

Effects of Preparation on the Properties of Mo, Al, and Ca Promoted Fe/MgO Catalysts

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The texture, morphology, and state of iron in the Fe/MgO catalyst with Mo, Al, and Ca promoters have been investigated. It was established that a new Fe-containing phase appeared in all promoted samples after calcination at 723 K, which might be attributed to MgFe_2O_4 . After reduction in hydrogen at 603 K, the phases identified by XRD were MgO and α -iron in all cases except for the aluminum promoted sample. Mössbauer investigation of this latter sample revealed that most of the iron remained in the Fe^{3+} state and only a small part of it was reduced to Fe^{2+} . The limited reduction is attributed to the prevailing presence of spinel-type oxides. Different preparation conditions (drying in air or in vacuum) resulted in morphological changes; smaller iron particles are formed upon reduction of samples dried in vacuum. Comparison of the size of the metal particles and that of the support shows that the characteristic size of iron considerably exceeds the size of the grains of the support. © 1992 Academic Press, Inc.

Introduction

For the Fischer-Tropsch process promoters for catalysts are widely used both in the bulk and supported states. The most common promoter is potassium, which alters the activity, selectivity, and thermal stability of iron catalysts (1, 2). On supported catalysts other promoters such as Ru (3), Rh, Ni, Cr (4) may also play a significant role. These effects have been related to alumina (3, 4), silica (3), and TiO_2 , SnO_2 , and MnO_2 (3, 5) supported iron catalysts.

Several advantages of magnesia supported iron catalyst (6-11) gained definite interest for promoter effects in this system. It has been shown that the reducibility of the Mo monolayer on alumina support is

hindered by strong interaction (12). Compound formation between Ca and any of the catalyst components has never been verified, but it cannot be entirely excluded as the data show in relevant phase diagrams (13). Aluminum may react either with the active component or with the support via formation of solid solutions and compounds like FeAl_2O_4 (14, 15) and MgAl_2O_4 (15).

The behavior of the MgO support itself in the Fe/MgO catalyst is also affected in a rather complex way by the procedure of the preparation (6, 8, 10, 17-19). The method of preparation (e.g., the drying conditions) can also influence the interaction of the promoters (Ca, Al, and Mo) with the catalyst precursor. For instance, for silica supported iron it has been shown that the size of the

iron particles noticeably depends on whether the impregnated sample was dried in vacuum or in air. Namely, the water makes the impregnating salt migrate on the support surface, so formation of the larger particles is facilitated in air dried samples. On the contrary, when drying occurs under vacuum small metal particles can be stabilized (7, 16).

In the present work the effects of Mo, Al, and Ca as promoters are studied on the Fe/MgO catalyst. Al and Ca are not reducible, but the former may interact with any of the catalyst components. Further, the study of the behavior of the molybdenum promoter is also worthwhile, since it can be reduced; however, its reducibility is influenced strongly by the support. In addition, we also intend to elucidate the relation of drying conditions of the catalyst precursor to the final morphology of the reduced catalyst.

Experimental

Catalyst precursors were prepared by precipitation of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution in a slurry of magnesium oxalate at $\text{pH} = 9.5$ using ammonium nitrate as described by Storm (20). The samples contained 10 wt% iron and 1 wt% of the respective promoter. The Mo, Al, and Ca promoted samples were prepared by coprecipitation. The appropriate amounts of solutions of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{MoO}_7 \cdot 4\text{H}_2\text{O}$, or $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, or $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, were simultaneously added dropwise to the slurry of magnesium oxalate in a basic media containing NH_4OH ($\text{pH} = 9.5$) for preparing the $M(\text{OH})_x/\text{Fe}(\text{OH})_3/\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (M : Mo, Al, or Ca) catalyst precursors. The suspensions were left overnight and then filtered. The precursors were dried either in air at 378 K for 20 hr (denoted by A), or in vacuum at 333 K for 12 hr (denoted by V). The dry material was then calcined in air at 723 K for 5 hr. The samples were pelletized into 10×2 mm pellets then they were crushed,

and the fraction in the size range between 1.25–2 mm was used. The samples were reduced in a stream of hydrogen (6 L/hr) at 703 K for 5 hr.

