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ACCEPTED MANUSCRIPT

<AT>Kinetic modelling of temperature-programmed reduction of cobalt oxide by hydrogen

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Highlights►

<ABS-Head><ABS-HEAD>Graphical abstract

<ABS-P>

<ABS-P><xps:span class="xps_Image">fx1</xps:span><ABS-HEAD> \blacktriangleright Highlights \blacktriangleright A 5-steps reduction mechanism for Co_3O_4 was proposed; \blacktriangleright The promoter improved the reducibility of Co_3O_4 while little on CoO; \blacktriangleright Reduction difficulties follow the order: Ru-Co-La/Al₂O₃ < Ru-Co/Al₂O₃ < Co/Al₂O₃; \blacktriangleright High crystallinity increases the difficulty of reducing Co₃O₄ instead of intermediates; \blacktriangleright The interaction between CoO and Al_2O_3 to form $CoAl_2O_4$ was modelled.

<ABS-HEAD>Abstract

<ABS-P>The reduction activities and mechanisms of cobalt-based catalysts are of great interest to industry and researchers, due to their applications in Fischer–Tropsch synthesis. Here, we investigated the reduction of alumina-supported cobalt catalysts by hydrogen using temperature-programmed reduction. We propose a five-step reduction mechanism that incorporates both amorphous and crystalline Co₃O₄, and includes the interaction between CoO and the Al₂O₃ support. Based on our proposed mechanism, we developed a kinetic model of the reduction process. The modelling results of catalysts promoted with ruthenium and lanthanum in contrast with un-promoted catalyst clearly show that the promoter improves reducibility of the catalyst. The effect of Co₃O₄ crystallinity was also investigated by the reduction of fresh in comparison of pre-oxidised catalyst. We conclude that high crystallinity significantly increases the difficulty of reducing Co₃O₄. The interaction between CoO and Al₂O₃ under reduction conditions to form CoAl₂O₄ was quantitatively simulated. The kinetic modelling confirms that the support plays an important role in catalyst reduction via the interaction between the catalyst and the support. Those kinetic modelling results are supported by in situ X-ray diffraction studies of the reduction process. <KWD>Keywords:

Catalysis; Temperature-programmed reduction; Cobalt oxide; Kinetic modelling; Reduction mechanism; Fischer–Tropsch synthesis

<td:DefL>Nomenclature **list**

 $<xps:span class=deft>I_i </xps:span> <xps:span class=defd>TCD signal intensity (a.u.) at time I;</xps:span>$

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