



Iron oxide based catalysts: a temperature programmed reduction study

Ajay Kumar^{1*} and Bharmana Malvi²

¹Analytical Sciences, T&I, SABIC Research & Technology Pvt. Ltd, Plot No. 81 to 85, Chikkadunnasandra, Sarjapura - Attibele State Highway, Bengaluru, Karnataka-562125, India

²Olefins Platform, SABIC Research & Technology Pvt. Ltd, Plot No. 81 to 85, Chikkadunnasandra, Sarjapura - Attibele State Highway, Bengaluru, Karnataka-562125, India
ajay.kumar@sabic.com

Available online at: www.isca.in, www.isca.me

Received 18th June 2021, revised 22nd August 2021, accepted 11th September 2021

Abstract

Reduction process of iron oxides using hydrogen is a complex phenomena which needs to be understood properly to know about role of various phases of iron oxide in the functioning of catalyst. A detailed Temperature Programmed Reduction (TPR) study of iron oxide based catalyst has been reported here. Apart from fundamental behavior in terms of phase transformation as a result of reduction, the effect of various parameters like preparation methods, use of iron precursors, promoters and additives have also been studied in the present study. The reduction was found to be a multistage and stepwise process depending strongly on various factors like catalyst preparation method, iron precursor and presence of additives. This H₂-TPR study further showed that, when Fe was more than 45%, reduction happened to be a three stage process (hematite Fe₂O₃ → magnetite Fe₃O₄ → wustite FeO → Fe), however when Fe is less than 30% it reduces through a two stage process (Fe₂O₃ → Fe₃O₄ → Fe). Also it was found that interaction of alumina (10%) with iron can make it possible to have reduction route through metastable FeO. However, with increasing Al content, alumina interacted strongly with iron oxide and resulted in the formation of spinel phase which was not easy to reduce. The presence of K and Mg in the catalyst shifted reduction towards high temperature.

Keywords: Temperature programmed reduction, Catalyst, Iron oxide, Hematite, Magnetite, Wustite.

Introduction

The reduction phenomena of iron oxides using hydrogen or carbon monoxide is known to play a significant role in several catalytic applications for example, Fisher-Tropsch (FT) process, production of styrene from ethylbenzene dehydrogenation, ammonia synthesis, etc.^{1,2}. Numerous articles have been published in literature to understand the iron oxide reduction behavior in hydrogen³⁻¹⁰.

The overall reduction process is known to be complicated which can be influenced significantly by the physicochemical properties of the iron oxide and reduction conditions. The published results show wide variations as there are several forms of iron oxides and oxyhydroxides (hematite (α -Fe₂O₃), magnetite (Fe₃O₄), wustite (FeO), goethite (α -FeOOH.xH₂O), and ferrihydrite (Fe₅HO₈.4H₂O)), and their reduction processes are different in terms of temperature range, and additives or impurities present. Iron oxides viz., Fe₂O₃, Fe₃O₄, and FeO show different oxidation states and further have propensity towards oxidation of Fe²⁺ to Fe³⁺. Further this problem become more complicated when iron oxide based catalysts are added with promoters or other additives to get better catalyst performance in terms of selectivity, mechanical strength etc. Thus the complex reduction phenomena of iron oxide based catalyst containing promoters and additives which influences reducibility of iron oxide due to the metal interaction (among

various metal constituents) and phase transitions, needs to be understood properly, including the effect of preparation condition on the reduction behavior (temperature, composition, content etc.). To address these important aspects and gaps, the present study has been carried out with focus on the temperature programmed reduction behavior of different iron oxide based catalysts. Based on the catalyst preparation method, catalyst composition and iron precursor involved in the catalyst preparation, H₂-TPR behavior was studied and findings of the present study are reported here.

Methodology

Sample preparation: The fresh catalyst was obtained by extrusion of a mixture of iron hydroxide/oxide along with alumina binder and potassium (K)/ magnesium (Mg) promoters. Iron hydroxide/oxide used is either obtained by thermal decomposition of ferric nitrate or commercially available iron oxide powder used, as received¹¹. Extrudates formed were dried and then calcined at temperature of 550°C in the presence of air. Alumina in form of Boehmite was used as modifier (binder) to provide the mechanical strength to the shaped calcined catalyst. These bulk catalysts have been prepared by varying composition in terms of iron, K and/or Mg promoter, and binder content. These preparations were divided into three sets as described in the Table-1.