Different methods were applied for characterization of the samples. Crystalline phase composition and average particle size, d_{ave} , determined by line broadening, were measured by XRD using a Philips PW 1050 with $\text{CuK}\alpha$ characteristic line. BET surface area and pore size distribution were determined by Sorptometer 212D Perkin-Elmer Shell and by Mercury Porosimeter 1500 Carlo Erba, respectively. The change of the structure of iron during calcination and reduction was followed by *in situ* Mössbauer spectroscopy. For these measurements a Co/Pd source was used. Spectra were recorded at ambient temperature on a KFKI spectrometer used in constant acceleration mode. The isomer shift values are related to α -iron, the accuracy of these data is ± 0.03 mm/sec. Spectra were fitted by Lorentzian lines, and no positional parameters were constrained. The *in situ* cell and further experimental details are reported in (21).

Results

Phase Composition by XRD Analysis

No influence either of the method of drying or of the promoters was revealed by XRD on the crystalline phases of the calcined samples. The precursor of the active component is in the form of Fe_2O_3 on the MgO support. The support phase does not show any trace of MgC_2O_4 , $\text{Mg}(\text{OH})_2$, or MgCO_3 , as was observed after calcination at lower temperature (19). The MgFe_2O_4 component, although identified by Mössbauer spectroscopy, could not be detected by XRD, since this component is probably a thin, layer-like phase formed between the Fe_2O_3 and MgO grains. Because of their low concentration, the promoter-containing phases cannot be observed by this method, either. After re-

TABLE I
PHASE COMPOSITION OF CALCINED AND REDUCED SAMPLES DRIED PREVIOUSLY IN AIR
(A) OR IN VACUUM (V)

Sample	Crystalline phase composition			
	A		V	
	Calcined	Reduced	Calcined	Reduced
Fe/MgO	Fe ₂ O ₃ ; MgO	α -Fe; MgO	Fe ₂ O ₃ ; MgO	α -Fe; MgO
MoFe/MgO	Fe ₂ O ₃ ; MgO	α -Fe; MgO	Fe ₂ O ₃ ; MgO	α -Fe; MgO
AlFe/MgO	Fe ₂ O ₃ ; MgO	Fe ₂ O ₃ ; MgO	Fe ₂ O ₃ ; MgO	Fe ₂ O ₃ ; Fe ₃ O ₄ ; MgO
CaFe/MgO	Fe ₂ O ₃ ; MgO	α -Fe; MgO	Fe ₂ O ₃ ; MgO	α -Fe; MgO

duction the samples contain MgO and α -Fe in the unpromoted sample and in those containing Mo and Ca. In the AlFe/MgO sample no α -Fe can be identified, only Fe₂O₃ or Fe₃O₄. The results XRD phase analysis are presented in Table I.

State of Iron Determined by Mössbauer Measurements

In all the calcined samples the iron is in the Fe³⁺ state. The most important characteristic of the spectra is the presence of the magnetic splitting. The hyperfine field (MHF) values found are close to those of α -Fe₂O₃ and MgFe₂O₄. The presence of spinel-structure species (MgFe₂O₄) is not surprising, especially in the case of Ca promoter; a promoting effect of small quantities of group II elements has been observed on formation of spinel compounds with MgO (22). A comparison of the air-dried (A series, Table II) and vacuum-dried (V series, Table III) samples reveals a slight difference; most of the air-dried samples contain a small amount of Fe³⁺ not incorporated into magnetic phases. The characteristic MHF values obtained on the Al-containing samples are significantly smaller both for the A and V samples. This might be attributed to presence of mixed (Fe,Al)₂O₃ and/or γ -Fe₂O₃ oxides of spinel structure (23).

The main feature of the spectra obtained after the reduction is the prevailing presence of metallic α -iron (Tables II and III). The exceptions were the alumina-containing samples, where only trace amounts of α -iron can be detected. The other striking characteristic of the alumina-containing sample is the overwhelming presence of a partly reduced oxide phase, the spinel-structure magnetite (Fe₃O₄). This means that only a part of the Fe³⁺ ions can be reduced to the Fe²⁺ state under the conditions at which in the other samples Fe²⁺ is fully reduced to the metallic state.

