcination step. After reduction large Co particles, mainly located on the external surface, are formed. The same is true for Ni/NaY [13,14]. Recently, Koh et al. modified this method by injecting a concentrated NaOH solution into dry Co/NaX; the authors report highly dispersed Co [3].

The present work focusses on a novel strategy which attempts to stabilize Co^{2+} ions in supercages of zeolite Y, while simultaneously neutralizing the protons formed during reduction (1), without favoring agglomeration of hydroxide particles or creating a concentration gradient between the surface of a zeolite crystallite and its interior. The concept is to introduce an alkali salt into the zeolite; during calcination this salt will decompose, leaving an oxide (e.g. Na_2O) inside the zeolite cages. This oxide might stabilize Co^{2+} ions in supercages and it will neutralize the protons during reduction. In this paper Na acetate has been used to test the validity of this idea.

2. Experimental

2.1. SAMPLE PREPARATION

A 2 wt% Co/NaY catalyst was prepared by ion-exchange of NaY (LZY-52) with a dilute aqueous $CoCl_2$ solution. Details of the ion-exchange program have

been reported elsewhere [15]. After thorough washing with distilled deionized water and drying at room temperature, the cobalt zeolite was further dried in air at 400°C. The dried sample was impregnated with a concentrated aqueous sodium acetate solution in a rotary evaporator ($T = 50$°C and $P = 130$ Torr) using a stoichiometric ratio of sodium acetate to Co^{2+}. The Co/NaY catalysts impregnated with Na acetate are denoted as Co/NaY–NaAc.

2.2. SAMPLE CHARACTERIZATION

The formation of the oxidation products of Na acetate salt was monitored by a computer interfaced Dycor M200 quadruple mass spectrometer. Temperature programmed oxidation (TPO) experiments were conducted in a flow of 60 ml/min of an O_2–Ar (5% O_2) gas mixture. The temperature was programmed at a rate of 8°C/min from 20 to 540°C. Two Na acetate impregnated samples (120 mg each) were studied by TPO: pure NaY and Co/NaY. Temperature programmed reduction (TPR) experiments were performed as described previously [9]. Two Co/NaY–NaAc samples (120 mg each) were calcined in O_2 (180 ml/min) at a heating rate of 0.5°C/min to either 300 or 500°C, and held at the final temperature for 2 h prior to TPR experiments. The heating rate during TPR was 8°C/min and the reducing gas was a mixture of 5% H_2 in Ar at a flow rate of 30 ml/min. Powder X-ray diffraction (XRD) studies were conducted and analyzed as described in a previous publication [15].

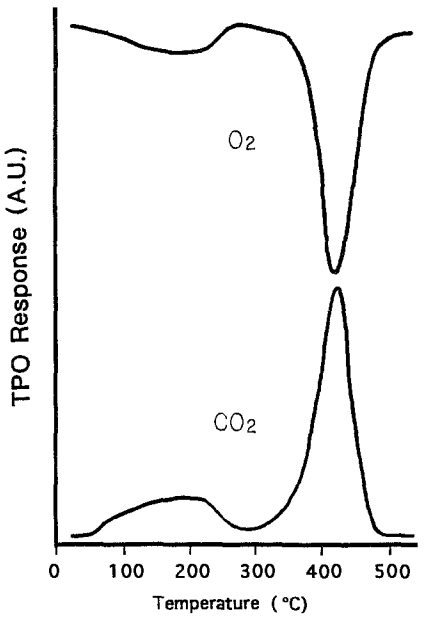

Fig. 1. Rate of O_2 consumption and CO_2 evolution during temperature programmed oxidation of NaY–NaAc.

3. Results

The TPO profiles of NaY–NaAc are presented in fig. 1 for O_2 consumption and CO_2 formation, respectively. The peak position for the oxidation of Na acetate in NaY zeolite appears at 415°C. For a Co/NaY–NaAc sample, however, the oxidation was completed at a remarkably lower temperature, i.e. 240°C as shown in fig. 2.