Table-1: Catalyst details.

Set no.	Catalyst	Synthesis details	Calcination temp. (°C)	Bulk catalyst composition (wt.%)				Fresh Catalyst phase
				Fe	K	Al	Mg	
Set A	CAT-1	Thermal decomposition of mixture of ferric nitrate & potassium nitrate (KNO ₃)	550	30-50	2-5	10-30	0	Fe ₂ O ₃
	CAT-2							
	CAT-3							
	CAT-4							
Set B	CAT-5	Commercial ferric oxide impregnated with KNO ₃	550-750	40	3-10	20	0	Fe ₂ O ₃
	CAT-6							
	CAT-7							
Set C	CAT-8	Thermal decomposition of mixture of ferric nitrate, KNO ₃ and magnesium nitrate.	550	30-50	2-4	8-25	1-3	Fe ₂ O ₃
	CAT-9							

TPR measurement method: The TPR measurements were made on Micromeritics Autochem-2920 instrument. In TPR method, the catalyst sample is subjected to a programmed linear temperature ramp under the flow of reduction gas. Before the reduction step, about 50mg of catalyst was dehydrated at 350°C by flowing pure argon for 30 minutes. Then argon containing 10% hydrogen (H₂-Ar) was flown through the sample at 50cm³/minute flow. The sample temperature was increased up to 850°C with constant ramp (5°C/min) and the hydrogen consumed was measured simultaneously with a thermal conductivity detector (TCD) against the reaction temperature.

Results and discussion

Iron oxide is known to exist in several phases (hematite, megamite, magnetite and wustite) which influence catalyst properties and behavior quite significantly. Conventionally, X-ray diffraction (XRD) and Raman spectroscopic methods have been employed to analyze the various forms of iron oxide based catalyst^{10,12-14}. Both provide valuable information about various iron oxide phase formed at different stages of the reaction (fresh, reduced and after reaction). However, both these techniques provide information in stationary state. Also, XRD does not give in formations about amorphous phases/structures and it also becomes difficult to identify the poorly or weakly crystalline phase. Raman, on the other hand, is not sensitive to produce signals for metallic forms (elemental iron). The other challenge with Raman study is, since iron phases have natural tendency to be oxidized thus Raman measurements with using laser can sometime cause in-situ phase transformation during measurements and make it difficult to measure the original phase¹⁴. To eliminate such limitations, here in present work we employed TPR technique to study the iron oxide phase formation/transformation during reduction using H₂ gas. Temperature programmed analysis (TPA) techniques have been applied to understand catalyst characteristics¹⁵⁻¹⁷. In fact TP analysis methods have ability to analyze a material in transient state where surface coverage, desorption-reaction rates, temperature etc. vary with time. This is advantageous over techniques like XRD or Raman. Among the various TPA

techniques, TPR has been found to be very useful tool to analyze the reduction behavior of catalytic materials¹⁷⁻²⁵. Further TPR has been treated as a powerful technique for the estimation of reduced components simply because hydrogen consumed during reduction gives a measure of the reduced product. In addition, the TPR provides the vital in formations on, how the support and promoters influence the reduction behavior.

In the present H₂-TPR study, various catalyst samples prepared, were divided in to three sets viz., A, B and C, based on iron precursors used, preparation method, and catalyst composition and their reduction behavior was studied. Various TPR profiles shown in Figures-1 to 3 showed multiple peaks which are broad and overlapped. These peaks were convoluted in order to elucidate the reduction stages and for the determination of H₂ consumption for relative and qualitative comparison. The important results and findings of the detailed and systematic H₂-TPR study are being discussed here.