The second component, which is present in each reduced sample of the series A and V (except the alumina-promoted ones), is Fe²⁺ with isomer shift (δ) and quadrupole splitting (ΔE_q) values close to those reported in (6) and assigned to Fe²⁺ ions incorporated in the bulk magnesia support phase.

Morphology of Samples

As shown in Table IV, no α -iron was detected in the alumina-promoted samples measured by XRD. In the other samples the average size of iron particles was in the range of 90–100 nm in samples of series A and 40–65 nm for the series V. The iron is more dispersed in the vacuum-dried samples, which proves the advantage of drying

TABLE II
MÖSSBAUER DATA OF AIR-DRIED SAMPLES OBTAINED FROM ROOM TEMPERATURE SPECTRA AFTER THE TREATMENTS LISTED

Phase	Sample															
	Fe/MgO				MoFe/MgO				AlFe/MgO				CaFe/MgO			
	δ	ΔE_q	MHF	RI	δ	ΔE_q	MHF	RI	δ	ΔE_q	MHF	RI	δ	ΔE_q	MHF	RI
Calcined sample, 450°C, 5 hr																
Fe ³⁺	0.39	0.19	51.3	70	0.37	0.19	51.2	49	0.32	(0.02)	49.4	39	0.37	0.19	50.9	54
Fe ³⁺	0.32	—	46.4	30	0.30	—	47.3	37	0.30	(0.03)	47.6	53	0.33	—	49.1	40
Fe ³⁺	—	—	—	—	0.32	0.68	—	15	0.36	1.46	—	8	0.26	0.72	—	6
Reduced sample, 430°C, 5 hr																
Fe ³⁺	—	—	—	—	—	—	—	—	0.27	—	48.0	22	—	—	—	—
Fe ³⁺	—	—	—	—	—	—	—	—	0.64	—	44.9	57	—	—	—	—
α -Fe	0.03	—	32.9	82	0.00	—	32.9	59	0.00	—	33.0	4	0.00	—	33.0	80
Fe ²⁺	1.07	0.78	—	18	1.04	0.73	—	41	0.91	1.25	—	17	1.05	0.72	—	20

Note. δ = isomer shift related to α -Fe, mm/sec; ΔE_q = quadrupole splitting mm/sec; MHF = magnetic hyperfine field, T; RI = relative intensity in the spectra, %. Accuracy of data is ± 0.03 mm/sec.

the impregnated sample in vacuum (16, 24–26). The influence of promoters on iron particle size is also more evident on the vacuum-dried samples. As far as the particle size of the MgO support is concerned, no significant differences are revealed in dependence of the promoter. A comparison of the primary crystallite size of the metal particles and that of the support—both deter-

mined by XRD line broadening—shows that the characteristic size of iron considerably exceeds the size of the grains of the support.

The influence of precursor drying conditions on the BET area is most prominent on the Al promoted and reduced samples; the surface area in sample A is lower than in the nonpromoted catalyst, while in sample V its value is the highest of the whole series

TABLE III
MÖSSBAUER DATA OF VACUUM-DRIED SAMPLES OBTAINED FROM ROOM TEMPERATURE SPECTRA AFTER THE TREATMENTS LISTED

Phase	Sample															
	Fe/MgO				MoFe/MgO				AlFe/MgO				CaFe/MgO			
	δ	ΔE_q	MHF	RI	δ	ΔE_q	MHF	RI	δ	ΔE_q	MHF	RI	δ	ΔE_q	MHF	RI
Calcined sample, 450°C, 5 hr																
Fe ³⁺	0.37	0.19	51.3	77	0.38	0.14	50.4	41	0.33	(0.00)	49.0	77	0.32	0.00	49.4	65
Fe ³⁺	0.30	—	47.8	23	0.35	—	48.1	59	0.27	(0.07)	46.2	15	0.30	—	46.7	21
Fe ³⁺	—	—	—	—	—	—	—	—	0.37	—	41.2	8	0.21	1.04	—	14
Reduced sample, 430°C, 5 hr																
Fe ³⁺	—	—	—	—	—	—	—	—	0.29	—	48.1	27	—	—	—	—
Fe ³⁺	—	—	—	—	—	—	—	—	0.63	—	44.9	73	—	—	—	—
α -Fe	0.03	—	33.0	87	0.02	—	33.0	86	—	—	—	—	0.02	—	32.7	82
Fe ²⁺	1.06	0.79	—	13	1.01	1.06	—	14	—	—	—	—	1.01	0.84	—	18

