Effect of Ammonia on Carbon Monoxide Hydrogenation Over Various Metal Oxides

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The effect of ammonia on CO hydrogenation over a number of irreducible metal oxides is to enhance the hydrogenation ability of the oxides due to heterolytic dissociation of the preabsorbed ammonia to form NH_2^- and H^+ species.

In the literature, there are very few examples of oxides used as CO hydrogenation catalysts. In this paper we report for the first time the observation of a significant effect of the preadsorption of ammonia over oxides such as MgO, CaO, SrO, BaO, TiO_2, ZrO_2, La_2O_3, CeO_2, MnO_2, ZnO, Al_2O_3 and SiO_2; however, Fe_3O_4 and CdO were exceptions.

All of the oxides used were analytically pure powdered reagents, which were pressed into a disc, calcined at 500 °C, pulverized and sieved to 20–40 mesh for use. The CO hydrogenation reactions were performed in a fixed-bed reactor with 2.0 ml of catalyst (blank test of reactor showed negligible activity). The reaction conditions were: 360 °C, 0.8 MPa syngas ($H_2 : CO = 4 : 1$), and 750 ml ml^{-1} cat h^{-1} space velocity. After the reaction began, the hydrocarbon products were analysed at 10 min intervals using an on-line chromatograph containing a capillary column coated with alumina and using a flame ionization detector.

In order to investigate the ammonia effect, 200 ml of ammonia gas were injected into the nitrogen stream and passed through the catalyst bed at 360 °C *in situ* to allow reaction to occur. After 5 min the residual ammonia in the reactor was purged with nitrogen. Thus, the effect of nitrogen could be excluded. Fig. 1 shows that nitrogen purging can slightly affect the CO conversion; this might be due to purging

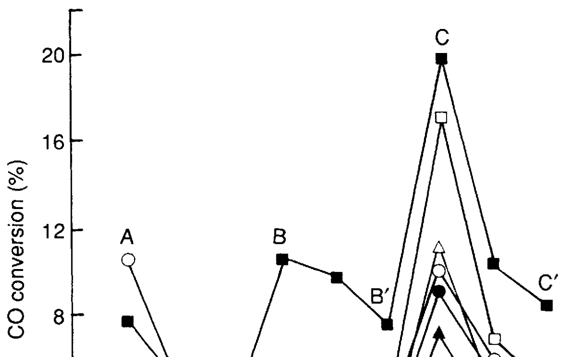

Fig. 1 Conversion of CO *versus* time on stream. Line A′, B for N_2 and B′ and C, for NH_3 treatment, respectively. ■, CeO_2; □ MgO; △, SrO; ▲, CaO; ○, BaO; ●, ZrO_2; ▽, TiO_2; and ▼, La_2O_3.

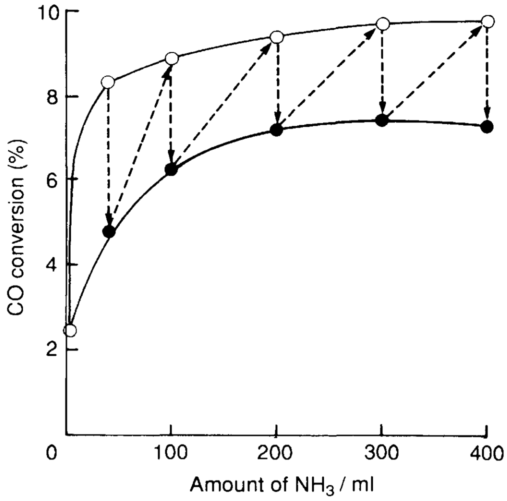

Fig. 2 Effect of the amount of ammonia on the conversion of CO on ZrO_2 (the arrows show the exposure sequence). ○, Obtained after 10 min of reaction after adsorption of the corresponding amount of NH_3; ●, 10 min after the first sample.

	C_1	C_2	C_3	C_4
	(mol %)			
○	47.1	27.4	20.1	5.4
●	52.9	26.2	16.5	4.4

of deposited carbon, which blocks the active centres. This explanation is supported by the fact that N_2 mixed syngas shows no CO conversion improvement. When ammonia was injected, CO conversion greatly increased. Apparently the ammonia is affecting this reaction.

For further clarification, the quantitative effect of ammonia on CO convesion over ZrO_2, used as a representative oxide, was studied in more detail. The results are shown in Fig. 2. The CO conversion is greatly enhanced at first, followed by a sharp decrease after 20 min. Subsequently injection of more NH_3 again increased the CO conversion to a slightly higher level than in the previous stage.

In order to explain the observed phenomena, ESR characterization of the O_2^- (formed through adsorbed oxygen attacking the dissociated NH_3) on ZrO_2 was performed. These results are the same as Stone *et al.*[1] obtained on MgO, which means that the NH_3 dissociated into NH_2^- and H^+. Thus, the H^+ formed increased the concentration of active hydrogen species on the oxide surface and resulted in an increase of the oxide hydrogenation ability. It is predicted that this ability will quickly disappear. This explanation is also supported by an observed decrease of the alkene to alkane ratio by the adsorption of ammonia.

The different behaviours of Fe_3O_4 and CdO can be explained as follows: X-ray diffraction patterns indicated that both are partly reduced to metals under the reaction conditions, so that sufficient hydrogen species for CO hydrogenation are formed; however, the hydrogen species required are lacking on the pure oxide surface. Therefore, the adsorbed ammonia only blocks the active centres rather than acting as a promoter; thus CO conversion decrease over a reducible oxide is predictable.

The effect that ammonia has on CO hydrogenation over the aforementioned unreducible metal oxides appears to be general. This may be a reflection of a fundamental property of the metal oxide. Therefore, it would seem to be useful for us to focus attention on the oxide catalysts used for the Fischer–Tropsch synthesis of light alkenes in view of the limited activity of the oxides in carbon chain propagation and hydrogenation.

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Reference

1 E. Garrone and F. S. Stone, *Proceedings of the 8th International Congress on Catalysts, Berlin (West)*, Dechema, 1984, vol. 3, p. 441.