Set-A: These catalysts were prepared via thermal decomposition of mixture of ferric nitrate and potassium nitrate¹¹. TPR profiles of these four samples (Figure-1) shows multiple reduction peaks indicating that the reduction is occurring at various stages. For CAT-1, the first two peaks are relatively close to each other. Both these peaks at 368°C and 397°C are appeared as a result of reduction of Fe₂O₃ to Fe₃O₄. These two peaks indicate that both maghemite (γ-Fe₂O₃) as well as hematite (α-Fe₂O₃) co-exist. Maghemite (γ-Fe₂O₃) is reported to be reduced at slightly low temperature as compared to hematite (α-Fe₂O₃)⁷. Further these peaks are not so well resolved indicating that before maghemite gets completely reduced, hematite starts reducing. The possible reason could be weak maghemite as compared to dominating hematite phase. After this there is broad and overlapped peaks. The peak at 512 °C shows the reduction of magnetite (Fe₃O₄) to wustite (FeO) which is metastable and reported unstable below 570°C^{1,13,26-28}. Thus immediately it is further reduced to metallic Fe (broad peak with maxima around 680°C).

Interaction of alumina (10% Al) with iron can make it possible to have reduction route through metastable FeO as reported in literature²¹. The sample CAT-2 with Fe 40% and increased amount of Al, showed first reduction (very weak) peak at $\approx 333^\circ\text{C}$ and strong reduction peak at 398°C for Fe_2O_3 to Fe_3O_4 transition. After that there is very weak and broad peak showing further reduction is weak and partial. The other samples CAT-3 and CAT-4 also possess similar type of TPR behavior. In CAT-3, the weak peak does not appear and strong bands showed significant shift towards low temperature and appear at 331°C . Where as in CAT-4 strong peak was observed to be shifted to higher temperature and appeared at $\approx 416^\circ\text{C}$.

These samples have variation in composition (Fe, K and Al content). Iron phase of fresh catalyst was same (Fe_2O_3). In case of CAT-2, Fe is reduced to 40% and Al is increased to 20%, after major reduction of Fe_2O_3 to Fe_3O_4 (at 398°C), subsequent reduction of FeO to Fe was found to be weak or retarded. This is due to the fact that with increasing Al content, alumina interacts

strongly with iron oxide^{21,29-30}. This leads to the formation of spinel structure of iron–alumina which is not easy to reduce¹⁰. This is also clearly evident from the trend of H_2 consumed (Table-2). In CAT-1 first reduction was found at about 400°C and the subsequent reductions were showing strong peaks with good H_2 consumption. Overall reduction is good in this sample. However in CAT-2 sample, Al content is increased, so first reduction itself is comparatively weak. Reduction in CAT-3 is further weak due to low content of iron oxide. The stable FeO phase may appear due to strong iron-alumina interaction²¹. This can result further a slow or delayed reduction of FeO to Fe (observed in CAT-3). Comparison of CAT-2 and CAT-4 (having same chemical composition) showed that observed differences are attributed to preparation method. KNO_3 impregnation in CAT-4 has been done after thermal decomposition step unlike other samples, which is causing reduction to be pushed towards higher temperature⁸. This in turn shows that catalyst preparation method has directly influenced the reduction profile of the sample.

Table-2: TPR results on iron based catalyst.

SET-A			SET-B			SET-C		
Samples	T _{Max} (°C)	H ₂ Quantity (mmol/g)	Samples	T _{Max} (°C)	H ₂ Quantity (mmol/g)	Samples	T _{Max} (°C)	H ₂ Quantity (mmol/g)
CAT-1	368	0.255	CAT-5	425	0.977	CAT-8	390	1.809
	397	2.173		511	2.535		437	1.364
	512	5.260		671	3.422		499	2.809
	679	5.814					666	5.211
	Tot. H ₂	13.503		Tot. H ₂	6.934		Tot. H ₂	11.193
CAT-2	333	0.252	CAT-6	365	0.106	CAT-9	327	0.297
	398	0.793		401	1.349		387	0.629
	471	2.162		465	0.319		479	0.734
	653	3.547		627	5.690		617	4.596
	Tot. H ₂	6.754		Tot. H ₂	7.464		Tot. H ₂	6.255
CAT-3	331	0.763	CAT-7	419	2.419			
	402	1.237		596	7.355			
	526	1.452						
	608	0.413						
	707	0.922						
	Tot. H ₂	4.787						
CAT-4	416	4.132		Tot. H ₂	9.774			