Note. δ = isomer shift related to α -Fe, mm/sec; ΔE_q = quadrupole splitting mm/sec; MHF = magnetic hyperfine field, T; RI = relative intensity in the spectra, %. Accuracy of data is ± 0.03 mm/sec.

TABLE IV

AVERAGE PARTICLE SIZE, d (nm), OF α -Fe AND MgO IN REDUCED AIR- (A) AND VACUUM DRIED (V) SAMPLES

Sample	A		V	
	α -Fe	MgO	α -Fe	MgO
Fe/MgO	89	10	65	12
FeMo/MgO	88	11	38	7
FeAl/MgO	—	12	—	11
FeCa/MgO	103	8	49	10

(Tables IV and V). This points to the lack of small size pores in the A sample. However, in the Ca promoted and reduced sample the situation is the opposite; the surface area is higher in the A sample. In regard of the BET data—reflecting the secondary surface properties as pores, capillaries, cracks, etc.—transformation from polydisperse to mainly monodisperse pore structure takes place during reduction.

Discussion

The method of preparation, in particular the drying conditions, has a primary influence on the size of the metallic iron particles formed. The smaller size of the iron particles in samples V (Table IV) could be related to the retarded surface mobility of the Fe^{3+} ions during drying in vacuum in absence of adsorbed water (7). On the contrary, during air drying the enhanced rate of surface migration of ferric ions results in the growth of iron oxide particles. The difference may primarily be due to the conditions and to a lesser extent to the difference in temperature (333 and 378 K for vacuum and air drying, respectively).

The differences in particle size after reduction should undoubtedly be manifested themselves in the rate of catalytic reaction. It is to be mentioned that the average size

of the iron particles reported in the present work is four to five times as high as that obtained on similar systems (6). This difference may be related to the different procedure of catalyst preparation.

Additionally, the different quantity of water caused by different drying conditions can also influence the final morphology of the magnesia support. Namely, MgO can be easily hydrated, by which the O^{2-} may migrate on the surface. Rapid sintering of magnesia due to the presence of water vapor can be attributed to the low charge and high mobility of magnesium ions (27).

Effects of the different promoters become obvious in all stages of catalyst preparation. Among the promoters used, only Mo can be expected to be reduced to the metallic state. Molybdena on alumina is spread over the support and therefore is difficult to reduce to lower valence states (12). The stabilizing effect of the oxide interface described might provide an explanation also in the case of MgO, indicated by the smallest iron particle sizes observed both in the air and vacuum dried Mo samples (Table IV).

As for the Ca promotion, the properties of the promoted and nonpromoted samples are similar. In fact, no particular effect can be expected upon addition of CaO to the MgO support, since CaO behaves as a non-reactive component toward iron and magnesia. Nevertheless, there are some differences in the particle size of iron, but the fraction of metallic iron is almost the same in the both promoted and unpromoted samples (Tables II and III).

