

## Oxidation of Carbon Monoxide with Silver-exchanged Mordenite Containing Cobalt in Framework Sites

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The catalytic activity of Ag-exchanged mordenite containing Co atoms in framework positions (Ag/CoMOR) was investigated for CO oxidation. The activity of the Ag/CoMOR catalyst was found to be higher than that of an aluminosilicate mordenite catalyst coexchanged with Ag and Co.

Various metallosilicates possessing a zeolitic structure have been synthesized, and their catalytic properties have been investigated for acid-catalyzed reactions and oxidation reactions.<sup>1</sup> Metallosilicates containing di- and trivalent transition-metal cations in framework positions have ion-exchange capacity, and bimetallic sites can be formed in the micropores of metallosilicates by ion exchange with different transition-metal cations. Komatsu et al. reported cooperative action of ion-exchanged Cu<sup>2+</sup> and framework Fe<sup>3+</sup> in MFI-ferrisilicate for the selective catalytic reduction of NO.<sup>2</sup> In addition, Inui et al. reported CO oxidation over rhodium-exchanged zeolite A containing Cu<sup>2+</sup> in framework sites.<sup>3</sup> Such bimetallic sites composed of ion-exchanged and framework transition-metal atoms are expected to be effective for various catalytic reactions. However, few examples of catalytic reactions using ion-exchanged metallosilicates have been reported thus far.<sup>2-4</sup>

The oxidation of CO has been used not only as a research tool to study heterogeneous catalysis but also for practical applications such as cleaning air.<sup>5</sup> In addition, the oxidation of residual CO in hydrogen fuels for polymer-electrolyte fuel cells has recently been studied extensively.<sup>6</sup> Supported Au nanoparticles have been reported to be active for low-temperature oxidation of CO.<sup>5</sup> Zeolite-supported metal catalysts also have been studied for CO oxidation.<sup>6</sup> One of the advantages of zeolite catalysts is that CO molecules with low concentration in the gas phase can be adsorbed in zeolite pores and be reacted with oxygen preferentially.<sup>7</sup> Therefore, the stabilization of active sites in zeolite pores is a promising way to develop a high-performance catalyst for CO oxidation.

Recently, Kato et al. have synthesized Co-containing mordenite, in which framework Al is partially substituted with Co.<sup>8</sup> As an active component for CO oxidation, the combination of framework Co of metallosilicates and ion-exchanged Ag is of interest, because a composite oxide of Co and Ag was reported to be active for CO oxidation at low temperature (<423 K).<sup>9</sup> In this study, the catalytic activity of Ag-exchanged mordenite containing framework Co was investigated for CO oxidation.

The synthetic procedure for a Na form of Co-substituted mordenite (CoMOR) was reported by Kato et al.<sup>8</sup> The atomic ratios of Si/Al and Co/Al for synthesized CoMOR were 9.8 and 0.059, respectively. A Ag-exchanged CoMOR sample (Ag/CoMOR) was prepared as follows. The as-synthesized CoMOR

sample was heated at 673 K for 1 h in air and then stirred in a 0.1 mol dm<sup>-3</sup> aqueous solution of AgNO<sub>3</sub> with a solution/zeolite ratio of 100 cm<sup>3</sup> g<sup>-1</sup> at room temperature for 1 h. This was followed by filtration, washing with water, and drying at room temperature. Silver-exchanged mordenite (Ag/MOR) was also prepared in the same way from a Na form of aluminosilicate mordenite (MOR) (HS-642, Wako Chemical) with a Si/Al atomic ratio of 9.6. Cobalt-exchanged mordenite (Co/MOR), and Co- and Ag-coexchanged mordenite (CoAg/MOR) were prepared by the ion exchange of MOR and Ag/MOR, respectively, using a 0.001 mol dm<sup>-3</sup> aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub> in the same procedure.

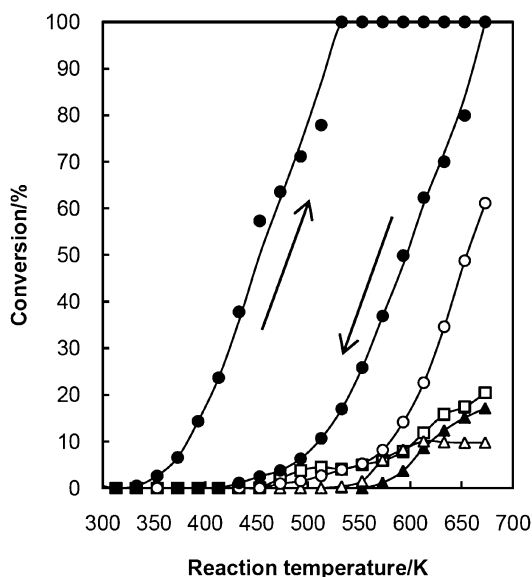
The amounts of Ag and Co in the mordenite samples were determined using an energy-dispersive X-ray fluorescence spectrometer (ED-05, X-tec). The X-ray diffraction (XRD) patterns were measured using a RINT-2200VK/PC diffractometer (Rigaku). Catalytic activity for CO oxidation was investigated by a temperature-programmed reaction. A reaction mixture composed of 0.8% CO, 20% O<sub>2</sub>, and He (balance) was fed to a glass tube reactor (4 mm in inner diameter) containing a mordenite catalyst (0.020 g) under atmospheric pressure, and the reactor was heated at a constant rate of 4 K min<sup>-1</sup> from room temperature up to 673 K. The outlet gases of the reactor were analyzed with a gas chromatograph (GL Science, GC-3200 with activated carbon columns).