The TPR profile of H_2 consumption after calcination at 300°C is shown in fig. 3. The maximum rate of reduction is at 390°C. Quantitative analysis indicates complete reduction of Co. H_2 consumption is in fact twice that required for the reduction of Co^{2+}; the excess H_2 is presumably consumed in the reduction of partially oxidized products which were retained in the zeolite. For the Co/NaY–NaAc calcined at 500°C, reduction is complete at 630°C (with the last reduction maximum at 550°C as shown in fig. 4.

XRD patterns of reduced samples showed no discernable diffraction peaks due to Co metal. No changes in crystallinity or crystal parameters of the zeolite host are observed; XRD lines are neither shifted nor broadened.

4. Discussion

The results of this work show the success of a novel strategy in preparing catalysts by design: enhanced reduction of Co^{2+} ions in zeolites by in situ neutralization in the presence of an alkali oxide buffer.

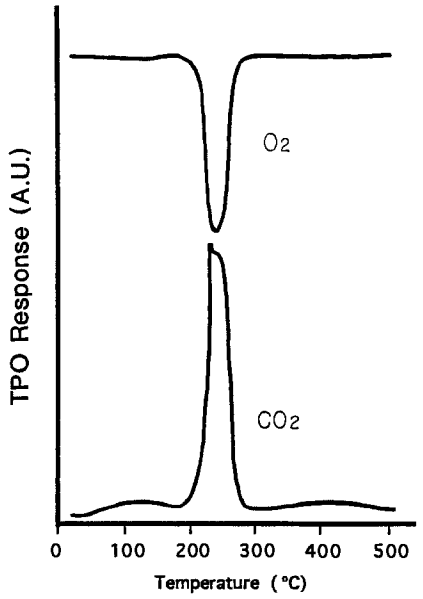

Fig. 2. Rate of O_2 consumption and CO_2 evolution in temperature programmed oxidation of Co/NaY–NaAc.

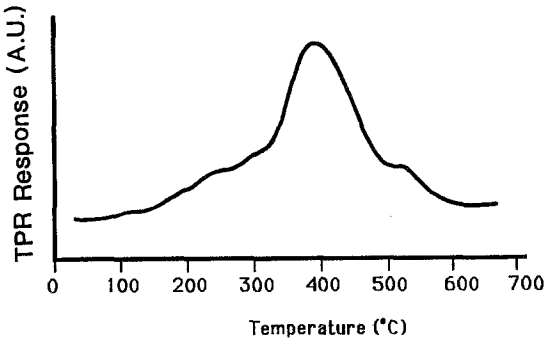

Fig. 3. Rate of H_2 consumption in temperature programmed reduction of Co/NaY–NaAc after calcination at 300°C.

The TPO results, shown in fig. 1 and fig. 2, of NaY–NaAc and Co/NaY–NaAc indicate a significant catalytic effect of Co ions on the oxidation of the acetate anion. The TPO (fig. 2) and TPR (fig. 3) profiles of the Co/NaY–NaAc catalysts indicate that calcination at 300°C and reduction at 500°C are optimum for efficient Co reduction. In the absence of a Na_2O buffer, calcination at 500°C induces migration of Co^{2+} ions into sodalite cages and hexagonal prisms [4] where they cannot be reduced below 750°C. The effect of introducing a precursor of a Na_2O buffer into the zeolite is illustrated by the TPR profiles in figs. 3 and 4. With respect to the 750°C reference case the downward shift of the TPR maxima by 200 or 350°C is striking. The fact that the TPR peak position still depends on the calcination temperature, 300 or 500°C respectively, suggests that Co^{2+} ions are still able to migrate from supercages to small cages. Presumably they will remain in their ionic state because the 2.2 Å window between supercage and sodalite cage does not permit migration of oxide species. In the samples calcined at 300°C, some partially oxidized product of (Co, Na) acetate may exist in the zeolite cages; its reduction will consume H_2. While bare Co^{2+} ions tend to migrate from supercages to sodalite cages upon dehydration at 300°C [4], the generation of Na_2O in the Co/NaY–NaAc sam-