The most specific modifying effect is displayed by Al_2O_3 . It is manifested by the absence of the metallic iron phase after reduction, measured by XRD and Mössbauer spectroscopy as presented in Tables II–IV. Instead, Fe_3O_4 of spinel-structure as major component was detected. As can be suggested, the restricted reducibility of the iron oxide phase can be attributed to the similar crystal structure of the starting $\gamma\text{-Fe}_2\text{O}_3$ and

TABLE V
SURFACE AREA, $S(\text{m}^2 \text{g}^{-1})$, AND PORE SIZE DISTRIBUTION, $r(\text{nm})$, OF CATALYST SAMPLES (A = AIR-DRIED SAMPLES, V = VACUUM-DRIED SAMPLES)

Sample	A						V					
	Calcined			Reduced			Calcined			Reduced		
	S	r	r^{*a}	S	r	r^{*a}	S	r	r^{*a}	S	r	r^{*a}
Fe/MgO	179	8; 18 140;2200	0.25	178	17;7500	0.35	174	7; 11 300;2200	0.50	135	25	0.10
FeMo/MgO	159	15; 30 95; 480	0.28	206	14	0.65	238	8; 28 170;1250	0.28	199	14	0.50
FeAl/MgO	196	7;23;500	0.35	157	60	0.10	211	9; 14 35; 950	0.28	229	—	0
FeCa/MgO	199	7;1000	0.45	255	14; 400	0.40	178	13; 50	0.18	175	9;2000	0.43

^a Asterisk (*) indicates fraction of pores with radius less than 20 nm.

the product Fe_3O_4 oxides. The change in the structure ($\alpha\text{-Fe}_2\text{O}_3$ vs. $\gamma\text{-Fe}_2\text{O}_3$) results in the incomplete reduction: $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, while in all other cases the reduction proceeds via the $\alpha\text{-Fe}_2\text{O}_3 \rightarrow (\text{Fe,Mg})\text{O} \rightarrow \alpha\text{-Fe}$ route (6).

The reducibility of iron ions affected significantly by alumina can be interpreted in several ways. Sushumna and Ruckenstein (24) showed a strong interaction between iron and alumina via formation of a compound with stoichiometrical composition (FeAl_2O_4) and of solid solution. Borghard and Boudart (14) investigated the iron catalyst in presence of 10 wt% alumina. They established that 85% of the aluminum is present in the form of Al_2O_3 in a separate phase at the surface of iron, thereby hindering the sintering of iron. The iron in the particles covered by alumina cannot be completely reduced, since hydrogen cannot penetrate into deeper layers where the iron is located.

The fraction of iron not covered by alumina is very small, the interaction with MgO is strong; therefore a part of the iron ions cannot be reduced into the metallic phase (14, 25). Borghard and Boudart (14) also

assumed the formation of FeAl_2O_4 which is incorporated into the metallic iron lattice, causing an increase the lattice parameters (structural promoter). However, in our case this compound was not detected; thus, the alumina covers most probably the iron oxide particles.

The observed properties of the Mo, Al, Co promoted Fe/MgO catalyst prepared in different ways are in a good correlation with their activity exhibited in hydrocarbon synthesis from a CO/H_2 mixture under 6 bar at 523 K and at 1500 h⁻¹ GHSV (28). The primary role of the zero valent iron can be suggested in the reaction, although the role of Fe^{2+} ions cannot be excluded either. Initially, when the major component is zero valent iron, the main products are hydrocarbons, and later, after several hours on stream, there is a change in the selectivity to form alcohols. The final catalytic phase, on which the significant alcohol formation proceeds after the incubation period, is probably an $\text{Fe}^{2+}/\alpha\text{-Fe}/\chi\text{-Fe}_5\text{C}_2$ system on each promoted catalyst studied. The major difference between the Al promoted and the Mo, Ca, and nonpromoted Fe/MgO is the absence of the bulk carbide phase in the

former sample, on which probably further reduction of the Fe_3O_4 takes place under reaction conditions, as indicated by the rate of reaction. A detailed explanation for the change in the reaction parameters has been discussed elsewhere (28, 29).