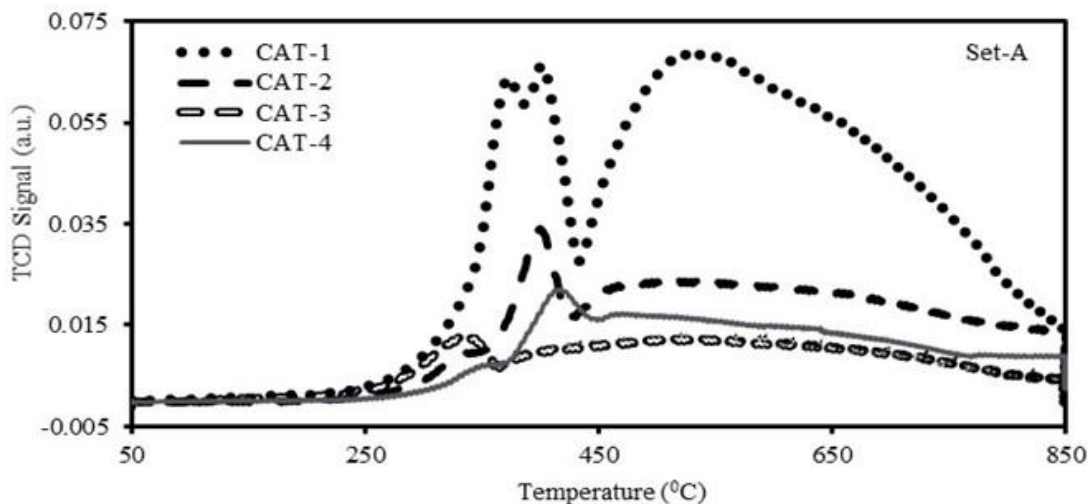


Figure-1: TPR profiles of iron oxide catalysts (Set-A).

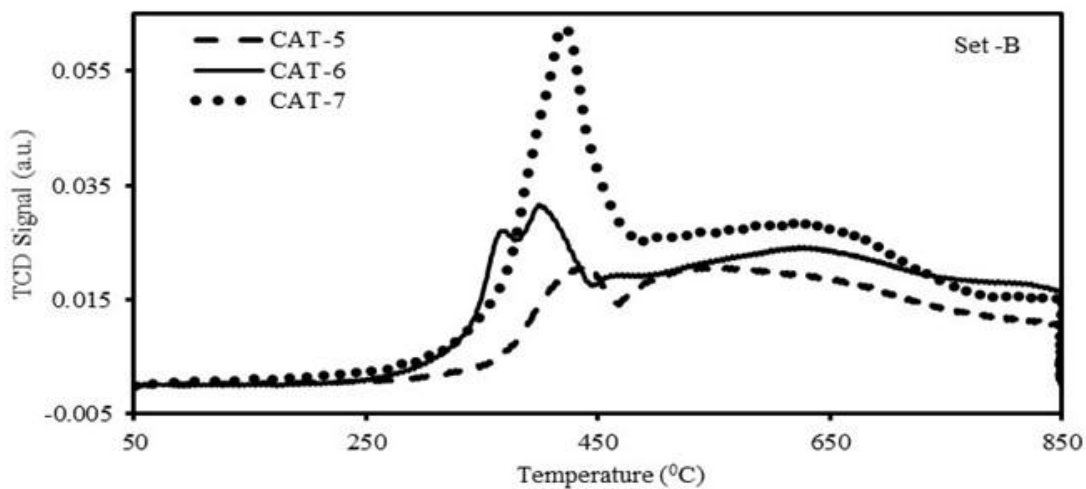


Figure-2: TPR profiles of iron oxide catalysts (Set-B).