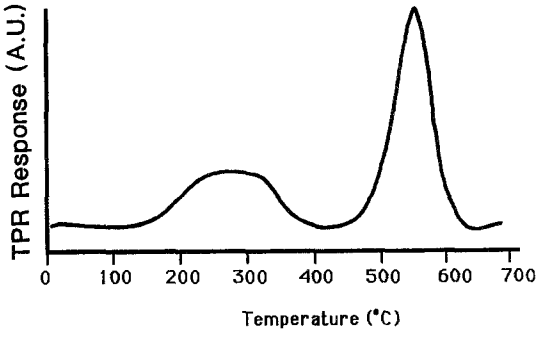

Fig. 4. Rate of H_2 consumption in temperature programmed reduction of Co/NaY–NaAc after calcination at 500°C.

ples evidently stabilizes Co^{2+} ions in the supercages. An ion coordination with Na_2O and supercage oxygens, O_z, such as

$$Na_2O–Co^{2+}(O_z)_3$$

appears probable, because it is unlikely that Na_2O will migrate to sodalite cages. At high calcination temperature, however, migration of Co^{2+} ions to hexagonal prisms will occur because of the favorable coordination in these sites. As a result, the reduction maximum shifts to higher temperature. However, the reducibility of the Co^{2+} ions is still markedly higher than in the untreated samples after calcination at the same temperature of 500°C. We attribute this remarkable phenomenon to an in situ neutralization of the protons, that are generated in (1). This phenomenon drives reaction (1) irreversibly toward Co^{2+} reduction.

5. Conclusion

Impregnating a gently dried Co/NaY catalyst precursor with sodium acetate dramatically enhances the reducibility of the Co^{2+} ions. As a result it becomes possible to reduce the Co^{2+} ions at a temperature up to 350°C lower than for samples that were not treated with sodium acetate. This provides a method to quantitatively reduce Co without damaging the zeolite framework. The results suggest that sodium acetate is partially or completely oxidized during calcination; the Na_2O apparently exerts two functions: (1) it impedes migration of Co^{2+} ion from large to small zeolite cages; and (2) it shifts the reduction equilibrium by neutralizing the protons that are formed during ion reduction with H_2. The chemistry is not specific for Co but should also be applicable to other zeolite supported metals with problematic reducibility, e.g. Ni.

Acknowledgement

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References

[1] Z. Zhang, S.L. Suib, Y. Zhang, W.A. Hines and J.I. Budnick, J. Am. Chem. Soc. 110 (1988) 5569.
[2] Z. Zhang, Y. Zhang, W.A. Hines, J.I. Budnick and W.M.H. Sachtler, J. Am. Chem. Soc. 114 (1992) 4843.
[3] D-J. Koh, J.S. Chung and Y.G. Kim, J. Chem. Soc. Chem. Commun. (1991) 849.
[4] Z. Zhang, W.M.H. Sachtler and S.L. Suib, Catal. Lett. 2 (1989) 395.

[5] M-S. Tzou, M. Kusunoki, K. Asakura, H. Kuroda, G. Moretti and W.M.H. Sachtler, J. Phys. Chem. 95 (1991) 5210.
[6] Z. Zhang, L. Xu and W.M.H. Sachtler, J. Catal. 131 (1991) 502.
[7] J.S. Feeley and W.M.H. Sachtler, J. Catal 131 (1991) 573–581.
[8] D. Fraenkel and B.C. Gates, J. Am. Chem. Soc. 102 (1983) 2478.
[9] Z. Zhang and W.M.H. Sachtler, J. Chem. Soc. Faraday Trans. 86 (1990) 2313.
[10] J.S. Feeley and W.M.H. Sachtler, Zeolites 10 (1990) 738.
[11] G. Lu, T. Hoffer and L. Guczi, Catal. Lett. 14 (1992) 207.
[12] M. Suzuki, K. Tsutsumi, H. Takahashi and Y. Saito, Zeolites 8 (1988) 381.
[13] M. Suzuki, K. Tsutsumi, H. Takahashi and Y. Saito, Zeolites 8 (1988) 284.
[14] W.M.H. Sachtler, Z. Zhang, A.Yu. Stakheev and J.S. Feeley, 10th Int. Congr. on Catalysis, Budapest 1992, preprint O9.
[15] Y.G. Yin, Z. Zhang and W.M.H. Sachtler, J. Catal., in press.