References

1. M. E. DRY, "The Fischer-Tropsch Synthesis", Catalysis-Science and Technology, Vol. 1, Chap. 4, Akademie-Verlag, Berlin (1981).
2. M. E. DRY, T. SHINGLES, L. J. BOSHOFF, AND G. J. OOSTHUIZEN, *J. Catal.* **15**, 190 (1969).
3. B. IMELIK, C. NACCACHE, G. COUDURIER, H. PRALIAUD, P. MERIAUDEAU, P. GALLEZOT, G. A. MARTIN, AND J. C. VEDRINE (Eds.), "Metal-Support and Metal-Additive Effects in Catalysis," Studies in Surface Science and Catalysis, Vol. 11, p. 337, Elsevier, Amsterdam (1982).
4. N. NAHON, V. PERRICHON, AND P. TURLIER, *React. Kinet. Catal. Lett.* **12**, 139 (1979).
5. V. LOCHNER, H. PAPP, AND M. BAERNS, *Appl. Catal.* **23**, 339 (1986).
6. M. BOUDART, A. DELBOUILLE, J. A. DUMESIC, S. KHAMMOUMA, AND H. TOPSOE, *J. Catal.* **37**, 486 (1975).
7. G. B. RAUPP AND W. N. DELGASS, *J. Catal.* **58**, 337 (1979).
8. R. DUTARTRE, P. BUSSIERE, J. A. DALMON, AND G. A. MARTIN, *J. Catal.* **59**, 382 (1979).
9. T. SEIYAMA AND K. TANABE (Eds.), "Proceedings of the 7th International Congress on Catalysis, Part A, Tokyo 1980," p. 418, Kodansha Ltd, Tokyo, (1981).
10. G. PONCELET, P. GRANGE, AND P. A. JACOBS (Eds.), "Preparation of Catalysts III," p. 385, Elsevier, Amsterdam (1983).
11. A. D. LOGAN AND A. K. DATYE, *J. Catal.* **112**, 595 (1988).
12. F. E. MASSOTH, *J. Catal.* **30**, 204 (1973).
13. N. A. TOROPOV, V. P. BARZAKOVSKII, V. V. LAPIN, N. N. KURCEVA, "Diagrammi silikatnih sistem," p. 126. Izdatelstvo Nauka, Moskva-Leningrad (1965).
14. W. S. BORGHARD AND M. BOUDART, *J. Catal.* **80**, 194 (1983).
15. I. FILIPOVIC AND S. LIPANOVIC, "Opca i anorganska kemija," p. 715. Skolska knjiga, Zagreb (1973).
16. J. R. ANDERSON, "Structure of Metallic Catalysts," p. 244. Academic Press, New York/London (1975).
17. M. A. McDONALD, D. A. STORM, AND M. BOUDART, *J. Catal.* **102**, 386 (1986).
18. T. E. HOLT, A. D. LOGAN, S. CHAKRABARTI, AND A. K. DATYE, *Appl. Catal.* **34**, 199 (1987).
19. P. PUTANOV, E. KIS, G. BOSKOVIC, AND K. LÁZÁR, *Appl. Catal.* **73**, 17 (1991).
20. D. STORM, Ph.D. Thesis, Stanford University (1978).
21. K. LÁZÁR, K. MATUSEK, J. MINK, S. DOBOS, L. GUCCI, A. VIZI-OROSZ, L. MARKÓ, AND W. M. REIFF, *J. Catal.* **87**, 163 (1984).
22. V. A. DZISKO, "Osnovi Metodov Prigotovlenia Katalizatorov, Nauka, Sibirskoe Otdelenie," p. 115, Novosibirsk (1983).
23. E. MURAD, U. SCHWERTMANN, AND J. D. CASHION, *Hyperfine Interact.* **54**, 619 (1990).
24. I. SUSHUMNA AND E. RUCKENSTEIN, *J. Catal.* **94**, 239 (1985).
25. L. GUCCI, *Catal. Rev. Sci. Eng.* **23**, 329 (1981).
26. M. ESZTERLE AND L. GUCCI, *Magyar Kémikusok Lapja* **39**, 429 (1981).
27. B. G. LINSEN, "Physical and Chemical Aspects of Adsorbents and Catalysis, Academic Press, New York/London (1970).
28. L. GUCCI, K. LÁZÁR, G. BOSKOVIC, E. KIS, AND P. PUTANOV, in "Studies on Surface Science and Catalysis" (A. Holmen, K.-J. Jens, and S. Kolboe, Eds.), Vol. 61, p. 251. Elsevier, Amsterdam (1991).
29. L. GUCCI AND K. LÁZÁR, *Catal. Lett.* **7**, 53 (1990).