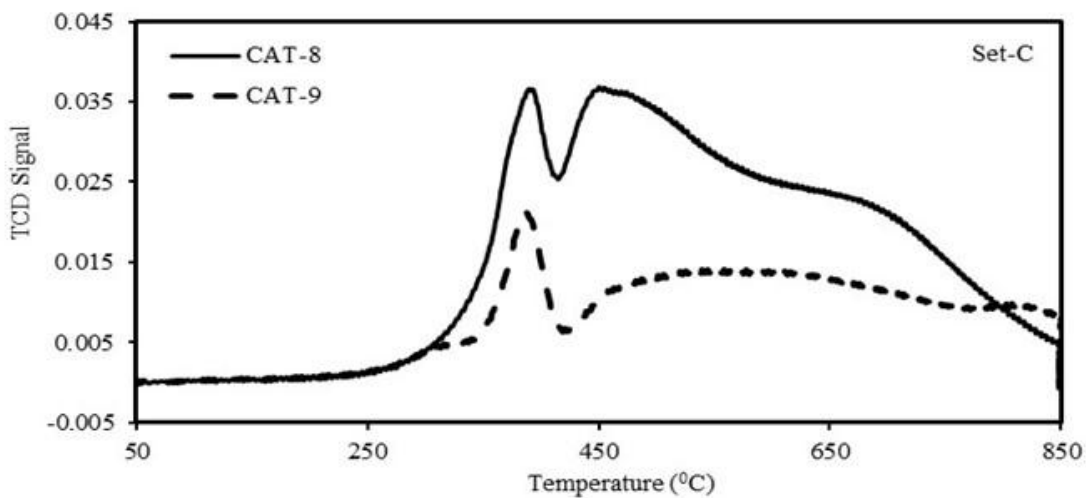


Figure-3: H₂-TPR profiles of iron oxide catalysts (Set-C).

Set-B: These catalysts were prepared using commercial ferric oxide after impregnating it with potassium nitrate (KNO_3). The H_2 -TPR profile of these three catalyst samples have been shown in Figure-2. The TPR characteristic of CAT-5 and CAT-7 are of similar type, with strong peak at about 425°C showing reduction of Fe_2O_3 to Fe_3O_4 . Further, we do not see reduction from Fe_3O_4 to FeO and instead it reduces directly to elemental Fe. The overall reduction is poor in CAT-5 which can be attributed to high calcination temperature (750°C). The TPR curve of CAT-6 has different reduction behavior as there are two clear peaks at 365 and 400°C indicating reduction is proceeding through FeO route. Further reduction is partial in temperature range 400 - 800°C . In CAT-7, sample with higher potassium content ($\approx 8\%$), the first reduction peak becomes strong with 2.4mmol.g^{-1} of H_2 consumption, but subsequent reduction was found to be weak and retarded. Further, additional KNO_3 impregnation in CAT-7 shifts the reduction peak towards higher temperature by about 25 - 30°C i.e. indicating its effect on reduction behavior. Similar results of potassium influence were obtained by Farias et al.⁸. This observed reduction behavior could be due to either strong interaction among various oxides (Fe & K) and /or electronic shifts/effects (as alkali metals are electron donor so electron affinity decreases for H_2 uptake)³¹.

Set-C: Here precursor compound is ferric nitrate. The catalysts preparation was carried via thermal decomposition of mixture of ferric nitrate, potassium nitrate and magnesium nitrate. The TPR profiles of these two catalyst samples i.e. CAT-8 and CAT-9 are shown in Figure-3. The first reduction peak is around 380 - 390°C owing to Fe_2O_3 reduction to Fe_3O_4 . Subsequently reduction to iron is occurring but peaks are broad and overlapped. In CAT-8 the reduction peaks are at about 450°C and 680°C due to magnetite (Fe_3O_4) reduction to wustite (FeO) and further wustite to elemental iron respectively. In CAT-9 the broad and relatively weak band in range 400 - 800°C showed that further reduction is poor. The sample CAT-8 with 46% Fe and starting phase of Fe_2O_3 shows reduction behavior similar to CAT-1. The total H_2 consumption is little lower in CAT-8 as compared to CAT-1.

However, peak maxima indicates that presence of Mg (about 2%) is delaying initial reduction, thereby shifting first two reduction peaks towards higher temperature by about 30°C . Strong interaction among Fe-Al-Mg-O components, solid solution formation and as described in potassium case electronic transfer could be the possible factors for the observed results as described in literature^{9,32,33}.