Table 1 shows the atomic ratios of Ag and Co to Al, as determined by X-ray fluorescence spectroscopy. The Ag content of Ag/CoMOR was close to the Ag contents of Ag/MOR and CoAg/MOR. The Co content of Ag/CoMOR was comparable to the Co contents of Co/MOR and CoAg/MOR.

Figure 1 shows the activity of the catalysts for CO oxidation as a function of reaction temperature. The conversion of CO over Ag/CoMOR started at 353 K increased with increasing reaction temperature and reached 100% at 533 K. The activity of Ag/CoMOR was much higher than that of CoMOR, which was inactive below 573 K. This indicates that the exchanged Ag in Ag/CoMOR plays an important role in CO oxidation. On the other hand, the activity of Ag/MOR was modest; CO conversion started at 473 K and was only 20% at a reaction temperature of 673 K. Conversion values with Ag/CoMOR were found to be

**Table 1.** Ratios of cobalt and silver to aluminum

Catalyst	Atomic ratio	
	Ag/Al	Co/Al
Ag/CoMOR	0.84	0.044
Ag/MOR	0.96	—
Co/MOR	—	0.050
CoAg/MOR	0.88	0.035



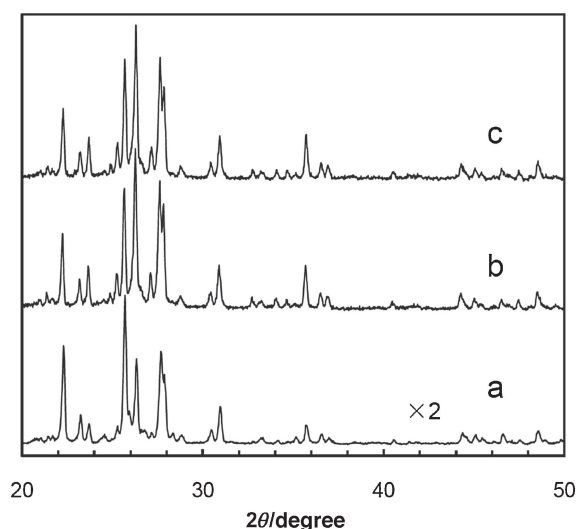
**Figure 1.** Carbon monoxide oxidation over CoMOR ( $\blacktriangle$ ), Ag/CoMOR ( $\bullet$ ), Ag/MOR ( $\square$ ), Co/MOR ( $\triangle$ ), and CoAg/MOR ( $\circ$ ). Reaction mixture: 0.8% carbon monoxide, 20% oxygen, helium (balance); flow rate:  $25 \text{ cm}^3 \text{ min}^{-1}$ ; catalyst weight: 0.020 g; heating rate:  $4 \text{ K min}^{-1}$ .

much larger than the sum of those with CoMOR and Ag/MOR at the same temperature, indicating that the Ag and Co of Ag/CoMOR exhibited a synergistic effect on CO oxidation.

Furthermore, the activity of Ag/CoMOR was much higher than that of coexchanged CoAg/MOR, which showed CO oxidation activity beyond 473 K. Conversion values with CoAg/MOR were nearly equal to the sum of those with Co/MOR and Ag/MOR at the same temperature below 633 K, indicating that ion-exchanged Ag and Co did not exhibit a synergistic effect on CO oxidation below 633 K. Therefore, it is suggested that the Co cations in framework positions are important to the synergistic effect on CO oxidation.

Figure 2 shows the XRD patterns of CoMOR, as-prepared Ag/CoMOR, and Ag/CoMOR after heating in the reaction mixture (0.8% CO, 20% O<sub>2</sub>, and He balance) up to 453 K (i.e., the point at which CO oxidation occurs). Only mordenite phase was detected in the XRD patterns of CoMOR and both Ag/CoMOR samples, although the relative intensities of the diffraction peaks changed after Ag exchange. It has been reported that Ag<sup>0</sup> metal particles are active for CO oxidation at low temperature (<423 K).<sup>10</sup> However, such particles are likely not the active sites of Ag/CoMOR, because diffraction peaks attributed to Ag bulk were not detected in the XRD pattern of Ag/CoMOR heated in the reaction mixture to 453 K. It is probable that active sites are created by the combination of framework Co atoms and ion-exchanged Ag ions dispersed in the micropores of the mordenite structure.

In the temperature-programmed reaction using Ag/CoMOR, the reactor was cooled in the reaction mixture at a constant rate of  $-2 \text{ K min}^{-1}$  after the temperature reached 673 K (Figure 1). Conversion values during cooling were lower than those during prior heating, indicating that Ag/CoMOR was deactivated by heating to 673 K in the reaction mixture. To test whether this deactivation was caused by heat alone, we



**Figure 2.** XRD patterns of CoMOR (a), as-prepared Ag/CoMOR (b), and Ag/CoMOR after heating in the reaction mixture (0.8% carbon monoxide, 20% oxygen, and helium balance) up to 453 K (c).

examined the activity of Ag/CoMOR heated previously in air at 673 K. Under these conditions, the activity of Ag/CoMOR was identical to that of as-prepared Ag/CoMOR, suggesting that the deactivation of Ag/CoMOR is not caused by heat alone.

In summary, we found a synergistic effect of ion-exchanged Ag ions and substituted framework Co atoms of Ag/CoMOR on CO oxidation. Further studies are required to elucidate the local structure and distribution of the active sites in the crystal and to improve catalytic stability.

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