In CAT-9, different reduction behavior was observed due to presence of increased Al content of 22% and decreased Fe (35%) content. The first reduction is normal but subsequent reduction is poor and prohibited. This overall observed reduction behavior of these catalysts are influenced by the complex interactions amongst the metal oxides as reported by several authors^{21, 29,30,34}.

Conclusion

The present H_2 -TPR study of iron oxide based catalyst showed that the reduction is multistage and stepwise process and depends strongly on various factors like preparation method, iron precursor and presence of additives. When Fe is more than 45% reduction is three stage process ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$). When $\text{Fe} < 30\%$ it becomes two stage process ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$). Similar type of behavior as reported by several other authors can be attributed to possible involvement of disproportionation reaction^{1,5,28}. Interaction of alumina (10%) with iron can make it possible to have reduction route through metastable FeO . With increasing Al content, alumina interact strongly with iron oxide and leads to the formation of spinel phase of iron– alumina which is not easy to reduce. The presence of K and Mg is shifting reduction towards high temperature. All these findings of the present study will be helpful in proper understanding about the reducibility of iron oxide catalysts in presence of additives, the effect of catalyst preparation method and further in optimizing the iron oxide based catalyst.

Acknowledgments

The authors thank Mr. Narayana Rao and Dr. B.V. Venugopal for their support and manuscript review.

References

1. Jozwiak, W.K., Kaczmarek, E., Maniecki, T.P., Ignaczak W., & Maniukiewicz W. (2007). Reduction Behavior of Iron Oxides in Hydrogen and Carbon Monoxide Atmospheres. *Appl. Catal. A: Gen.*, 326(1), 17–27. [https://doi: 10.1016/j.apcata.2007.03.021](https://doi.org/10.1016/j.apcata.2007.03.021).
2. Ndlela, S.C. and Shanks, B.H. (2003). Reducibility of Potassium-Promoted Iron Oxide Under Hydrogen Conditions. *Ind. Eng. Chem. Res.*, 42(10), 2112-2121.
3. Messi, C., Carniti, P., & Gervasini, A. (2008). Kinetics of Reduction of Supported Nanoparticles of Iron Oxide. *J. Therm. Anal. Cal.*, 91(1), 93-100.
4. Lin, H.Y., Chen, Y.W., & Li, C. (2003). The Mechanism of Reduction of Iron Oxide by Hydrogen. *Thermochim. Acta*, 400(1-2), 61- 67.
5. Fakeeha, A.H., Ibrahim, A.A., Naeem, M.A., Khan, W.U., Abasaeed, A.E., Alotaibi, R.L., & Al-Fatesh, A.S. (2015). Methane Decomposition Over Fe Supported Catalysts for Hydrogen and Nano Carbon Yield. *Catal. Sustain. Energy*, 2(1), 71-82. <https://DOI10.1515/cse-2015-0005>.
6. Jeong, M.H., Lee, D.H., & Bae, J.W. (2015). Reduction and Oxidation Kinetics of Different Phases of Iron Oxides. *Int. J. Hydrogen Energy*, 40(6), 2613. <http://dx.doi.org/10.1016/j.ijhydene.2014.12.099>.

7. Li, K., Haneda, M., & Ozawa, M. (2012). The Synthesis of Iron Oxides with Different Phases or Exposure Crystal Planes and Their Catalytic Property for Propene Oxidation. *Adv. Mater. Res.*, 463-464,189-193. [https://doi:10.4028/www.scientific.net/AMR.463-464.189](https://doi.org/10.4028/www.scientific.net/AMR.463-464.189).
8. Farias, F. E. M., Rabelo Neto, R. C., Baldanza, M. A. S., Schmal, M., & Fernandes, F. A. N. (2011). Effect of K Promoter on The Structure and Catalytic Behavior of Supported Iron-Based Catalysts in Fischer–Tropsch Synthesis. *Brazilian J. Chem. Engg.*, 28(3), 495-504.
9. Vulic T. J., Reitzmann, A. F. K., & Lázár, K. (2012). Thermally Activated Iron Containing Layered Double Hydroxides as Potential Catalyst for N₂O Abatement. *Chem. Eng. J.*, 207-208, 913–922. <http://dx.doi.org/10.1016/j.cej.2012.06.152>.
10. Al-Fatesh, A.S., Fakeeha, A.H., Ibrahim, A.A., Khan, W.U., Atia, H., Eckelt, R., Seshan, K., & Chowdhury, B. (2018). Decomposition of Methane over Alumina Supported Fe and Ni–Fe Bimetallic Catalyst: Effect of Preparation Procedure and Calcination Temperature. *J. of Saudi Chem. Soc.*, 22(2), 239-247. <http://dx.doi.org/10.1016/j.jscs.2016.05.001>.
11. Wiczorek-Ciurowa, K. and Kozak, A.J. (1999). The Thermal Decomposition of Fe(NO₃)₃·9H₂O. *J. Therm. Anal. Cal.*, 58(3), 647-651.
12. Wei, X., Zhou, Y., Li, Y., & Shen, W. (2015). Polymorphous Transformation of Rod-Shaped Iron Oxides and Their Catalytic Properties in Selective Reduction of NO by NH₃. *RSC Adv.*, 5, 66141. [https://DOI:10.1039/c5ra08254d](https://doi.org/10.1039/c5ra08254d)
13. Lübbe, M., Gigler, A. M., Stark, R.W., & Moritz, W. (2010). Identification of Iron Oxide Phases in Thin Films Grown on Al₂O₃ (0001) by Raman Spectroscopy and X-Ray Diffraction. *Surf. Sci.*, 604(7-8), 679-685. [https://doi:10.1016/j.susc.2010.01.015](https://doi.org/10.1016/j.susc.2010.01.015)
14. Hanesch, M. (2009). Raman Spectroscopy of Iron Oxides and (Oxy) Hydroxides at Low Laser Power and Possible Applications in Environmental Magnetic Studies. *Geophys. J. Int.*, 177(3), 941–948. [https://doi:10.1111/j.1365-246X.2009.04122.x](https://doi.org/10.1111/j.1365-246X.2009.04122.x)
15. Bhatia, S., Beltramini, J, & Do, D. D. (1990). Temperature Programmed Analysis and its Applications in Catalytic Systems. *Catal. Tod.*, 7(3), 309.
16. Boaro, M., Vicario, M., Leitenburg, C., Dolcetti, G., & Trovarelli, A. (2003). The Use of Temperature Programmed and Dynamic/Transient Methods in Catalysis: Characterization of Ceria-Based, Model Three-Way Catalysts. *Catal. Tod.* 77(4), 407-417. [https://doi.org/10.1016/S0920-5861\(02\)00383-8](https://doi.org/10.1016/S0920-5861(02)00383-8)
17. Che, M., & Védrine, J. C. (2012). Characterization of solid materials and heterogeneous catalysts: from structure to surface reactivity. John Wiley & Sons. Ist edn. Wiley-VCH Verlag Gmb H & Co. KGaA, pp 747-852.
18. Jin, Y., & Datye, A.K. (2000). Phase Transformations in Iron Fischer–Tropsch Catalysts during Temperature-Programmed Reduction. *J. Catal.*, 196, 8–17.
19. Antonella Gervasini (2013). Temperature Programmed Reduction/Oxidation (TPR/TPO) Methods, Calorimetry and Thermal Methods in Catalysis. Springer-Verlag Berlin Heidelberg, pp 175-195. http://DOI:10.1007/978-3-642-11954-5_5
20. Wimmers, O. J., Arnoldy, P., & Moulijn, J.A. (1986). Determination of the Reduction Mechanism by Temperature- Programmed Reduction: Application to Small Fe₂O₃ Particles. *J. Phys. Chem.*, 90(7), 1331-1337. <https://doi.org/10.1021/j100398a025>
21. Wan, H.J., Wu, B.S., Zhang, C.H., Xiang, H.W., Li, Y.W., Xu, B.F., & Yi, F. (2007). Study on Fe–Al₂O₃ Interaction over Precipitated Iron Catalyst for Fischer-Tropsch Synthesis. *Catal. Commun.*, 8(10), 1538-1545. <http://doi:10.1016/j.catcom.2007.01.002>
22. Nicholas, W.H., Stephen, J.G., Alan, J., & Brian, D. M. (1982). Temperature Programmed Reduction. *Catal. Rev. Sci. Eng.*, 24(2), 233-309. <http://DOI:10.1080/03602458208079654>
23. Thomé, A.G., Peters, S., & Roessner, F. (2017). iTPR - A New Methodical Approach for Temperature Programmed Reduction of Catalysts with Improved Sensitivity. *Catal. Commun.*, 97, 10-13. <http://dx.doi.org/10.1016/j.catcom.2017.04.011>
24. Einemann, M., Neumann, F., Thomé, A.G., Wabo, S.G., & Roessner, F. (2020). Quantitative Study of the Oxidation State of Iron-Based Catalysts by Inverse Temperature-Programmed Reduction and Its Consequences for Catalyst Activation and Performance in Fischer-Tropsch Reaction. *Appl Catal A, Gen.*, 602, 117718. <https://doi.org/10.1016/j.apcata.2020.117718>
25. Jozwiak, W., Maniecki, T., Mierczynski, P., Bawolak, K., & Maniukiewicz, W. (2009). Reduction Study of Iron-Alumina Binary Oxide Fe_{2-x}Al_xO₃. *Pol. J. Chem.*, 83(12), 2153-2162.
26. Gao, X., Shen J., Hsia, Y., & Chen, Y. (1993). Reduction of Supported Iron Oxide Studied by Temperature-Programmed Reduction Combined With Mossbauer Spectroscopy and X-Ray Diffraction. *J. Chem. Soc. Faraday Trans.*, 89(7), 1079-1084. <https://doi.org/10.1039/FT9938901079>
27. Parkinson, G.S. (2016). Iron Oxide Surfaces. *Surface Science Reports*, 71(1), 272–365. <http://dx.doi.org/10.1016/j.surfrep.2016.02.001>
28. Kock, A.J.H.M., Fortuin, H.M., & Geus, J.W. (1985). The Reduction Behavior of Supported Iron Catalysts in

- Hydrogen or Carbon Monoxide Atmospheres. *J. Catal.*, 96(1), 261-275. [https://doi.org/10.1016/0021-9517\(85\)90379-3](https://doi.org/10.1016/0021-9517(85)90379-3).
29. Yuan, T.R., Su, Z., Chengyu, W., Dongbai, L., & Liwu, L. (1987). An in Situ Combined Temperature Programmed Reduction-Mössbauer Spectroscopy of Alumina-Supported Iron Catalysts. *J. Catal.*, 106(2), 440-448. [https://doi.org/10.1016/0021-9517\(87\)90256-9](https://doi.org/10.1016/0021-9517(87)90256-9)
30. Kumar, A.&Malvi, B. (2019). Temperature Program Reduction (TPR) Study of Iron Oxide Based Catalysts. Proceedings from Indian Analytical Congress IAC-2019.N. Delhi, India, 12th-14th Dec. pp165.
31. Wan, H., Wu, B., Zhang, C., Xiang, H., & Li, Y. (2008). Promotional Effects of Cu and K on Precipitated Iron-Based Catalysts for Fischer-Tropsch Synthesis. *J. Mol. Catal. A: Chem.*, 283(1-2),33-42
32. Yang, J., Sun, Y., Tang, Y., Liu, Y., Wang, H., Tian, L., Wang H., Zhang, Z., Xiang, H., & Li, Y. (2006). Effect of Magnesium Promoter on Iron-Based Catalyst for Fischer-Tropsch Synthesis. *J. Mol. Catal. A: Chem.*, 245(1-2), 26-36
33. Rajesh, M., Minh, D.P., & Nzihou, A. (2018). Effect of support and its surface modifications in cobalt-based Fischer-Tropsch synthesis: Review. *Ind. Eng. Chem. Res., Am. Chem. Soc.*, 57(48), 16137-16161.
34. Kishan, G., Lee, M.W., Nam, S.S., Choi, M.J., & Lee, K.W. (1998). The Catalytic Conversion of CO₂ to Hydrocarbons Over Fe-K Supported on Al₂O₃-MgO Mixed Oxides. *Catal. Lett.*, 56(4), 215-219. <https://doi.org/10.1023/A:1019089919614>